

# Measurement of the Apparent Diffusion Coefficient of *N*-Butane in Soil

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**ABSTRACT:** Measurements of in-soil diffusion coefficients and the application of an appropriate diffusional model can allow for a more accurate prediction of soil gas concentrations and movement to locate subterranean contamination of volatile materials. The present study was undertaken to measure and evaluate the "apparent in-soil diffusion coefficient" for *n*-butane through soil columns under non-steady-state conditions. The term "apparent in-soil diffusion coefficient" refers to a numerical coefficient that primarily describes the movement of the material by diffusion but also contains effects due to other mechanisms (e.g., adsorption and solubility).

Six test columns were evaluated at three soil porosity levels ranging from 0.30 to 0.43 and at two column temperature conditions, nominally 18°C and 7°C. Soil columns measured 25.4 cm in diameter by 84 cm in height and contained a moist sand/silt/clay mixture. The numerical range for the apparent in-soil diffusion coefficients for *n*-butane was  $0.447 \times 10^{-3} \text{ cm}^2/\text{s}$  to  $0.561 \times 10^{-3} \text{ cm}^2/\text{s}$ . The lower coefficient values were associated with lower soil porosity levels and cooler column conditions.

**KEY WORDS:** volatile, gas, model, porosity, soil, adsorption.

## I. INTRODUCTION

A significant percentage of soil-based contamination involves the unintended release of organics from both surface and subsurface sources. It is estimated that nationally, there are more than 10,000 leaking underground tanks that contain petroleum-range hydrocarbon products. The detection of the presence and extent of such leaks can include the collection and analysis of soil gases trapped within the soil matrix in the vicinity of the release. Numerous authors have reported the

successful use of soil-gas surveying as an inexpensive screening tool for finding and defining the profiles of volatile organics present in the soil (Chiou and Shoup, 1985; Kerfoot and Barrows, 1987; Kuhlmeier, 1986; Runyon and Thompson, 1987). Detection of leaks from underground gasoline storage tanks presents an interesting application of this technology because of the multiple chemical components in commercial gasoline and the large numbers of such tanks potentially requiring leak monitoring and detection.

In the application of soil-gas surveying to determine the presence of gasoline-range hydrocarbons, it would be helpful to know how quickly various gaseous chemical components of gasoline move through the soil matrix. Because one of the primary mechanisms involved in gas-phase movement is diffusion, a numerical evaluation of an in-soil diffusion coefficient for one or more gasoline-range hydrocarbons would be useful. Although many diffusion coefficients for these gas-phase gasoline components have been determined for mixtures in air, measured values for the diffusion coefficients for the gas-phase components in soils generally are not available. In-soil diffusion coefficients have been empirically determined by adjustments to in-air diffusion coefficients. Such adjusted coefficients do not necessarily include the secondary effects of adsorption, interactions with soil water, or thermal effects and, thus, are subject to considerable variation when applied to actual soil-gas movement predictions.

The present laboratory study was undertaken to measure and evaluate the apparent in-soil diffusion coefficients for one gasoline-range hydrocarbon, *n*-butane, at three soil-porosity levels and at two temperature ranges, using a simple semi-infinite column diffusion model. This testing utilized a form of Fick's second law under non-steady-state conditions. Previously, a similar approach had been used successfully and reported on the measurement of the apparent in-soil diffusion coefficient for trichloroethylene (Hutter *et al.*, 1992).

The term "apparent in-soil diffusion coefficient" refers to a numerical coefficient that primarily describes movement by diffusion but also contains secondary effects due to other mechanisms (e.g., adsorption, buoyancy, and solubility) and is a term that has been commonly used by others (Bruell and Hoag, 1986; Farmer *et al.*, 1980; Herrera *et al.*, 1988; Karimi *et al.*, 1987; Letey and Farmer, 1974). These lumped effects, as they actually occur in the environment, combine to control vapor-phase movement through soils.

The objectives of this research were to determine how well a semiinfinite column diffusion model accounts for the mass transport of *n*-butane through soil under controlled conditions, to quantify the apparent in-soil diffusion coefficients for *n*-butane under two soil temperature conditions, and to evaluate this methodology for modeling in-soil, vapor-phase mass transport.

## II. BACKGROUND INFORMATION

Soil-gas surveys have recently become a popular tool for screening an area suspected of containing subsurface contamination of volatile materials. The appeal of the methodology is that it allows for a relatively quick and inexpensive means of determining the presence and extent of subsurface contamination.

Of particular interest in applying this technology to surveying for leaks associated with underground gasoline storage is the selection of a gasoline-range hydrocarbon component that is easy to measure and common to the multiple compositions of gasolines, is not encountered naturally in the suspect soil environment, and is thought to move relatively quickly through the soil matrix so as to be an early indicator of a leaking condition.

Hydrocarbon components of gasoline with a relatively high vapor pressure will preferentially volatilize and, consequently, would be good soil gas indicators for gasoline. Several such components exist in gasoline. Cline *et al.* (1991) lists major categories of leaded and unleaded gasoline components. Because normal butane (*n*-butane) has a relatively high vapor pressure and is listed as ranging from 4 to 5% of both fuels, it was selected as the component of study in this experiment.

### A. Semiinfinite Diffusion Model and Assumptions

There are several forms of diffusion-based mass-transfer relationships for gases moving through porous materials based on Fick's law of diffusion:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial X^2} \quad (1)$$

Where  $C$  = concentration,  $t$  = time,  $x$  = position,  $D$  = diffusion coefficient.

Several researchers have used the semiinfinite column form of Fick's Law of diffusion, which will be applied in this testing (Lindstrom *et al.*, 1967; Van Genuchten and Alues, 1982; Johnson, R. L., 1992). This modeling uses the following integrated form of Fick's equation based on the assumptions listed below for a semiinfinite column.

$$\frac{C_{(x,t)}}{C_{(0,0 \rightarrow \infty)}} = \operatorname{erfc} \left[ \frac{X}{2\sqrt{DT}} \right] \quad (2)$$

Where:  $C_{(0,0 \rightarrow \infty)}$  = source concentration, is a constant,  $C_{(x,t)}$  = concentration in buried reservoirs at location ( $x$ ) and time ( $t$ ),  $x$  = distance from source,  $t$  = time from

initiation of experiment,  $D$  = in-soil diffusion coefficient in  $x^2/t$ ,  $\text{erfc} = 1 - \text{erf}$ , where  $\text{erf}$  is the error function for initial boundary conditions of:

$$\begin{aligned}C &= C_0, \quad x = 0, \quad t \geq 0 \\C &= 0, \quad x \geq 0, \quad t = 0 \\ \frac{\partial C}{\partial x} &= 0 \quad \text{at } x \rightarrow \infty\end{aligned}$$

A more complete treatment of the development of this relationship is contained in Carslaw and Jaeger (1959); Crank (1975); Jost (1960); and Skelland (1974).

Assumptions:

1. There are no significant chemical reactions.
2. There is a homogeneous soil column structure.
3. There is one-dimensional movement without conduits, which would accelerate or retard the movement of the diffusing gas.
4. Soil adsorption, *n*-butane degradation, and reaction processes were secondary compared with the diffusion mechanism.
5. There are no other significant gas-transfer driving forces or gradients (e.g., pressure, temperature, convection, and buoyancy).
6. The duration of the testing is short compared with the time to reach steady state.
7. There are no other significant *n*-butane sinks (e.g., water solubility, side wall adsorption, and biological activity) that would predominate over the primary mass transport mechanism of diffusion.
8. Column lengths are sufficient to treat the system as a semiinfinite column for the course of the experiment. The use of the concept of a semiinfinite column means that no boundary is reached by the diffusing material.

The semiinfinite column approach and assumptions required for this model allow for measuring the apparent diffusion coefficient under non-steady-state conditions. Such an approach means data collection can commence before an equilibrium condition is established within the column. Under steady-state conditions, adsorption, solubility, and other mechanisms would not play a role in the movement of the subject gas. In this non-steady-state test methodology, these mechanisms are reflected in the final numerical result. Additional discussion

concerning these assumptions and effects of various test parameters are contained in prior work done with trichloroethylene (Hutter *et al.*, 1991, 1992).

### III. MATERIALS AND METHODS

#### A. Soil Columns

These tests incorporated six large vertical stainless-steel columns (92 cm high and 25.4 cm in diameter) packed with a premixed soil/sand composition and exposed to a relatively constant *n*-butane source concentration at the bottom end (source chamber) and a near-zero concentration at the top of each column (exhaust chamber). A humidified sweep air stream was maintained through the exhaust chamber to assure a near-zero concentration of *n*-butane at the top of the column.

The soil was supported at the bottom of the stainless-steel jacketed column by a layer of galvanized wire screen (0.4 cm<sup>2</sup> square grid, 0.076 cm diameter wire) and nylon mesh. Pretesting evaluation of this support indicated that it provided minimum resistance to diffusional gas movement when compared with the impedance of the soil column.

The soil was placed by hand into each column from the top opening. Manual tamping, generally following the ASTM method D698–78 as described by Bowles (1979), was used to attain the range of porosity levels used in this experiment. Reported porosity levels reflect values representative of each entire column.

Each column was wrapped with approximately 9 m of copper tubing in which a coolant circulated. Column temperatures were adjustable by control of the temperature and flow rate of the coolant. The entire column and coolant tubing assembly was covered with a 2-cm-thick fiberglass insulation.

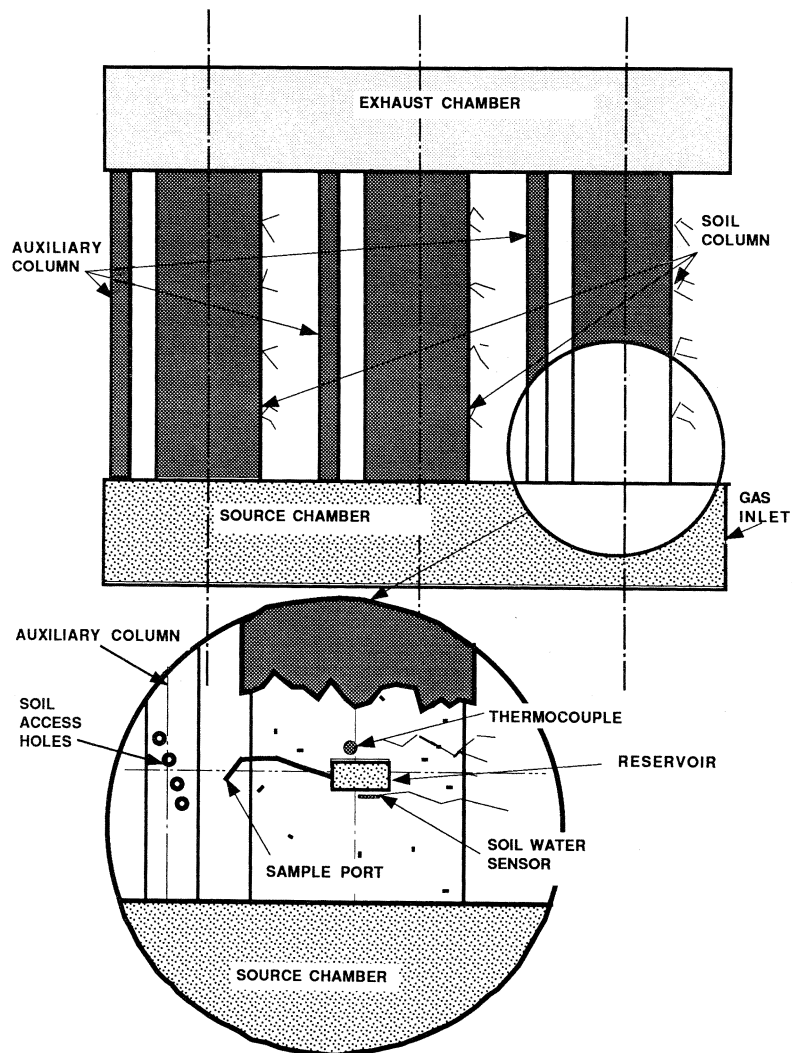
In parallel with each test column was an auxiliary 91 cm long by 6.35 cm inside diameter auxiliary column that was used exclusively as a means to obtain supplemental data on soil-water content and potential soil-water movement. These auxiliary columns were filled with the same soil mixtures, following the same filling procedures. Each auxiliary column had four groups of four sampling ports spaced at 16.5 cm increments along their length. These ports were used for soil sample removal during the course of the experiment to quantify the soil-water level.

#### B. Source and Exhaust Chambers

Groups of three columns were placed atop a single source chamber with a volume of 0.075 m<sup>3</sup>. The source gas, *n*-butane, was fed into this chamber to maintain a relatively constant concentration. After initially flooding the source chamber with *n*-butane, about 2.5 cm of water column pressure was maintained in the source chamber through an exhaust bubble port. A small fan located inside the source

chamber enhanced mixing, and multipoint source-chamber gas sampling assured an even distribution. The exhaust chamber was mounted at the top of each group of three columns and provided a humidified sweep air stream of approximately 1 cfm to assure a near zero concentration at the top of each column while minimizing water loss through the top of the soil column.

Figure 1 depicts the configuration of the columns, source and exhaust chambers, and other column features described in later sections.



**FIGURE 1.** Experimental soil column with soil gas sample ports, thermocouples, and soil water sensors.

### C. Soil

Each test and auxiliary soil column was filled using a 1:1 mixture (based on weight) of Ottawa silica sand and Ashkum Series 232 soil (see Table 1 for soil mixture analysis). This soil mixture was chosen to represent some commonly encountered soil conditions and to provide porosity levels that are representative of many uncompacted naturally occurring soil conditions.

Prior to the column-filling operation, the soil mixture was screened through a 0.0625 cm<sup>2</sup> size sieve, and visually observable vegetation matter was removed. The mixture was oven dried for a minimum of 24 h at 150°C to reduce the potential for biodegradation of the *n*-butane from organisms within the soil mixture and for better control of the soil-water level.

Water was manually added to the dried soil to achieve an intended initial 10% (based on weight) soil-water content. After the water was blended into the soil, it was allowed to equilibrate in sealed containers before it was packed into the columns. Actual soil-water levels were in the range of 7.6 to 8.9%.

### D. Soil-Gas Collection Reservoirs and Other In-Column Devices

Soil-gas collection reservoirs were fabricated from glass and were buried at 16.5 cm increments from the bottom of the column along the vertical axis of each column. The design of the reservoirs consisted of approximately 2.5-cm long (3.22 cm<sup>3</sup>) hollow glass cylinders that were open at each end. To prevent soil from filling the reservoirs, each end was covered with a fine nylon mesh that still allowed the adjacent soil gas to migrate into the inner void space of the reservoir. A small-bore flexible tygon tube connected each soil-gas reservoir to the exterior of the soil column where samples could be taken by syringe. The exposed ends of the

TABLE 1  
**Characteristics of the Test Soil/Sand Mixture**

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Total organic carbon: 8.71%	
Soil characteristics: fine/core with little clay and trace silt	
Soil constituents (by % weight)	
Sand	73.3
Gravel	10.0
Silt	7.5
Clay	9.2
Composed of Ottawa silica sand and Ashkum series soils 232:	
Clay 35 to 40%	
Moist bulk density 1.20 to 1.40	
pH 5.6 to 7.8	

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sampling tubing were sealed with a silicone sealant, which minimized *n*-butane loss and acted as a septum for sampling.

Y-type thermocouples and gypsum-block soil-water sensors were positioned in the area of each soil-gas collection reservoir. The gypsum blocks were used to provide an electrical resistance measure that was proportional to the soil-water level. Electrical connections for these devices were also routed through the outer wall of the column. Silicone sealant was used to assure an airtight closure where the sampling tubing and gypsum block leads exited the columns.

### **E. Soil-Gas Sample Collection**

After appropriate increments of time, soil-gas samples were retrieved from the soil-gas collection reservoirs by use of gas-tight syringes. Samples were withdrawn from the closed end of the tubing connecting the reservoirs with the exterior of the columns. Soil-gas sampling was typically performed at 7-d intervals. The volume withdrawn from the reservoirs remained a constant at 0.6 ml (approximately 20% of the reservoir volume), although smaller volumes were often required for analysis. Replicate gas-sample analysis was performed on 30% of the reservoir samples for quality control purposes. No statistical difference could be detected between test and replicate data. Gas samples from the source and exhaust chamber were also removed on a regular basis to assure a near-zero concentration level in the exhaust chamber and constant concentration in the source chamber.

### **F. Gas-Sample Analysis**

Sample analyses utilized a Gow Mac Gas Chromatograph model 69–750P equipped with a dual flame ionization detector. Calibration of the instrument was performed at the time of sampling. Residence time was approximately 1.8 min and the column was operated at 200°C. Constant gas-sample volumes of 0.6 ml were removed from each reservoir, but gas chromatograph injection volumes ranged from 0.1 to 0.6 ml, depending on expected sample concentration levels.

### **G. Soil-Column Temperatures**

The tests for *n*-butane soil-gas movement were divided between two column temperature levels. Soil-column temperatures were measured at four locations in each column in the area of each soil-gas reservoir. Three *n*-butane soil columns were simultaneously tested at approximately 18°C (64°F), and a second set of three



columns were simultaneously tested at soil-column temperatures of approximately 7°C (45°F). During testing, one column that was to be tested at 7°C actually had a median column temperature 1.6°C warmer than its companion columns.

Column temperatures were attained by circulating and controlling a cooled solution around the outer steel shell that provided the structural support for the soil column. A Poly Science Refrigerated Constant Temperature Circulator, model 9100, and Lab Line Instrument, Inc. Safety Refrigerator were used to provide and circulate the chilled coolant.

## H. Soil-Gas Diffusion Coefficient

Determination of the in-soil diffusion coefficient,  $D_{\text{soil}}$  was made by numerical evaluation of the slope of the erfc equivalent of  $C/C_o$  vs.  $X/2(t)^{0.5}$  curve through linear regression. The erfc equivalent of  $C/C_o$  from Equation 2 is defined as

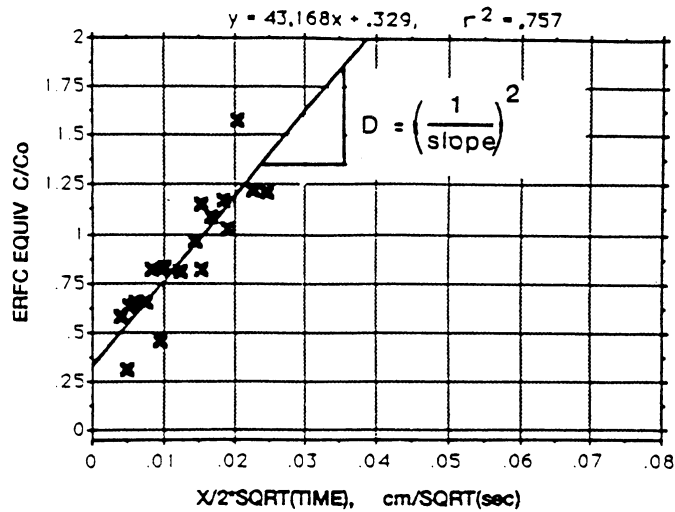
$$\text{erfc equivalent } [C/C_o] = \frac{X}{2\sqrt{Dt}} \quad (3)$$

The relationship of the erfc function to the erfc equivalent function is analogous to the relationship of the sine function to the arc sine function. Its values range from zero to infinity. Figure 2 shows a sample linear regression of the data in this form. The slope of this graph is inversely proportional to the square root of the diffusion coefficient as follows:

$$\text{slope} = \left( \frac{1}{D_{\text{soil}}} \right)^{0.5} \quad (4)$$

Because of some variability in the source-chamber concentration throughout the course of the test period, weighted average source-concentration levels were used for individual  $C_o$  values. These weighted average concentrations represent the cumulative average source-chamber concentration level for each column from the beginning of the test through the time of each soil-column sampling. The average source concentration level was determined by taking the sum of the products of the daily concentration levels and the time increment they represented divided by the total number of days of the soil-gas sampling. This relationship is represented by the following equation:

$$\sum_i^n \frac{C_i(\Delta T_i)}{T_n} = \text{weighted average concentration} \quad (5)$$



**FIGURE 2.** Sample graph showing regression relationship between erfc equivalent vs. distance and time.

Where  $C_i$  = concentration in bottom chamber for period  $i$ ,  $T_i$  = time increment corresponding to  $C_i$ ,  $T_n$  = total time interval between soil gas samples,  $i$  = corresponding individual bottom chamber test.

### I. Test Categories

Table 2 contains the source concentration of *n*-butane, the average soil column temperatures, air filled soil column porosity levels, and the final soil water content.

## IV. RESULTS AND DISCUSSION

An analysis of the data collected daily from the gypsum soil-water blocks and at approximately 10-d intervals from the auxiliary columns indicated minimum soil-water loss or movement. The buried sensors indicated a maximum soil-moisture deviation for any one location within a column of 2% from equilibrium levels. Over 90% of the data from the test columns indicated no more than a 0.5% change in soil-water concentration from column equilibrium levels. Gravimetric analyses for soil water of soils removed from the auxiliary columns all indicated loss of water. The maximum loss was 1.2% with an average loss of 0.8%. On completion of the tests and disassembly of the columns, gravimetric samples were also removed from the test columns. These results also indicated similar soil-water losses uniformly among the six columns.

TABLE 2  
**N-Butane Concentrations, Soil Column  
 Temperature, Soil Porosity, and Final Moisture Content**

Source chamber final weighted conc. <sup>a</sup> (ppm)	Median soil column temperatures with ranges (°C)	Air-filled soil porosity	Final water content (%)
330	17.7, 16.66–20.00	0.30	8.0
	18.3, 16.66–20.56	0.34	8.0
	18.3, 17.22–21.66	0.43	7.6
330	8.8, 6.66–14.44	0.30	8.1
	7.2, 5.55–10.00	0.37	8.0
	7.2, 5.55–10.00	0.43	8.1

<sup>a</sup> Source chamber weighted final concentrations are the time-weighted average results based on individual source gas concentration measurements and the corresponding time period that they represent (see Equation 5).

The measured in-soil diffusion coefficients for *n*-butane ranged from  $0.447 \times 10^{-3} \text{ cm}^2/\text{s}$  to  $0.561 \times 10^{-3} \text{ cm}^2/\text{s}$  and are presented in Table 3. Using a reference value of  $9.6 \times 10^{-2} \text{ cm}^2/\text{s}$  for *n*-butane in air (Boyd *et al.*, 1951; Cussler, 1984), the measured  $D_{\text{soil}}$  coefficient values are lower than those predicted by porosity only models, but are consistent with expected trends when accounting for the general effects of porosity, soil moisture, temperature, and adsorption. Millington and Shearer (1971) discuss the fact that measured  $D_{\text{soil}}/D_{\text{air}}$  ratios can be from 20 to 90% lower than calculated values using porosity alone. They tabulated the results from 15 diffusion studies in which all the measured ratios were lower than the corresponding porosity-based calculated values.

Table 4 contains the diffusion coefficients calculated from the data generated by this study compared with the predicted values of other diffusion models based solely on the application of various theoretical models using empirical data. These approaches are described in the work of Troech *et al.* (1982) wherein numerical curve-fitting coefficients are used to allow for adjustment of in-air diffusion coefficients to estimate in-soil diffusion coefficients. The various constants used in these empirical adjustments (see Table 4 for numerical values) account for the collective effects of diffusion path tortuosity, soil porosity, and other soil structure parameters. The air-adjusted values provide a range of calculated values for *n*-butane in soil of this type and are all larger than that measured in this experiment. Because this experimentation was conducted under non-steady-state conditions, loss of migrating gaseous *n*-butane due to transient sinks such as adsorption onto the soil components and into available water in the soil would be expected to lower the in-soil diffusion coefficient. These affects may account for the measured *n*-butane  $D_{\text{soil}}$  coefficient values being lower than the predictions based solely on soil-structure parameters.

TABLE 3  
**Measured In-Soil N-Butane Diffusion Coefficients and Associated Statistical Results**

Source chamber final weighted conc. <sup>a</sup> (ppm)	Median column temp. (°C)	Air-filled soil porosity	Lower 90% confidence limit	Measured in-soil diffusion coef. (10 <sup>-3</sup> cm <sup>2</sup> /s)	Upper 90% confidence limit	Corresponding r <sup>2</sup> value	Number of data points
330	17.7	0.30	0.398	0.537	0.676	0.757	19
	18.3	0.34	0.437	0.566	0.688	0.758	19
	18.3	0.43	0.422	0.561	0.700	0.728	18
330	8.8	0.30	0.406	0.498	0.590	0.745	18
	7.2	0.37	0.397	0.518	0.640	0.774	18
	7.2	0.43	0.333	0.447	0.561	0.847	18

<sup>a</sup> Source chamber weighted final concentrations are the time-weighted average results based on individual source-gas concentration measurements and the corresponding time period that they represent (see Equation 5).

TABLE 4  
**Comparison of Measured *N*-Butane Diffusion Coefficients with Predicted Values Based on Porosity**

Source chamber final weighted conc. <sup>a</sup> (ppm)	Median column temp. (°C)	Air-filled soil	Measured $D_{\text{soil}} \cdot D_{\text{air}} \times 10^{-2}$	Predicted values ( $\times 10^{-2}$ ) based on porosity only <sup>b</sup>		
				$D_{\text{soil}} \cdot D_{\text{air}} = a(S-b)$	(1)	(2)
330	17.7	0.30	0.559	4.8	13.3	8.1
	18.3	0.34	0.579	6.3	15.8	9.7
	18.3	0.43	0.585	9.5	21.7	13.8
330	8.8	0.30	0.519	4.8	13.3	8.1
	7.2	0.37	0.540	7.5	18.0	11.2
	7.2	0.43	0.466	9.5	21.7	13.8

<sup>a</sup> Source chamber weighted final concentrations are the time-weighted results based on individual source-gas concentration measurements and the corresponding time period that they represent (see Equation 5). The numerical values for these coefficients are empirical results that account for such effects as soil-path tortuosity, porosity, soil packing, and geometry characteristics.

<sup>b</sup> As reported in Troeh *et al.* (1982), (1)  $a = 0.37$ ,  $b = 0.17$ ; (2)  $a = 0.66$ ,  $b = 0.1$ ; and (3)  $K = 0.49$ ,  $m = 1.5$ ,  $S = \text{air-filled porosity}$ ,  $D_{\text{air}} \text{ n-butane} = 0.096 \text{ cm}^2/\text{sec}$  (Cussler, 1984).

Several researchers have developed retardation factors to account for partitioning of the diffusing gas into the soil moisture and onto the solid organic phase in the porous media. These relationships rely on steady state partitioning coefficients and parameters such as Henry's constant, soil organic content, bulk density, and organic partitioning coefficients for the subject gas and soil (Jury *et al.*, 1983; Mendoza and Frind, 1990; Mendoza and McAlary, 1990; Weeks *et al.*, 1982). Under the non-steady-state conditions of this testing, such terms cannot be directly applied. However, such coefficients and parameters would decrease the rate of apparent movement of *n*-butane and decrease the size of the resulting diffusion coefficient. This is consistent with the trends observed in this experiment.

Lyman *et al.* (1982) also report that estimates of diffusion coefficients can be made for various soil conditions based on the molecular weights of the test and candidate gases:

$$D_1 / D_2 = (M_2 / M_1)^{0.5} \quad (6)$$

where D and M represent the diffusion coefficients and molecular weights, respectively, for the two materials. Using this method, they report estimated values for the diffusion coefficients of trichloroethylene through various soils. Table 5 contains similarly calculated values for *n*-butane for comparison with the results of this testing. It can be seen that these estimates, like those predicted in Table 4, are approximately one order of magnitude greater than that measured in this present study.

Few comparable measured experimental diffusion coefficients for *n*-butane are found in the literature. This may be due to proprietary research by the petroleum industry where butane may be used as a marker for prospecting for petroleum reserves, *n*-butane's potentially short-lived nature when exposed to oxidizing conditions in soils, or the fact that *n*-butane generally represents less than 0.5% of natural gas. Therefore, the diffusion characteristics of other alkanes were used for comparison purposes. Table 6 contains various diffusion-related parameters for *n*-hexane, *n*-butane, propane, and methane, and show that *n*-hexane and propane have characteristic values that bracket those of *n*-butane.

Shonnard and Bell (1987) studied the diffusion of gasoline vapors in soils, reported as propane, and found a  $D_{\text{soil}}$  coefficient value of  $2.2 \times 10^{-4}$  cm<sup>2</sup>/s for a soil moisture ranging from 31 to 35%. This value is within a factor of two lower than that measured in this study, which had a characteristic soil water level of approximately 10%.

The finite element modeling and field evaluation for in-soil diffusion of methane is described by Mohsen *et al.* (1978; 1980). They reported that an in-soil diffusion coefficient in the range of  $0.63 \times 10^{-4}$  to  $0.59 \times 10^{-3}$  cm<sup>2</sup>/s produced a good relationship between their model and field tests. Their results are comparable with those reported for *n*-butane in this study (see Table 3).

TABLE 5  
**N-Butane Diffusion Coefficient (D) Estimates Based on  
 Diffusion Coefficients and Molecular Weights of Other Compounds**

Chemical name	Experimental values <sup>a</sup>					Calculated values	
	Mol wt.	D (cm <sup>2</sup> /s)	Temp. (K <sup>o</sup> )	Soil type	Soil porosity	D, N-butane (cm <sup>2</sup> /s)	
Ethylene dibromide	187.9	0.015	293	Garden soil	0.389	0.027	
Ethylene dibromide	187.9	0.005	293	Amhurst	0.199	0.009	
Ethylene dibromide	187.9	0.011	293	Amhurst	0.303	0.020	
Carbon dioxide	44.0	0.043	296	Dry	—	0.037	
Carbon disulfide	76.0	0.193	288.6	Dry sand	0.374	0.221	
Ethanol	46.0	0.042	294.5	Dry quartz sand	0.415	0.033	
Oxygen	32.0	0.105	298	32.7% Moist	0.38	0.078	
Oxygen	32.0	0.056	298	45.7% Moist	0.27	0.041	
							Mean 0.058

<sup>a</sup> Source: Lyman *et al.* (1982).

A comparison of the three  $D_{\text{soil}}$  values from columns at approximately 18°C with those values from columns maintained at approximately 7°C indicates an 11% decrease in the  $D_{\text{soil}}$  values. This drop in measured diffusion coefficients with decreasing column temperatures was an expected trend due to thermodynamic considerations. Letey and Farmer (1974) report a tenfold decrease in diffusion rates when comparing data at 40° and 20°C. In the work of Ehlers *et al.* (1969), a nonlinear relationship between  $D_{\text{soil}}$  and temperature was reported. Again, the decreased  $D_{\text{soil}}$  was associated with the lower temperature. In modeling gas movement in soil, Currie (1960) uses the following simple relationship between temperature and in-air diffusion coefficients:

$$\frac{D_{T_1}}{D_{T_2}} = \left( \frac{T_1}{T_2} \right)^{1.73} \quad (7)$$

Where  $D_{T_1}$  and  $D_{T_2}$  = diffusion coefficients at  $T_1$  and  $T_2$ ,  $T_1$  and  $T_2$  = corresponding absolute temperatures.

This approach is intended for conversion of diffusion coefficients in air at various temperatures and does not include the effects of temperature on other mechanisms (e.g., solubility, Henry's constant). Using Currie's simple approach, however, one would expect a  $D_{18^\circ\text{C}}: D_{7^\circ\text{C}}$  ratio of 1.07. Based on the averages for both temperature ranges, this experimentation produced an in-soil  $D_{18^\circ\text{C}}: D_{7^\circ\text{C}}$  ratio of 1.13, which is close to that predicted based solely on temperature differences.

One unexpected result of this experimentation was that the measured  $D_{\text{soil}}$  coefficients for *n*-butane did not strongly follow the expected trend of decreasing  $D_{\text{soil}}$  values with decreasing soil porosity over the range of these tests (i.e., porosity = 0.429 to 0.301). The magnitude of the change in the diffusion coefficients over the range of temperatures was relatively small and changes in soil porosity were not strong predictors of the resultant diffusion coefficient. The expected trend of decreasing  $D_{\text{soil}}$  values with decreasing soil porosity was apparent for a study using trichloroethylene (Hutter *et al.*, 1992). However, data by Farmer *et al.* (1973) for the volatilization of dieldrin in soils indicated that over narrow bulk-density ranges (1.00 to 1.25 gm/cc) or soil-porosity ranges, the apparent flux remained relatively constant. These tests for *n*-butane were conducted in the same bulk-density range as those performed by Farmer *et al.* (1973) and perhaps did not traverse a wide enough porosity range to allow detection of a trend.

In addition, reported porosity levels represent the gross calculated porosity of the entire column. It is possible that additional soil compaction may have accrued at the bottom of a column. This effect could have resulted in an overall narrowing of the range of porosities for all columns.



The *n*-butane  $D_{\text{soil}}$  coefficients also may not strongly follow the expected trend for porosity because soil porosity may not be the limiting factor, and other parameters such as solubility, adsorption, advection, or gas density may have a stronger individual or collective influence. Mendoza (1989) found density-dependent advection enhanced downward movement for certain hydrocarbons like propane that have high vapor pressures and high molecular weights. *N*-butane has a slightly greater molecular weight and a lower vapor pressure than propane. If one assumes that *n*-butane has a similar density-dependent advection characteristic, one would expect that this advective mechanism would inhibit upward mass transfer and would yield reduced apparent  $D_{\text{soil}}$  coefficient values. In effect, if density-dependent advection is a significant influence, then such a measured apparent diffusion coefficient would be directional.

Another consideration obscuring the influence of soil porosity on these  $D_{\text{soil}}$  values could be the effect of oxidation of the *n*-butane in the test columns. An oxidation reaction would produce a maximum of 1.2 mol of reaction gases (assuming water as vapor) for every mol of reactant. Moreover, such reactions would result in a depressed apparent diffusion by the increased molar volume, the increased soil water available to inhibit diffusion, and a loss of diffusional material (e.g., loss of *n*-butane). Measures were taken to minimize the potential for biological degradation. Not only was the soil heat treated prior to testing, but the columns were also maintained at moderately cool temperatures to reduce biological activity. Garner and Beynon (1951) state that nonbiological oxidation of *n*-butane can occur well below the ignition point, but this is a very slow progression. *N*-hexane, for example, oxidizes one order of magnitude less than *n*-butane. During this testing, no sampling was performed to assure that  $\text{CO}_2$ , a degradation and oxidation product, was not an exhausting gas. In future experiments, sampling for  $\text{CO}_2$  should be included to confirm that this is not an active process.

TABLE 6  
Select Properties of *N*-Hexane, *N*-Butane, Propane, and Methane

	Molecular	Water solubility <sup>a</sup>	Vapor pressure at 25°C <sup>b</sup>	Henry's constant <sup>c</sup>	Diffusion coefficient in air or N <sub>2</sub> <sup>d</sup>
<i>N</i> -Hexane	86	9.5	0.205	1.85	0.0757
<i>N</i> -Butane	58	61.4	2.4	0.947	0.0960
Propane	44	62.4	9.3	0.707	0.0860
Methane	16	24.1	269.0	0.665	0.24

<sup>a</sup> Devitt *et al.*, 1987

<sup>b</sup> Thibodeaux, 1979

<sup>c</sup> Fuller *et al.*, 1966

<sup>d</sup> Metcalfe and Farquhar, 1987

## V. CONCLUSIONS

A simple one-dimensional diffusion model applied under non-steady-state conditions can account for a significant portion of the mass transport of *n*-butane through slightly moist soil columns under a constant concentration gradient. This model may be useful to predict soil-gas concentration levels as a function of position and duration of soil exposure. The apparent in-soil diffusion coefficients for *n*-butane varied from  $0.447 \times 10^{-3}$  cm<sup>2</sup>/s to  $0.561 \times 10^{-3}$  cm<sup>2</sup>/s. These values are approximately one order of magnitude lower than values based on porosity-only models. Variations in the measured apparent in-soil diffusion coefficients could not be solely predicted by adjustments made to column porosity levels. The effect of lower soil-column temperatures resulted in consistently lower apparent diffusion coefficient values.

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