

Transport of chemical vapors through soil: A landfill cover simulation experiment

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Abstract

Experimental simulation studies of the transport of volatile organic chemical vapors by both diffusion and convection through soil covers, as in landfills, are reported. Three organic compounds — methanol, methyl cyclohexane, and dichloropropane — and one type of soil were used in this study. An existing mathematical model incorporating the chemical and soil properties, temperature, pressure, and decomposition gas velocity was used to estimate effective diffusivities from the experimental data. The experimental effective diffusivity for each chemical was found to be greater than that predicted from the Millington–Quirk model of diffusion in porous media. An enhancement factor was defined as the ratio of the observed effective diffusivity to the predicted one. The average enhancement factor was 2.7 with a range of 1.6 to 4.9. Relative humidity effects and surface diffusion are postulated as factors in the observed enhancement.

Introduction

There is solid evidence that volatile chemicals are emitted to the air from subsurface sources created by the burial of domestic and industrial wastes in landfills. At least one hundred chemicals have been identified in landfill gas [1]. These included hydrocarbons, esters, terpenes and organic sulfur compounds. Vinyl chloride and benzene were present at significant concentrations at an industrial waste landfill [2]. Similar compounds were also detected in the vents of an inactive landfill [3]. The fact that hydrocarbon vapors migrate upward from subsurface petroleum reservoirs has been exploited in petroleum exploration; the first such report dates to 1929 in Germany [4].

In this paper we describe pilot scale experimental studies of chemical vapor transport from landfills (Fig. 1). These enclosures range from chemical dump

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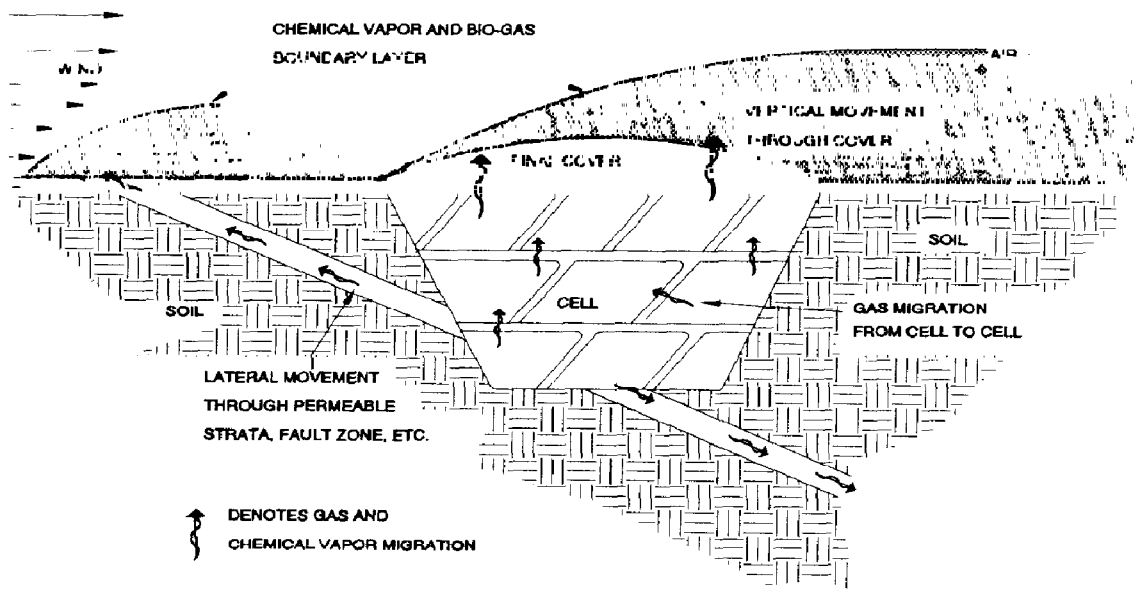


Fig. 1. Chemical transport from landfills.

sites with inadequate earthen covers to modern well-constructed chemical waste landfills. In the absence of strong synergistic effects, the results of this study should apply for pure chemicals as well as mixtures involving solids, sludges and liquids.

The pathway resulting in vapor emission to the atmosphere of chemicals stored in landfills begins with the chemical in a free solid or liquid state either pure or as a component of a mixture. The chemical must exist in a free state to be mobilized by transport processes (solidification or other pretreatment prior to placement in the landfill may attenuate or eliminate the vapor emission pathway). Vapor phase transport commences with vaporization. This process is relatively fast and should not limit the transport rate. As a vapor, the chemical exerts a partial pressure in the gas-filled pore spaces in the cell environment. The actual partial pressure will, of course, depend on the state and nature of the chemical source. The steady state emission rate of volatile organic chemicals (VOCs) is directly proportional to the partial pressure exerted in the landfill cell. The available models for estimating the equilibrium partial pressures in gas-filled pore spaces of landfills and transport rates of VOCs to the soil surface have been described elsewhere [5]. The existence of a chemical partial pressure within the cell environment creates a concentration gradient across the cell cap, providing a driving force for diffusive transport through the cap to the soil surface, provided that the chemical partial pressure in the air boundary layer above the soil surface is less than that in the cell. This assumption is reasonable since breezes are likely to sweep away any chemical emitted at the surface.

A number of factors, such as gas production from degrading materials, waste composition, depth of the landfill, mean ambient temperature and soil type, govern the rate at which VOCs are emitted from a landfill. Soil characteristics important in emission modelling include particle size distribution, organic matter content, soil porosity, water holding capacity, soil moisture level and the chemical composition as determined by weathering and climate. Soils have an inherent capacity to adsorb many volatile and non-volatile pollutants [6,7]. Thus chemical mobility may be affected by interactions with the soil [8]. The extent of adsorption is primarily dependent on the percentage of soil organic matter and surface area of dry soils [9].

Several key processes must be understood and quantified in the laboratory before reliable models can be developed that are capable of predicting chemical vapor emissions from subterranean enclosures. The present study focuses on the following factors:

- (a) chemical equilibrium between air, soil and soil-water phases in the cap,
- (b) the effect of chemical properties on the transport, and
- (c) the effect of decomposition gas produced in the landfill and atmospheric air flow through the soil cap on vapor emission.

A description of the experimental apparatus and methodology follows.

Experimental

A pilot-scale apparatus was built to simulate the major features of soil-covered landfills, and vapor transport through the soil layer was investigated. Detailed construction and operation of this device has been presented elsewhere [10,11]; the following is a brief review.

The experimental apparatus is shown in Fig. 2. It was constructed of galvanized steel (18×18×36 inches). The soil support consisted of a metal frame, iron grating, cheese cloth and screen, which could be raised or lowered to accommodate up to 38 cm of soil. For each experiment, a recording pan-evaporator was placed inside the chamber below the soil and filled with the liquid chemical. A small fan in the chamber was used to eliminate vapor phase concentration gradients. The gas and liquid temperatures were measured by thermocouples and recorded throughout the experiment by a chart recorder. Dry carbon dioxide introduced via a gas distribution tube simulated decomposition gas generation and flow through the soil. Its flow rate was varied from 0 to 6.4 cm³ s⁻¹ at 735 mmHg pressure. The CO₂ flow rate was measured with an inline wet test flowmeter. Silicone rubber cement sealed all joints to assure that the vapor exited via the soil column rather than through leaks. A fan was used to keep the external soil surface free from vapor accumulation during initial experimental runs; however, it was observed that this fan did not affect the chemical flux through the soil cap. This indicated that the effect of wind velocity on emission rates was insignificant. One might anticipate such a result

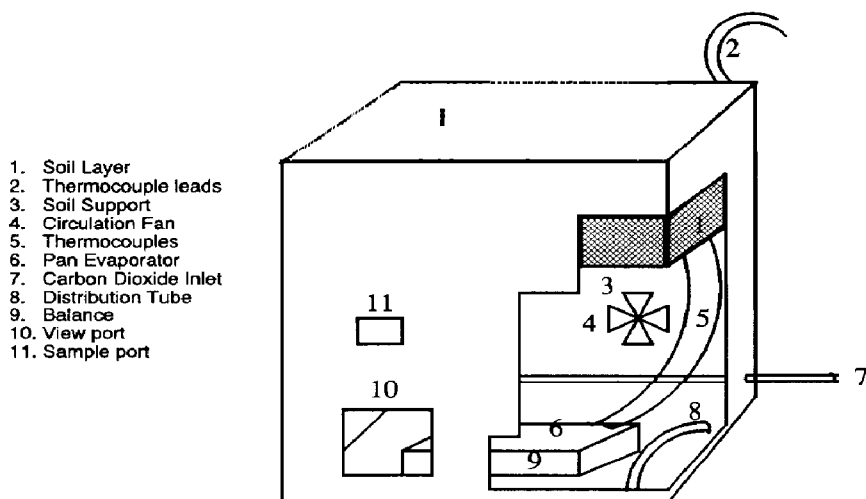


Fig. 2. Schematic of experimental apparatus.

TABLE 1

Soil characteristics

Percentage sand	30
Percentage silt	47
Percentage clay	22
Percentage carbon content	1.4
Percentage water content	2.4
Porosity	0.56
Bulk density (g cm^{-3})	1.29

since the soil-side resistance is greater (for unsaturated soils) than the air-side resistance for vapor transport [12].

The entire apparatus was placed in a temperature and humidity controlled room. The evaporative loss of the chemical was recorded by the pan evaporator, and flux was calculated as the rate of weight loss through the soil cross-sectional area of 2090 cm^2 . Vapor samples were taken from the lower chamber of the simulator using an evacuated gas sampling bulb to determine partial pressure of the chemical in the vapor phase beneath the soil. The samples were analyzed on a Perkin Elmer (Sigma 3) gas chromatograph equipped with a flame ionization detector.

Table 1 presents the soil characteristics. The soil depth was 7.6 cm in all the experiments. The soil was not compacted because of difficulty in reproducing compaction. It was simply broken up and carefully placed inside the chamber.

The chemical compounds used were: methanol (MeOH), methylcyclohexane (Mch) and 1,2-dichloropropane (Dcp). Table 2 presents a summary of

TABLE 2

Chemical properties

Compound	Molecular weight	Vapor pressure at 25°C (mmHg)	Aqueous solubility (mg l ⁻¹)	Diffusivity ^{a,b} in air at 25°C (cm ² s ⁻¹)
Methanol	32	125	∞	0.17
Methylcyclohexane	98	46	14	0.077
1,2-Dichloropropane	113	50	2800	0.04

^aEstimated from the Wilke-Lee modification of the Hirschfelder-Bird-Spotz relation [14].

^bValues used for D_{eff} calculation estimated at experimental temperatures.

relevant chemical properties. The chemicals were chosen based on the range of chemical properties exhibited.

The extent of chemical adsorption to the soil used was determined. Oven-dried soil (60°C overnight) was placed in clean, tared vials, then placed in a desiccator containing the chemical of interest in the lower section (one chemical per desiccator). Six samples ranging in weight from approximately 1 to 20 grams were used. The sealed desiccators were undisturbed for sixty days. The weight gain due to chemical adsorption was noted. Significant amounts were found to be adsorbed: 0.0469 ± 0.0016 g MeOH/g soil, 0.0649 ± 0.0026 g Dcp/g soil, and 0.0440 ± 0.003 g Mch/g soil. To eliminate transient sorption effects, pre-treatment of the soil within the apparatus was deemed necessary. Soil pre-treatment, which typically took two days, was performed prior to all experiments. Experimental measurements were begun after the observed flux stabilized, indicating that steady state conditions had been achieved.

To prevent introduction of moisture to the soil the wet test flow meter was removed from the line after the carbon dioxide flow rate was set. A Dri-Rite cartridge was placed in line to adsorb water present in the CO₂ gas cylinder prior to introduction of the gas into the experimental chamber. The CO₂ gas line had to be clamped shut to prevent chemical vapor loss into the Dri-Rite cartridge during runs without CO₂ flow.

In order to determine whether all the vaporized chemical actually passed through the soil, a specially designed hood was placed over the apparatus. A known rate of air was pumped through the hood, across the soil surface, to collect the emitted vapor. The flux calculated from this information was compared directly to the flux measured by the weight lost from the pan evaporator beneath the soil layer. These experiments were performed without carbon dioxide (decomposition gas) flow through the soil. The results, shown in Table 3, indicate that the flux from the chamber was in fact the same as that through the soil column.

TABLE 3

Chemical flux through soil hood

Chemical	Gas rate (ml s ⁻¹)	Chamber flux (ng cm ⁻² s ⁻¹)	Hood flux (ng cm ⁻² s ⁻¹)
Methanol	17.8	621	505
Methanol	17.4	598	491
Methylcyclohexane	24.0	609	624
Methylcyclohexane	22.7	621	619
1,2-Dichloropropane	26.7	1320	1372
1,2-Dichloropropane	27.4	1328	1394

Results and discussion

Thirty-nine experimental runs were performed. The chemical flux with and without 'decomposition' gas flow are shown in Table 4 for each compound. The gas temperature in these experiments ranged from 23.1°C to 26°C while the liquid temperature ranged from 20.8°C to 24.5°C. The effect of gas flow was quite discernible; as expected, the flux increased with increased gas flow rate through the soil.

The measured fluxes were used to calculate effective diffusion coefficients for the chemicals in the soil, providing a mechanism for extrapolating laboratory data to the field. These coefficients were calculated using a relation previously described [5]. It is

$$D_{\text{eff}} = \left[\frac{N_A RT}{M_A P_T} + V_g \right] L / \ln \left[1 - \frac{P_A}{P_T} \left(1 + \frac{M_A P_T V_g}{N_A RT} \right) \right]^{-1} \quad (1)$$

where N_A denotes the flux of chemical (g cm⁻² s⁻¹), V_g the decomposition gas velocity (cm s⁻¹), M_A the molecular weight of chemical (g mol⁻¹), P_A the partial pressure of the chemical at the bottom of the soil layer (atm), P_T the total pressure (atm), L the soil cover depth (cm), T the temperature (K), R the gas constant (atm cm³ mol⁻¹ K⁻¹), and D_{eff} the effective diffusivity (cm² s⁻¹).

The effective diffusivities for each chemical as calculated by eq. (1) are presented in Table 5. These diffusivities were found to be independent of the CO₂ flow rate (velocity). The mean values were in the order methanol > dichloropropane > methylcyclohexane. The molecular diffusivities in air of Mch and Dcp are in the reverse order to that of the calculated effective diffusivities. A partial explanation of this observation is the fact that the relative vapor saturation for these chemicals was not the same in the sub-soil chamber. As shown in Table 4, Dcp had a greater degree of saturation than Mch. Examination of

TABLE 4

Chemical flux through soil cover with and without CO₂ flow

Chemical	Gas rate (ml s ⁻¹)	Flux ^a (ng cm ⁻² s ⁻¹)	Degree of vapor saturation ^a	Number of exptl. runs
Methanol	0	924 ± 37	0.52 ± 0.07	7
	5.7	1196 ± 4	0.66 ± 0.03	3
1,2-Dichloropropane	0	1417 ± 46	0.62 ± 0.03 ^b	12
	3.9	1727 ± 9	0.58 ± 0.02	3
	6.3	2298 ± 172	0.85 ± 0.02	7
Methylcyclohexane	0	677 ± 38	0.51 ± 0.05	4
	3.9	943 ± 2	0.63 ± 0.03	3

^aMean ± S.D.^bFor eight runs, the four remaining runs had a degree of saturation of 0.45 ± 0.02.

TABLE 5

Effective diffusion coefficients

Chemical	Effective diffusivity ^a (cm ² s ⁻¹)	Number of exptl. runs
Methanol	0.115 ± 0.017	10
1,2-Dichloropropane	0.083 ± 0.004	22
Methylcyclohexane	0.051 ± 0.003	7

^aMean ± S.D.

eq. (1) indicates that, since the vapor pressures are nearly identical, a higher degree of saturation should result in a larger effective diffusivity.

The experimental effective diffusivities were compared with those predicted by the Millington-Quirk model [13] which is given by

$$(D_{\text{eff}})_{\text{MQ}} = D_m \epsilon_1^{10/3} / \epsilon^2 \quad (2)$$

where ϵ is the soil porosity, ϵ_1 is the air-filled porosity, and D_m is the molecular diffusivity of the chemical in air (cm² day⁻¹). This model is presently the preferred relationship for estimating effective diffusion constants in porous media from chemical and soil properties [5]. Molecular diffusivities, D_m were estimated from the Wilke-Lee modification of the Hirschfelder-Bird-Spotz relation [14]. The values calculated using the Millington-Quirk model were always lower than the experimental values. Hence an "enhancement factor" was defined to aid in the data analysis

$$E = D_{\text{eff}} / (D_{\text{eff}})_{\text{MQ}} \quad (3)$$

Table 6 presents the calculated enhancement factors for each chemical. The

TABLE 6

Enhancement factors

Chemical	Soil depth (cm)	Pore gas	No. of exptl. runs	Enhancement factor ^a	Reference
Methanol	7.6	Dry CO ₂	3	2.85 ± 0.15	This work
	7.6	Dry air	7	2.25 ± 0.35	This work
Methylcyclohexane	7.6	Dry CO ₂	3	2.65 ± 0.07	This work
	7.6	Dry air	4	2.02 ± 0.15	This work
1,2-Dichloropropane	7.6	Dry CO ₂	10	4.93 ± 0.39	This work
	7.6	Dry air	12	3.28 ± 0.26	This work
Hexachlorobenzene	1.8	Humid air	6	1.83 ± 0.20	[17]
Benzene	2.5	Humid air	20	1.58 ± 0.28	[2]
Mercury	2.7	Humid air	10	2.68 ± 0.52	[19]

^aMean ± S.D.

experimental results exceed the model predictions by factors as large as 4.93 (for Dcp).

Several mechanisms can be postulated to explain the observed enhancement of diffusion. An explanation offered by some researchers for anomalous results is a phenomenon called surface diffusion [15]. Two transport processes may occur in parallel. The first, simple molecular diffusion, occurs within the pore. This process is slow relative to the second phenomenon, surface diffusion, which occurs on the pore walls. Surface diffusion is thought to include rapid adsorption, rapid transport while adsorbed and rapid desorption. Our data does not permit distinction between competing transport mechanisms, so surface diffusion remains a conjecture.

Flux enhancement may also result from the influence of water on adsorption/desorption processes in the soil, since water effectively competes for adsorption sites [9]. Relative humidity (RH) fluctuations will effect changes in soil moisture content and thus the amount of water sorbed on the available sites. In spite of RH control measures, the moisture level in the experimental room fluctuated around a level in equilibrium with 2.5 to 3.2% (w/w) water. As RH cycles from low to high, water molecules will dislodge adsorbed molecules of the VOC. These molecules would diffuse towards the soil-air interface. As RH cycles from high to low, the water would desorb, leaving the adsorption sites free to adsorb the chemical again. The net result would be an increase in the chemical flux as this cycle continued. The enhancement may also result from vapor transport through large cracks or pores which would invalidate the tortuosity correction of Millington and Quirk.

Air turbulence, caused by the exhaust fan, may enhance soil air movement in coarse textured mulches and through shallow depths in dry soil [11,16,17].

However, the fan was observed to have no effect on the measured flux through the soil cap in this study.

Relevant experimental values of vapor diffusion through soil layers exist in the literature. Diffusion of hexachlorobenzene (HCB) through soils [18], benzene diffusion through soil covers [2], and diffusion of elemental mercury through soils [19] have been reported. These literature values were used to calculate effective diffusivities for each case using eq. (1). These were compared with the effective diffusivities calculated using the Millington-Quirk relation described earlier and enhancement factors calculated. The molecular diffusivities used were: $0.0625 \text{ cm}^2 \text{ s}^{-1}$ for HCB, $0.085 \text{ cm}^2 \text{ s}^{-1}$ for benzene and $0.0131 \text{ cm}^2 \text{ s}^{-1}$ for mercury. Enhanced values for experimental effective diffusivities over the predicted values were found in these cases also. The enhancement factors are presented in Table 6. The nature of the soil does not seem to play an important part in these enhancements since the level of enhancement is in the same range for our experiments as well as those from the literature. Due to the limited data set, statistical analysis of E with candidate independent variables was not attempted.

Conclusions

The emission of chemical vapors through landfill soil covers has been shown to be a function of the rate at which decomposition gas moves through the soil and the chemical properties, particularly the vapor pressure and the diffusion coefficient. We observed that the Millington-Quirk relation for estimating the effective diffusivity of a chemical in a porous medium consistently underpredicted the magnitude of the experimentally measured diffusivities. This result is corroborated by previously published data. The mechanism for the enhancement is not known at the present time. Nevertheless, modelers and designers should be aware of this phenomenon when predicting the vapor phase chemical loss rate through soil covers. The following specific conclusions from this work can be stated:

- (1) The flow of decomposition gas (carbon dioxide in this case) can enhance the chemical transport process.
- (2) The effective diffusion coefficient calculated from experimental data is independent of the decomposition gas flow.
- (3) The experimental effective diffusivities were larger than those predicted by the Millington-Quirk model. Enhancement factors ranged from 1.6 to 4.9 with a weighted average of 2.7.
- (4) Air turbulence did not affect the chemical flux. This substantiates the claim that the soil-side mass transfer resistances dominate the emission of vapors through soil covers.

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