MATHEMATICAL MODELS FOR PREDICTING CHEMICAL VAPOR EMISSIONS FROM LANDFILLS

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Summary

Mathematical models are described for estimating steady-state chemical vapor emissions from landfills. The various vapor-transport mechanisms that give rise to the chemical flux rates through soil cover layers are reviewed. Four different vapor-transport models are described and comparisons made between them by simulating results on benzene and Aroclor 1248 volatilization from a landfill cover. Specific recommendations are made as to the use of algorithms and procedures for computing vapor emissions from sources beneath the ground. The limitations of the models are also discussed.

Introduction

The objective of this manuscript is to provide a state-of-the-art methodology to predict the steady-state air emissions of volatile chemical disposal facilities that involve the confinement of the chemicals in contact with the environment. It is presumed that the methods presented here will be used by facilities designers, permit writers and any other project viewer to assess the impact of either existing or proposed facilities which involve the confinement of volatile chemicals for which there is some need to limit air emissions.

Immediately upon placement of a volatile liquid into the subsurface or the release of it as a result of a leak in its container, physicochemical processes are set up which initiate vapor migration. The equilibrium and transport aspects of the process of vapor migration are discussed below.

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Equilibrium.

The principles involved concerning equilibrium lead to practical results for understanding both the qualitative and quantitative aspects of the chemical source term that establishes the high concentration condition and the starting point for chemical vapor molecules in diffusive and advective transport pathways. Depending upon the physical state of the liquid mixture, concentration levels and soil conditions, the nature of equilibrium conditions can be different. It is likely that four separate phases may exist in the subterranean environment in addition to the original liquid phase. These phases are: soil gas, soil–water (free), soil-inorganic matter and soil natural organic matter. Precise knowledge concerning the make-up of these phases will be required in order to make reasonable chemical partial pressure predictions in the soil gas.

Transport

Once a state of disequilibrium exists between two spatial positions, transport commences. Chemical vapor-transport mechanisms in the subterranean environment include primarily molecular diffusion and advection processes. Both are effected somewhat by flow induced dispersive phenomena on the soil particle but this is usually negligible. Either transport mechanism, diffusive or advective, can occur in transient or steady-state conditions. Only the latter will be considered since it yields the highest emission rate to the adjoining air boundary layer.

Chemical vapor transport under steady-state gradient conditions applies across the cap of a landfill. In the following sections, the state of knowledge to quantify both the equilibrium condition of the source in the cell region and the transport rate across a soil cap will be reviewed in detail.

Chemical equilibrium within cells

The partial pressure of the individual volatile chemical species within the gas filled pore spaces is usually expressed in pressure units of atmospheres or more frequently millimeters of mercury (the use of bar or Pa would be more proper following the SI system). The mass concentration in the pore spaces (ρ_{A1}) is related to this partial pressure, molecular weight and cell temperature through the ideal gas law:

$$\rho_{A1} = P_A M_A / RT \tag{1}$$

where P_A is the partial pressure of the chemical in equilibrium with the solid or liquid source substance (atm), M_A is the molecular weight (g/mol), T is the cell gas temperature (K) and R is the Universal Gas constant (82.1 atm·cm³/mol·K).

The concentration from eqn. (1) is in g/cm³ and at cell conditions of temperature and pressure.

Since p_{A1} in eqn. (1) is related to the equilibrium partial pressure, its value will depend on the properties of the chemical species, the quantity in the cell, the quantity of other substances in the cell, and the state of association with the other substances including the soil and water. Table 1 is an attempt to categorize the state of chemical substances in landfill cells. This categorization of states then forces one to consider what theories and methodologies are available by which to obtain P_A or p_{A1} in the individual cases.

The available equilibrium vapor pressure laws are listed in Table 2. Symbols for each law in Table 2 are keyed to chemical substance state in Table 1. Use of any estimating techniques presumes that one knows the composition of the waste material by chemical species, the number of solid and liquid phases, the mass (or mole) fractions of each species, along with water content, inert material content, organic material (waste paper, plant tissue, etc.) content, pore air (or gas) content, temperature and total pressure. Rarely is all of the above information available concerning the chemical waste in any particular cell.

The distinction of high and low chemical concentration in Table 1 is not

TABLE 1

State of chemical substances in landfills and vapor pressure laws

State	Equilibrium law (Table 2)
High Concentration[a] ($\geq 5\%$ by weight)	
pure substance, solid form mixture,	PV
solid flakes, powers, granules	PV
pure substance, liquid	PV
oil mixture, liquid or sludge (homologs)	RL, KF
liquid or sludge mixtures (non-homologs)	AC
aqueous solution of dissolved chemicals (miscible and immiscible)	AC, HL
liquid or sludges mixtures "solidified" with:	
a. surface soil or sub-soil[b]	PV, BET
b. fly ash, sand, inorganic slag[b]	PV, BET
c. waste paper, garbage, other cellulose material[b]	PV, AWS
oil-in-water sludges, emulsions, mousse	RL, HL, AC
water based micelles	AC
Low Concentration ($< 5\%$ by weight)	
substances (pure or mixtures) admixed with fill material, fly ash, sand, inorganic slag, etc. without water[b]	BET, PV
substances (pure or mixtures) admixed with natural soil; water and soil organic water	AWS, PV
substances (pure or mixtures) admixed with waste paper, garbage or other organic material of cellulose base	AWS, PV

[a]0.05 g/g cell material.
[b]Denotes methodology unclear, untested and research needed.

TABLE 2

Equilibrium vapor pressure laws

Symbol	Law	Sources
AC	Activity coefficients	32, 33
AWS	Air, water, soil–solid model	28
BET	Brauner, Emmett, Teller	34, 35, 28
HL	Henry's law	32, 36
KF	Equilibrium vaporization ratio	37, 38
PV	Pure component vapor pressure	32, 33, 38
RL	Raoult's law	32, 33, 38

arbitrary. High concentration in a terrestrial or aquatic environment is taken to mean a level of single or joint chemical content in a phase (i.e., water or soil) that constitutes $\geq 5\%$ (wt.) (or $\geq 500,000$ ppm (wt.)) of the mixture [1].

Generators and disposers of hazardous organic waste are extremely creative and as a consequence, there are many more mixture-composition states than there are equilibrium laws. Table 1 contains a list of a few common states of mixtures and compositions that organic wastes can assume in landfill cells. Fortunately, many of these disposed states can be categorized to correspond to a few well known states of matter for which there are theories, modeling formulas and procedures for estimating chemical partial pressures. Table 2 contains a list of seven common equilibrium laws.

The available equilibrium laws by which one can estimate the partial pressures of specific chemical species in an organic waste material have been reviewed by Groves et al. [2]. The document provides guidelines for estimating the equilibrium chemical concentration in air (or soil gas) associated with disposal sites containing complex organic/soil mixtures. In general, these laws are fairly easy to use once the state and composition of the waste material is known. As was pointed out above, this is rarely known. Matters are made worse because often the original waste is mixed with other waste or fill material prior to final placement in the cell. The accuracy of any vapor pressure estimate depends upon knowing the state of the chemical as it exists in the final mixture.

The approach used by Groves et al. [2] was to: a) present the equilibrium law in its basic form giving the general concept; b) give some entrees to literature sources through which one can make specific vapor pressure estimates; and c) cover selected organic waste disposal scenarios that result in states of matter for which equilibrium law will yield a reasonable quantitative estimate of the vapor pressure (i.e., P_A in eqn. (1)).

Transport through soil covers

Due to the presence of volatile chemicals in a pure solid or liquid state or in mixture form there will exist a finite partial pressure for each species in the

adjoining gas filled pore spaces of the disposal cell. The source of volatile is typified by a leaking drum in the center cell of a landfill. Several transport processes cause the volatile substance to move to adjoining cells. These processes can involve the transport of the chemical as a liquid or as a vapor.

In general, very little is known about the transport of chemical substances, either in liquid form or in vapor form, within and between disposal cells of landfills. The processes and rates of movement within and between cells will effect the area extent of the "vapor cloud" within the landfill and hence the vapor emission rate through the cover. Without any information on these in-cell processes and rates it seems appropriate, at this time, to consider the landfill cover as the only barrier regulating transport to the air boundary layer.

The modeling of volatile organic chemical emisssions from landfills is based on the highly idealized single-celled source proposed by Thibodeaux [3]. The idealized landfill consists of two compartments. The lower compartment, containing the source of the volatile, in uniform and constant concentration throughout, is a subterranean chamber. The upper compartment is a soil cover that separates the lower chamber from the atmosphere.

The models presented in this section are only concerned with steady-state vapor transport processes through the soil cover layer. Other restrictions on the conceptual model include a constant chemical concentration in the lower chamber and a constant chemical flux rate through the layer. In the following paragraphs various vapor transport mechanisms will be reviewed with regard to obtaining chemical flux rates through soil cover layers.

Diffusion mechanism

Early work aimed at developing quantitative volatile organic chemical emission models for landfill type disposal operations was performed by Farmer et al. [4,5]. The volatilization or vapor loss of hexachlorobenzene from a landfill was treated as a molecular-diffusion controlled process through the soil cover over the waste. For steady state diffusion, Fick's first law was used for the vapor flux. The apparent diffusion coefficient relation developed by Millington and Quirk [6] was employed for the transport coefficient. The combined equations yielded the following expression:

$$N_A = D_{A1}(\epsilon_1^{10/3}/\epsilon^2)(\rho_{A1}^* - \rho_{A1})/L \tag{2}$$

where N_A is the vapor flux from the soil surface ($ng/cm^2 \cdot s$), D_{A1} is the molecular diffusivity of the vapor in the soil gas (cm^2/s), ϵ_1 is the soil gas filled porosity (cm^3/cm^3), ϵ is the total porosity (cm^3/cm^3), ρ_{A1}^* is the concentration of the volatilization material in soil gas at the bottom of the air-soil surface (ng/cm^3 or $\mu g/l$), and L is the soil depth (cm).

Farmer et al. [4,5] performed laboratory experiments to verify that Fick's first law and the Millington–Quirk effective diffusivity would predict the emis-

sion of hexachlorobenzene (HCB). They concluded that HCB diffusion was primarily in the vapor phase through air-filled pores and that this was the primary process controlling movement of HCB molecules to the soil surface of a landfill cover. HCB has a vapor pressure of 1.91×10^{-5} mmHg at 25°C.

Karimi [7] studied the emission of benzene from a refinery sludge waste using coverings of soil, montmorillonite, kaolinite, activated charcoal and polyethylene films in a simulated landfill under controlled laboratory conditions. The waste had sufficient benzene to exert a vapor pressure of 0.3 to 0.8 mmHg. The simulation apparatus was identical to that used by Farmer et al. [4,5] and maintained a soil cover thickness of 2.54 cm. The measured benzene flux data was correlated by eqn. (2). Sallam et al. [8], using a diffusion cell with Freon 1 (CCl_2F_2) at a concentration of 200 $\mu l/l$, generated data that resulted in a slight modification to the Millington-Quirk effective diffusion equation. They recommended $\epsilon_1^{3.10}$ in place of $\epsilon_1^{10/3}$ in eqn. (2).

Murphy [9] developed a diffusion/mass-transfer model for emission of volatile species from buried waste. He postulated that the volatiles must diffuse through the bulk waste, then through the soil, then into the lower atmospheric boundary layer. The air boundary layer resistance was modeled using a mass-transfer coefficient. The diffusion process through the soil and waste was modeled using the Farmer et al. equation [4,5]. The chemical was assumed to be in water and Henry's constant was used to obtain the concentration in the cell gas. A time dependent rate equation resulted. The flux into the atmosphere decreased the amount of volatile chemical in the landfill and thus increased the transport distance. The model equations were not used to make any specific predictions of emission rates and no verification was reported.

Waste elemental mercury has been disposed of by burial in trenches. Orebaugh and Hale [10] developed a mathematical model that accounted for the countercurrent upward flux (diffusion) of gaseous mercury vapor to the atmosphere and simultaneous downward dissolution in soil-water (wash-down). Elemental mercury has a vapor pressure of 1.3×10^{-3} mmHg at 25°C. The basic modeling of the transport modes assumed: (1) uniform soil porosity; (2) free air circulation at the soil surface with zero concentration of mercury vapor; (3) equilibrium distribution between mercury vapor and dissolved mercury related by Henry's constant; (4) steady state diffusion related by Fick's first law; (5) isothermal conditions; and (6) one-dimensional geometry. The resulting equation for the flux of mercury vapor to the atmosphere was:

$$N_A = F p_{A1}^* / H (\exp[FL/D_{A3}] - 1) \tag{3}$$

where F is the soil-water infiltration rate (g/cm²·s) and D_{A3} is the effective diffusion coefficient of the volatile chemical through the soil (cm²/s).

Model calculations were performed by Orebaugh and Hale [10] for vapor emission rates to air from 10 tons of elemental mercury buried in containers in trenches at the Savannah River Plant burial ground. The trenches were 20

feet (6.1 m) deep with a minimum burial depth specification of 4 feet (1.2 m). The containers were assumed randomly distributed both horizontally and vertically in the trenches. A total of 5 mg/h was calculated to be emitted to air at a water infiltration rate of 0.027 g/cm^2 h. With no water infiltration, the emission rate was calculated to be 12.9 mg/h. It therefore appeared that soil-water can down-wash rising chemical vapors and reduce the emission rate. In this case the emission rate was reduced by a factor of 2.6.

Convection mechanism

Fick's first law is valid for low volatile chemical concentrations in air or gas. As the concentration of the volatile chemical approaches 5% (volume) significant deviations from Fick's first law result. At 25°C, benzene has a vapor pressure of 95 mmHg which results in a 12.5% (volume) mixture with air at one atmosphere total pressure. At this concentration level the flux of benzene cannot be adequately modeled by Fick's first law.

At high concentrations (i.e. > 5% (v/v)) the diffusion process itself creates a significant apparent velocity in the gas-filled pores. This induced velocity need be accounted for as a modification of Fick's first law [11]. For high concentrations the appropriate flux equation is:

$$N_A = (D_{A3} P_T M_A / RTL) \ln \left[\frac{(P_T - P_A)}{(P_T - P_A^*)} \right] \tag{4}$$

Where D_{A3} is the effective diffusion coefficient (cm^2/s), P_T is partial pressure of the volatilizing material in soil gas at the bottom of the soil layer (mmHg), and P_A is the partial at the air-soil surface (mmHg).

The pressure in the logarithm term on the right hand side of eqn. (4) can be replaced with concentrations by the use of eqn. (1). The effective diffusion coefficient in eqn. (4) can be as in eqn. (2), i.e. D_{A1} ($\epsilon_1^{10/3}/\epsilon^2$), or D_{A1} ϵ/τ as proposed by Thibodeaux [3]. For P_A^* and P_A < 0.05 P_T (i.e., low concentration) the logarithm term can be closely approximated by $(P_A - P_A^*)/P_T$ so that when the ideal gas relationship is used eqn. (4) reduces to eqn. (2).

Gas convection through the soil cover is a vapor transport mechanism common to landfills in which codisposal of conventional solid waste and hazardous organic waste has been practiced. Methane and carbon dioxide are generated within landfill cells and escape through the cover, creating apparent velocities (i.e., volumetric flow/area) with averages up to 3.2×10^{-4} cm^3/cm^3·s [12]. The molecular diffusion model represented by eqn. (2) and the corrected form of Fick's first law represented by eqn. (4) are both inadequate when methane and carbon dioxide are moving through the cover. Thibodeaux [3] developed an emission model that treated the decomposition gas convection as an "add on" mechanism to the diffusion. This diffusion plus convection model equation is

$$N_A = \frac{D_{A3}/L}{\exp(LV/D_{A3})} \left[(\rho_{A1}^* - \rho_{A1}) + V\rho_{A1}^* \right] \tag{5}$$

where V is the apparent decomposition gas velocity. When the gas velocity is zero eqn. (5) reduces to eqn. (2). $D_{A3} \equiv D_{A1} (\epsilon_1^{10/3}/\epsilon^2)$.

The effect of decomposition gas convection as an enhancement to diffusion was simulated by using apparent gas velocities of 0.0 and 1.63×10^{-3} cm^3/cm$^2 \cdot$s. Calculations with benzene, chloroform, vinyl chloride and a PCB suggest that decomposition gas flow can enhance the volatile chemical emission by a factor of seven. An effective diffusion coefficient based on field measurements of radon gas (^{222}Rn) and the data of Farmer et al. [5] on hexachlorobenzene was used to establish the general credibility of the model.

The above model was combined with Darcy's law to study the dynamics of gas flow in the landfill cover [13]. Landfill decomposition gas dynamics flow was simulated to account for barometric pressure effects on emission. Based on *in situ* gas permeability measurements in a waste trench containing tritium, seasonal cap permeabilities and seasonal emission rates for benzene were computed. The fluctuation of the barometric pressure was found to increase the emission rate by 13% as compared to constant pressure conditions. A sensitivity analysis of the effect of season, cover thickness, cell porosity, cell depth, and decomposition gas generation rate on emission of benzene was also performed. Without decomposition gas production, the cover thickness plays the dominant role in controlling the emission rate. For benzene in the presence of decomposition gas, the depth of buried waste was found to be the most sensitive parameter. Karimi [7] noted that the vapor diffusion coefficient observed in his laboratory experiments with benzene was close to the one used in the above simulation.

Continuing study of the diffusion/convection mechanisms in soil covers has resulted in a theoretically consistent equation that avoids the "add on" approach presented above [14]. The equation is

$$N_A = \frac{VP_A^* M_A}{RT} \bigg/ \left[1 - \frac{P_A^*}{P_T} \right.$$
$$\left. - \frac{P_A^* - P_A}{P_A^* \exp\{ [N_A/M_A + VP_T/RT] LP_T/RT \, D_{A3} - P_A \}} \right] \tag{6}$$

It should be noted that N_A, the flux of the volatile through the landfill cover, also appears on the righthand side of eqn. (6). This is a necessary inclusion for chemicals of high vapor pressure in the range $P_A \geq 0.05 \, P_A$. An iterative scheme is required for solution. The flux computed from eqn. (4) should be used to commence the iterative solution.

Alzaydi et al. [15] developed a similar model for predicting the migration of methane and carbon dioxide in soils around sanitary landfills. The presence of small pressure gradients and high gas concentrations required the use of the combined mechanisms since neither could be ignored.

Employing a transient model and using atmospheric flow data, Weeks et al. [16] showed that various theoretical and empirical models tend to confirm the utility of diffusion theory to predict soil gas concentrations even in very thick and heterogeneous unsaturated zones.

Altogether there are four vapor transport models that can be used to quantify volatile chemical emission rates from subterranean burial. The Farmer et al. model is expressed as eqn. (2). Equation 4 is the logarithm gradient model. The convection "add on" to diffusion model is expressed by eqn. (5) and the exact model by eqn. (6). It is of interest to compare the predictions of each model.

Calculations were performed with each of the four model equations using benzene and Aroclor 1248. A dry soil layer one meter thick with porosity of 51% was used as the landfill cap material. Benzene and the PCB were assumed to be present under this layer at pressures of 95 and 0.375 mmHg respectively and to have molecular diffusivities of 0.088 and 0.048 cm^2/s. The calculated emission rates appear in Figs. 1 and 2.
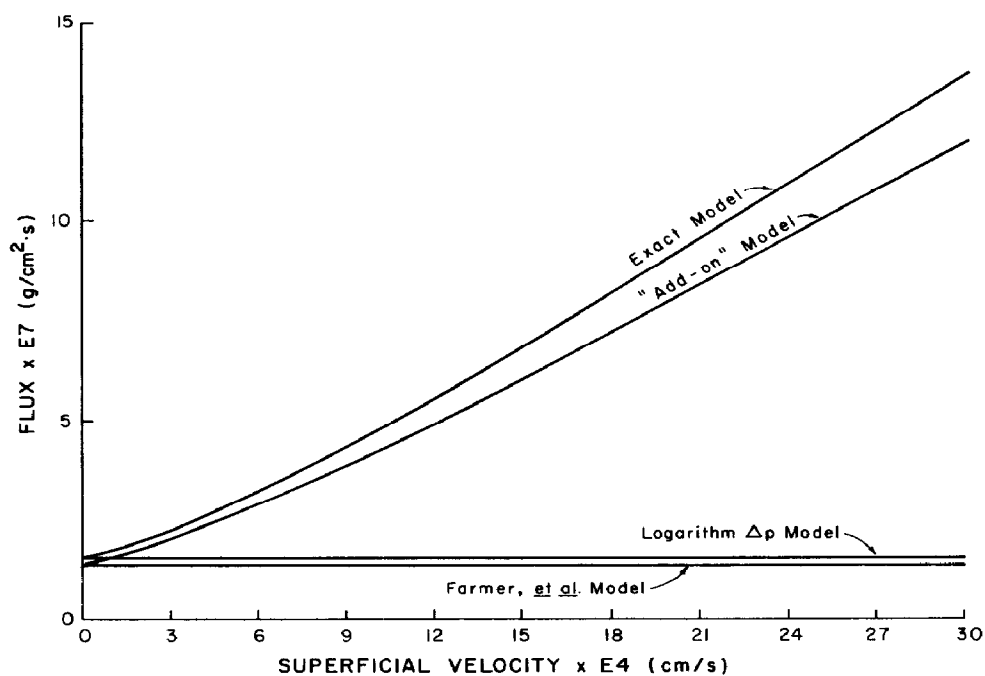

Fig. 1. Benzene emission from landfill to air-model calculations. (Flux $\times 10^7$ vs. superficial velocity $\times 10^4$).
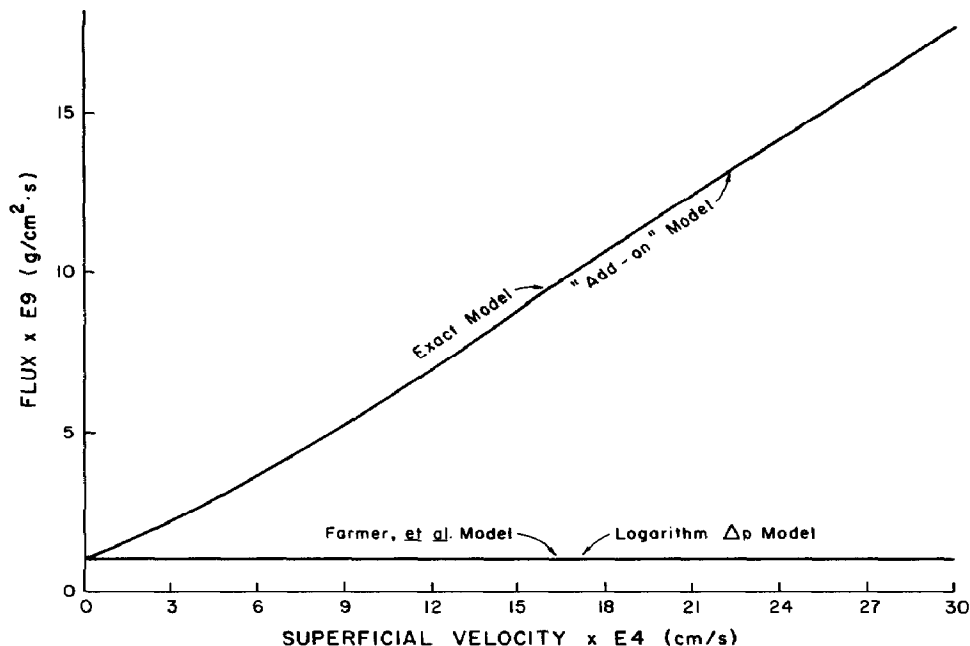
Fig. 2. Aroclor 1248 emission from landfill to air-model calculations. (Flux × 10⁹ vs. superficial velocity × 10⁴).

There are some significant differences in the numerical predictions. Convection plays a dominant role in transport of vapors through the cover. This is apparent from the results of the exact model and the "add on" model compared to the pure diffusion models. This convective effect was significant for both chemicals. Benzene is the more volatile of the two chemicals, and can produce a convective component due to its high vapor pressure. This effect is accounted for in the logarithm Δp model and is responsible for the 7% increase in rate over that predicted by the Farmer et al. model. Due to its low vapor pressure the same rate results with either the logarithm Δp model or the Farmer et al. model for Aroclor 1248. The "add on" model under-predicts the exact model result for the more volatile benzene. The exact model accounts for added convection generated by the high volatility (i.e., vapor pressure) of the diffusing substance. Except for zero decomposition gas flow and low vapor pressure chemicals the Farmer et al. model underestimates the emission rate.

Gas can be forced into and out of porous subterranean chambers such as landfills by the action of the atmosphere. Barometric pressure pumping is a common descriptor of this process. Table 3 contains some typical ranges of common atmospheric pressure fluctuations.

The effect of large barometric pressure changes are typically associated with the passage of weather fronts. A few investigators have studied the effects of

TABLE 3

General characteristics of atmospheric pressure fluctuations

Parameter	Frontal passage	Diurnal variation	Local gustiness
Pressure amplitude (mmHg)	10–20	1–3	0.1– 0.2
Duration period	4– 8(d)	24(h)	10 –30(s)

these larger pressure variations on the transport of chemicals from subterranean sources. Clements and Wilkening [17] investigated the effect of the large scale atmospheric changes on ^{222}Rn flux across the soil-air interface. Field data showed that pressure changes of 1–2% associated with the passage of frontal systems produced changes in the ^{222}Rn flux from 20 to 60%, depending upon the rate of change of pressure and its duration. By using an "add on" type model for convection and diffusion, this finding was confirmed in laboratory experiment with a vertical column of ^{226}Ra-bearing sand. Lu and Matuszek [18] observed similar atmospheric pressure-induced gas flow of tritiated compound from waste in a commercial radioactive-waste land burial site. The pressure differential between trench gas and atmosphere was measured with a transducer. Trench covers were found to be highly permeable to pressure-induced flow of gases and air. Interconnected fractures apparently penetrate through the trench cap and determine the rate of flow of ^{3}HCH$_3$ and other radioactive gases from the trenches. The model used was entirely convective (i.e., Darcy's law) and ignored the diffusion of radioactive compounds through the cap.

The pumping effect of the diurnal barometric variations in the extracting gases and vapors from subterranean cavities has apparently not been investigated. Fukuda [19] investigated air and vapor movement in soil due to wind gustiness. The soil depth to which air can penetrate as a result of wind gustiness is very slight. It was found that in sandy soil for particles of mean diameter of 0.25–0.5 mm, air penetrates only 5 mm below the surface. A Darcy's law model for convective air movement was applied to experimental data involving short-duration pressure changes in a soil column.

Other transport mechanisms

There are other transport mechanisms that may be operative either to enhance or suppress chemical movement through the soil cap. These processes have not been systematically observed or quantified in soil systems, however, several of the more important are presented here. This presentation serves as an introduction to these processes and provides a means of hypothesizing mechanisms that can enhance or modify the known processes.

Soil-suction effects (capillary migration of fluids)

If the soil cap is in direct contact with liquid or sludge waste, capillary rise may be active. Cairney and Mice [20] described the capillary rise of fluids, against gravity, up a column of soil materials. Soil materials partially dry out in the upper layers as the soil column experiences a drought condition. The pressure in the spaces, which lie below the soil surface, but above the fluid level, are always negative. A pressure will always exist in partially "dried" soils which create conditions for the upward rise of "moisture" from deeper layers. The stage is reached at a relatively low degree of dewatering when "clay" will actually pass significantly greater quantities of fluid than will "sand". Thus, soil-suction will be a significant factor in fine-grained soil materials, but only in long, dry, hot summers. In such conditions upward migrations of meaningful large flow rates of soil moisture, with water soluble contaminants, will occur through soil columns in excess of 1 meter thick.

The above described "wicking effect" occurs with water. Corvanos [21] and Buff [22] observed the same phenomenon in the laboratory when studying the evaporation of volatile liquids from and through soil layers. Both observed three zones: a "wet" or liquid-soaked zone, a "damp" zone above and a top most "dry" zone. The "damp" zone was formed apparently due to capillary rise of the liquid chemical in the soil. The rise positions the liquid level closer to the soil surface and effectively reduces the distance of diffusion (i.e., L in eqn. (2) to (6)) the chemical vapors must traverse.

Surface diffusion

Surface diffusion is a term often used as an excuse for many unexpected observations [23]. Evidence for a surface flux arose from the observation of gas fluxes higher than those predicted for the viscous, transition or Knudsen regimes. Cussler [24] described surface diffusion as two physical processes occurring in parallel. The first of these processes, taking place within the pore, is the usual form of diffusion. This diffusion is relatively slow. The second process, on the walls of the pores, is the relatively fast diffusion. Such a process includes rapid solute adsorption, rapid transport while adsorbed, and rapid solute desorption. Cussler commented that although the observations certainly were correct, the interpretation as surface diffusion remained incomplete and unsatisfying.

Heat transport limitations

If the volatile organic is a liquid within the landfill cell, it must vaporize prior to being transported through the soil. If the chemical is in a sludge form or sorbed onto the soil, a similar vaporization process must occur. In either case energy is necessary to cause the chemical to change phase.

A source of energy (or heat) is needed if vaporization and/or desorption

processes are to occur. The energy sources can be from within the cells, from above or from below. The likely energy sources within the cell originate from exothermic chemical or biochemical reactions. Aerobic processes are present during the very early stages of sanitary landfilling when molecular oxygen is present [25]. During a very short period of time (i.e., few weeks) anaerobic processes begin to dominate. Under anaerobic conditions, energy release in virtually nil and no temperature rise is manifest. It appears that if biochemical anaerobic processes do occur in hazardous waste landfills, these reactions provide no thermal energy for vaporization process. However, other reactions, such as nuclear decay, decomposition, hydrolysis or neutralization (i.e., acid–base reactions), can produce energy. Limitations on placing unreactive materials in landfills reduce the likelihood of the latter occurring.

The soil or rock layers underneath the cells are a possible source of some small amount of energy. From observations and measurements made in tunnels, shafts, wells and deep borings, it is known that there exists a temperature, viz. geothermal, gradient in the earth's crust from the interior to the exterior of the earth [26]. There exists a terrestrial heat flux from the hot interior of the earth toward the cooler ground surface. The world wide average rate of geothermal heat flow is 6.3×10^{-6} Watt/cm^2. This amount of heat is only one thousandth of the average influx of solar heat received during the day and re-radiated during the night, so that the geothermal effect on the temperature near the surface is negligible. Therefore, the temperature of soils and rocks near the earth's surface is determined largely by the mean annual air temperature rather than by the geothermal heat flow. The possible exception to the above is the positioning of a landfill above more intense sources of geothermal energy such as hot springs.

The land surface is the most likely source of energy. Solar energy is the dominant source. In this case, the rate of sensible heat transfer through the soil cap must be equal to the rate of energy needed to vaporize (or desorb) the chemical:

$$-k\frac{\mathrm{d}T}{\mathrm{d}y} = \lambda N_{\mathrm{A}} \tag{7}$$

where k is the average thermal conductivity of the soil (Watt/cm·K) in the cap, $\mathrm{d}T/\mathrm{d}y$ is the temperature gradient across the cap (K/cm), and λ is the latent heat of vaporization of the volatile chemical (J) at the cell temperature. If the chemical is sorbed on to the soil an additional heat of desorption term (J/ng) must be added to λ. The above equation relating energy transfer places an upper bound on N_{A} for land surface energy sources.

Conclusions, recommendations and limitations

In this section, the conclusions are given in terms of model recommendations and limitations. Specific recommendations are made as to the use of al-

gorithms and procedures for computing chemical vapor emission from sources beneath the ground. Recommendations include the equilibrium vapor pressure of the volatile as it exists in the soil/waste environment and the emisson rate from the underground source. The final section discusses some limitations of the methodology.

Equilibrium vapor pressure. Equation 1 is recommended for the computation of the volatile chemical concentration within the landfill cell zone at the start of the transport pathway to the soil-air interface. Table 2 is a guide to the state of the chemical substances in the cell zone. This "shopping list" provides the user with a choice of fourteen possible chemical disposal states. Once the disposal state is chosen and the equilibrium law is pin-pointed (2 or 3 letter code), then Table 3 is used to access the algorithm. Seven equilibrium laws are available, literature sources are given for the equilibrium laws. Due to the complexity of data required it is impractical to cover all seven in this document. However, this has been done and the user should consult Groves et al. [2]. The latter document categorizes the states and illustrates each with an example calculation.

Emission flux rate. Equation 6 is recommended for computing the chemical flux rate through a soil cap of thickness L. A number of investigators have shown that the Millington–Quirk equation correctly accounts for the presence of the porous media. Therefore effective diffusion coefficient should be estimated by the Millington and Quirk equation which is:

$$D_{A3} = D_{A1} \epsilon_1^{10/3} / \epsilon^2 \tag{8}$$

It should be noted that N_A also appears on the righthand side of eqn. (6). An iterative scheme is required for the solution. Equation 5 needs to be used to commence the iterative solution.

In addition to chemical and soil properties information is needed on the decomposition gas flow and barometric pressure induced gas flow through the cap. Information on decomposition gas flow is readily available [27]. Barometric pressure induced flows are more difficult to estimate (see Ref. 13).

Besides the factors described above, another important factor in determining the extent of VOC emissions from landfills is adsorption on soil constituents. It has been often found that dry soil has a larger adsorption capacity than wet soil. Thus soil moisture content should also be considered an important parameter in determining VOC emissions from landfills [28].

The flux equation can accommodate a composite cap by use of the "resistance in series" concept. The L/D_{A3} term in eqn. (6) is replaced by

$$\frac{L}{D_{A3}} = \sum_{i=1}^{n} \frac{L_i}{D_{A3i}} \tag{9}$$

where L_i and D_{A3i} are the respective soil depths and effective diffusion coefficients of each layer of the composite cap. Springer et al. [29] employ this

resistance in series concept to estimate PCB flux through a composite landfill cover.

Heat transport limitations. Equation 7 is recommended for computing the limiting emission rate for a chemical that exists in liquid or solid form within the cell. No heat transport limitation need be applied if the chemical is in gaseous form within the cell.

The computation methodology is based upon well established transport theory and some major factors unique to landfills have been verified by laboratory scale and pilot scale experiments [14]. There remains some major factors that need further laboratory investigation. Field verification needs to be performed. There are some factors that will always defy exact model or parameter quantification due to the extreme complexity and variability of this element of the natural ecosystem (i.e., soils). The following are some of the obvious limitations to the methodology.

Limitations of the model equations:
· The model is limited to one-dimensional vertical transport. No provisions are made to account for the lateral and downward migration of the volatile "vapor cloud" in flux calculation.
· The diffusion path length is assumed constant. In reality the path length increases as the volatiles in the upper layers of cell become depleted with time. The model is steady state whereas the real flux is a falling rate.
· Barometric pressure pumping due to the atmosphere is not accounted for. This may result in increased emission rates of the order of 13%.
· Unknown transport mechanisms are sometimes operative what may increase the flux rate.
· Infiltration of rainwater may washdown the upward moving vapors and decrease the rate. A 39% reduction was estimated for mercury vapors.
· Thermal energy will under some conditions control the chemical flux rate. This is likely to occur in the winter in regions where the soil surface is very cold and the net heat flux is out of the soil rather than into the soil. Under these conditions the chemical emission rate may cease altogether.

Limitations of parameter estimates:
· The partial pressure of a particular volatile chemical within a landfill cell is extremely difficult to estimate. Equilibrium is assumed to exist between the chemical and the cell environment. This may not be correct. Even if it were a correct assumption, details of the chemical substance within the cell are unknown. This makes the choice of which equilibrium law to use a very uncertain procedure. The realistic quantification of chemical partial pressure is possibly the weakest link in the entire methodology.
· There appears to be no observations of decomposition gas flow rates from hazardous waste landfills. Methane and carbon dioxide rates from sanitary and co-disposal operations are not generally available.

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· Soil properties such as density and water content are extremely variable in time and space. The use of constant value is only an approximation. In general, the effect of chemical adsorption onto soil and the resulting effect on porosity is unknown.

Acknowledgement

Appendix

Fick's first law in a stationary coordinate system (eqn. (3.1–7) Ref. 31 for a component in the gas phase):

$$F_A = -cD\frac{dy_A}{dy} + y_A(F_A + F_B) \tag{A.1}$$

where $A \equiv VOC$, $B \equiv$ bio-gas or air, $y = L$ represents the depth of the landfill cap. The assumptions involved in the following derivation are steady state diffusion, binary system, constant total pressure and isothermal system. Rearranging eqn. (A.1) gives

$$\frac{cD}{(F_A + F_B)}\frac{d[y_A(F_A + F_B)]}{dy} = y_A(F_A + F_B) - F_A \tag{A.2}$$

Separation of variables and integration gives

$$\int_{y_A = y_A*}^{y_A = 0} \frac{d[y_A(F_A + F_B)]}{y_A(F_A + F_B) - F_A} = \frac{(F_A + F_B)}{cD}\int_{y=0}^{y=L} dy \tag{A.3}$$

$$\ln\{1/[1 - y_A^*\frac{(F_A + F_B)}{F_A}]\} = \frac{(F_A + F_B)L}{cD} \tag{A.4}$$

After rearranging we obtain

$$F_A = y_A^* F_B / \{1 - y_A^* - \exp[-(F_A + F_B)L/cD]\} \tag{A.5}$$

Using

$$F_A = N_A/M_A,\ c = P_T/RT,\ y_A^* = P_A^*/P_T \text{ and } F_B = P_T V/RT$$

we get $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (A.6)

$$N_A = \frac{VP_A^* M_A}{RT} \Big/ \{1 - \frac{P_A^*}{P_T} - \exp(-[\frac{N_A}{M_A} + \frac{VP_T}{RT}]\frac{LP_T}{DRT}\}$$

Eqns. (A.6) and (6) are the same if $P_A = 0$.

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