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Techniques for Modeling Hazardous Air Pollutant Emissions from Landfills

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ABSTRACT

The Environmental Protection Agency's Landfill Air Estimation Model (LAEEM), combined with either the AP-42 or CAA landfill emission factors, provide a basis to predict air emissions, including hazardous air pollutants (HAPs), from municipal solid waste landfills. This paper presents alternative approaches for estimating HAP emissions from landfills. These approaches include analytical solutions and estimation techniques that account for convection, diffusion, and biodegradation of HAPs. Results from the modeling of a prototypical landfill are used as the basis for discussion with respect to LAEEM results.

INTRODUCTION

The EPA Landfill Air Estimation Model (LAEEM) is a PC-based automated estimation tool, for calculating uncontrolled gas emissions from municipal solid waste (MSW) landfills (EPA 1995, 1996). It was intended to serve as a quick method for screening potential methane and hazardous air pollutant (HAP) emissions from MSW landfills to determine the applicability of the control requirements of the Clean Air Act (CAA) regulations. This role is reflected in its simplicity since it is based on the assumption that gases are generated from the first-order decay of organic materials, a concept which has been widely used in the past to model methane emissions from MSW landfills (Tchobanoglous et al. 1993).

This paper begins with a discussion of the theoretical basis for LAEEM, so that in subsequent sections extensions can be made that account for other factors expected to have an influence on HAP emissions. Alternative theoretical models will then be presented, followed by a series of example calculations based on a typical MSW landfill.

LAEEM METHOD FOR ESTIMATING HAP EMISSIONS

The LAEEM method for estimating HAP emissions is based on a number of assumptions, including the following: 1) landfill gas from MSW consists primarily of an equimolar mixture of methane and carbon

dioxide, with trace amounts of other constituents, 2) there is a lifetime methane generation potential for the solid waste, and 3) the landfill gas generation process occurs as the result of first-order decomposition.

Let L_0 represent the lifetime methane generation potential, and k the first-order decay constant. Then the rate of methane generation from N layers of solid waste can be expressed as:

$$Q_{CH_4}(t) = \sum_{i=1}^{N} [kL_0 e^{-kt} V \rho]_i \qquad (1)$$

where $Q_{CH_4}(t)$ = rate of methane generation, m^3 CH_4 / year

k = first - order decay constant, $year^{-1}$

L_0 = lifetime methane generation potential, m^3 CH_4 / Mg solid waste

t = time since solid waste material was deposited, year

V = volume of solid waste in layer i, m^3

ρ = in - place compacted density of solid waste, Mg / m^3

Assuming the landfill gas to be primarily an equimolar methane-carbon dioxide mixture, and that landfill gas emissions occur through vertical flux through a horizontal surface area, the vertical velocity can be calculated as:

$$v(t) = \frac{\sum_{i=1}^{N} [2kL_0 e^{-kt} V \rho]_i}{A} \qquad (2)$$

where v(t) = vertical velocity, m / year

A = surface area of landfill, m^2

By further assuming that the landfill gas has a HAP concentration (either an individual constituent, or the sum of all constituents) of c_v ppmv, the HAP emission brought about by convection can be calculated as:

$$Q_{HAP}(t) = 44.6 \times 10^{-6} \, v(t) \, c_v \qquad (3)$$

where $Q_{HAP}(t)$ = HAP emission rate, mol HAP / m^2 · year

c_v = HAP volumetric concentration in landfill gas,

m^3 HAP / 10^6 m^3 landfill gas (ppmv)

ALTERNATIVE APPROACHES FOR ESTIMATING HAP EMISSIONS

Generalized HAP Movement Equations

HAP movement in landfills can be influenced by a variety of factors, including convection with the methane-carbon dioxide mixture (as calculated by LAEEM), through diffusion caused by concentration gradients, by depletion caused by biodegradation, and by retardation induced by adsorption. Assuming a linear adsorption isotherm, which is common at low concentrations, first-order HAP biodegradation, and vertical gas movement, results in the following equations describing the effect of these factors on HAP movement:

$$\phi(1+\rho)\frac{\partial c_g}{\partial t} = -v\frac{\partial c_g}{\partial z} + D\frac{\partial^2 c_g}{\partial z^2} - k_b \phi c_g \qquad (4)$$

where c_g = gas-phase HAP mass concentration, kg / m^3

ϕ = landfill gas porosity, m^3 / m^3

ρ = linear adsorption coefficient, kg / kg

D = effective diffusivity, m^2 / year

k_b = first-order biodegradation coefficient, year^{-1}

t = time, years

$$Q_{HAP}(t) = \frac{[vc_g - D(\frac{\partial c_g}{\partial z})]_{\text{top of landfill}}}{M} \qquad (5)$$

where $Q_{HAP}(t)$ = HAP emission at time t, mol HAP / m^2 · year

M = average molecular mass of landfill gas, kg / mol

The complexity of these equations encourages the search for simplified approaches, as will be explored in the following section.

Simplified Solutions to HAP Equations

Several alternative methods are available for estimating HAP emissions based on Equations (4) and (5). The choice of method may be aided by an assessment of the relative importance of each of the four terms in Equation (4), using the method of scaling analysis.

Scaling analysis

In the method of scaling analysis, an order-of-magnitude estimate is made for each of the terms in the governing differential equation, as follows:

$$\phi(1+\beta)\frac{\partial c_g}{\partial t} = -v\frac{\partial c_g}{\partial z} + D\frac{\partial^2 c_g}{\partial z^2} - k_b \phi c_g \qquad (4)$$

Order - of - magnitude estimate for each term :

$$\phi(1+\beta)\frac{\Delta c_g}{\Delta t} \quad \frac{v\Delta c_g}{L} \quad D\frac{\Delta c_g}{L^2} \quad k_b \phi c_g \qquad (6)$$

Accumulation Convection Diffusion Biodegradation
Adsorption

where Δc_g = characteristic concentration difference, kg/m^3
L = characteristic length, m

Based on the relative size of each of the terms in Equation (6), a number of specialized cases can be defined:

Convection predominates

Convection can be expected to be the predominant factor affecting HAP movement if each of the following criteria is satisfied:

a. $$\frac{v\Delta c_g}{L} >> D\frac{\Delta c_g}{L^2}$$

$$\therefore v >> \frac{D}{L} \qquad (7a)$$

b. $$\frac{v\Delta c_g}{L} >> k_b \phi \Delta c_g$$

$$\therefore v >> k_b \phi L \qquad (7b)$$

Assuming that convection predominates, one can determine an order-of-magnitude estimate for the length of time that unsteady-state effects, represented by the first term in Equation (4), are expected to be important:

$$\phi(1+\beta)\frac{\Delta c_g}{\Delta t} \sim \frac{v\Delta c_g}{L}$$

$$\therefore \Delta t \sim \frac{\phi(1+\beta)L}{v} \qquad (8)$$

It can be shown that the unsteady-state solution consists of a wave equation type of HAP transport to the landfill surface, and that the steady-state solution leads to the method of LAEEM, as encapsulated in Equation (3).

During the period of active landfill decomposition, it is commonly expected that convection will be more important than diffusion as a transport mechanism. However significant biodegradation can preclude satisfaction of Equation (7b), leading to the following case.

Biodegradation predominates

Criteria for this case are determined in the same fashion as for the previous case, leading to the following equations:

$$\text{a. } k_b >> \frac{v}{\beta L} \qquad (9a)$$

$$\text{b. } k_b >> \frac{D}{\beta L^2} \qquad (9b)$$

The length of time that unsteady-state conditions are important can then be estimated as follows:

$$\Delta t \sim \frac{1+\beta}{k_b} \qquad (10)$$

The only steady-state solution of Equation (4) with predominant biodegradation can be shown to be the zero solution, that is to say that all of the HAPs have been biodegraded and hence are not being emitted.

The unsteady-state solution for this case results in the following expression for in-place HAP concentration:

$$c_g = c_0 e^{\frac{-k_b t}{1+\beta}} \qquad (11)$$

where c_0 = initial HAP concentration, kg/m^3

Diffusion predominates

A landfill that has been closed for an extended period of time may have negligible convection, but may have continued off-gassing occurring through diffusion, if the following criteria are satisfied:

$$\text{a. } D >> vL \qquad (12a)$$

$$\text{b. } D >> k_b \beta L^2 \qquad (12b)$$

The steady-state emission rate through a landfill barrier of thickness L can be shown to be the following:

$$Q_{HAP} = \frac{Dc_0}{L} \qquad (13)$$

where Q_{HAP} = steady-state HAP emission rate through barrier, $kg/m^2 \cdot year$

c_0 = HAP concentration at bottom of barrier, kg/m^3

L = thickness of barrier, m

Unsteady-state emissions can be expected to be important for a time estimated as follows:

$$\Delta t \sim \frac{\phi(1+\phi)L^2}{D} \qquad (14)$$

No effect predominates

Steady-state HAP emissions can be expected to occur for this case, after the following time:

$$\Delta t > \max\left(\frac{\phi(1+\phi)L}{v}, \frac{\phi(1+\phi)L^2}{D}, \frac{1+\phi}{k_b}\right) \qquad (15)$$

The complete description of the steady-state convection-diffusion-biodegradation equation is the following:

$$D\frac{d^2c_g}{dz^2} - v\frac{dc_g}{dz} - \rho k_b c_g = 0 \qquad (16)$$

Boundary condition 1: At $z = 0$, $c_g = c_0$

Boundary condition 2: At $z = L$, $c_g = 0$

Through the methods of ordinary differential equations (Rabenstein 1972), the following expression for HAP emissions results:

$$Q_{HAP} = D(a_1 R_1 e^{R_1 L} + a_2 R_2 e^{R_2 L}) \qquad (17)$$

where $a_1 = \frac{c_0 e^{R_2 L}}{e^{R_2 L} - e^{R_1 L}}$

$a_2 = c_0 - a_1$

$R_1 = \frac{v + \sqrt{v^2 + 4\rho k_b D}}{2D}$

$R_2 = \frac{v - \sqrt{v^2 + 4\rho k_b D}}{2D}$

The complete solution of the unsteady-state equation would most likely use a numerical solution, and is beyond the scope of this paper.

ESTIMATING HAP MOVEMENT FROM AN EXAMPLE LANDFILL

To demonstrate the variety of solution techniques described in previous sections, an example landfill with characteristics described in Table 1 will be used. The LAEEM method will first be applied to define the gas velocity time profile, and to determine a baseline estimate for HAP emissions. Then the alternative methods will be used in an effort to quantify the potential effects of biodegradation, diffusion, and adsorption on HAP emissions.

Table 1: Landfill characteristics used for HAP emission examples

Parameter	Value
Number of layers	10
Depth per layer	3.05 m (10 ft)
Total depth	30.5 m (100 ft)
Layer placement rate	1 layer per year
Cover thickness	0.91 m (3 ft)
First-order decay coefficient for solid waste	0.05 / year
Lifetime methane generation potential	100 m^3 CH_4 / Mg solid waste
In-place compacted density of solid waste	0.593 Mg / m^3 (1000 lbs / yd^3)
HAP concentration in landfill gas, unless otherwise stated	595 ppmv
Gas phase effective diffusivity	150 m^2 / year
Gas phase porosity	0.40

LAEEM Solution

Using the method described by Equations (2) and (3), the velocity and HAP emission time profiles for the example landfill described in Table 1 can be calculated, resulting in Figure 1. The rising portion of the curve corresponds to the period of solid waste deposition, followed by the declining portion resulting from the summation of the exponentially decaying releases of the completed landfill.

Alternative Solutions

In addition to the transport by convective velocity described by LAEEM, HAPs are subject to transport by gas phase diffusion, and in-situ biodegradation. For reference, a listing of current default HAP concentrations for air pollutants listed in LAEEM is included in Table 2, along with reported values in the literature for the biodegradation rate constants for these compounds.

Table 2: Air pollutants listed in LAEEM for non-codisposal landfills

Compound	Concentration (ppmv)	First-order biodegradation rate[a] (1/year)
1,1,1-Trichloroethane	0.48	230
1,1,2,2-Tetrachloroethane	1.11	23 – 32

1,1,2-Trichloroethane	0.1	Nil
1,1-Dichloroethane	2.35	7.0 – 14
1,1-Dichloroethene	0.20	NA
1,2-Dichloroethane	0.41	Nil
1,2-Dichloropropane	0.18	13
2-Propanol	50.1	3.4 – 10
Acetone	7.01	1.0 – 7.4
Acrylonitrile	6.33	4.9 – 28
Benzene	1.91	16 – 84
Bromodichloromethane	3.13	56
Butane	5.03	NA
Carbon Disulfide	0.58	Nil
Carbon Monoxide	141	NA
Carbon Tetrachloride	0.004	16
Carbonyl Sulfide	0.49	NA
Chlorobenzene	0.25	74 – 150
Chlorodifluoromethane	1.30	Nil
Chloroethane	1.25	NA
Chloroform	0.03	630
Chloromethane	1.21	5.0
1, 4 Dichlorobenzene	0.21	Nil
Dichlorodifluoromethane	15.7	NA
Dichlorofluoromethane	2.62	Nil
Dichloromethane	14.3	3.6
Dimethyl Sulfide	7.82	NA
Ethane	889	NA
Ethanol	27.2	2.6
Ethylbenzene	4.61	7.9
Ethyl Mercaptan	2.28	NA
Fluorotrichloromethane	0.76	NA
Hexane	6.57	NA
Hydrogen Sulfide	35.5	NA
Mercury	2.92×10^{-4}	NA
Methyl Ethyl Ketone	7.09	1.6 – 2.4
Methyl Isobutyl Ketone	1.87	10 – 25

Methyl Mercaptan	2.49	NA
Pentane	3.29	20
Perchloroethylene	3.73	NA
Propane	11.1	NA
Trichloroethene	2.82	84
t-1,2-Dichloroethene	2.84	110
Vinyl Chloride	7.34	28 – 63
Xylene	12.1	5.0 – 130

[a]After Howard 1989; Howard 1990; and Howard 1993

Unsteady-state in-situ biodegradation

From Figure 1, the velocity time profile has been determined to vary up to a maximum value of 146 m / year, and so the parameter $v / \phi L$ described in Equation (9a) will vary up to a maximum of 10 $year^{-1}$. From Table 2, it can be seen that the first-order biodegradation rate, k_b, varies from 0 – 630 $year^{-1}$, and hence has the potential to be a significant factor when compared with convection.

For the purpose of illustration, assume that the effect of biodegradation on benzene is to be considered. From Table 2, the range of literature values for the biodegradation is

16 – 84 $year^{-1}$. Comparing k_b to $v / \phi L$, it is seen that biodegradation may play a significant role, especially during those years with lower gas velocities.

The HAP concentration reductions resulting from in-situ biodegradation, calculated using Equation (11), are shown in Figure 2, and demonstrate that significant reductions are achievable.

Diffusion from an inactive, non-biodegrading landfill

Application of the criteria of Equations (12a) and (12b) for the example landfill would quickly lead one to conclude that a typical gas phase effective diffusivity of 150 m^2 / year would not be sufficiently large relative to the convection term, vL, or the biodegradation term, $k_b \phi L^2$, unless the landfill is both inactive ($v = 0$), and non-biodegrading ($k_b = 0$).

$$\Delta t \sim \frac{\phi(1+\beta)L^2}{D} \qquad (14)$$

$$\therefore \Delta t \sim \frac{0.4(1+0)30.5^2 m^2}{150\, m^2 / year}$$

$$\therefore \Delta t \sim 2.5\, years$$

Unsteady-state emissions via diffusion may play a role for a time estimated by Equation (14), as follows:

Using the example HAP benzene, with a default concentration of 1.91 ppmv (see

Table 2), the steady-state benzene emission can be calculated using Equation (13), as follows:

$$Q_{HAP} = \frac{Dc_0}{L} \qquad (13)$$

$$c_0 = 1.91\,\text{ppmv} = 8.53 \times 10^{-5}\ \text{kg/m}^3$$

$$\therefore Q_{HAP} = \frac{(\frac{150\,\text{m}^2}{\text{year}})(8.53 \times 10^{-5}\ \frac{\text{kg}}{\text{m}^3})}{30.5\,\text{m}}$$

$$\therefore Q_{HAP} = 4.2 \times 10^{-4}\ \frac{\text{kg}}{\text{m}^2 \cdot \text{year}} \quad \text{(source of HAP at bottom of landfill)} \qquad (18)$$

Note that this represents diffusion from the bottom of the landfill through to the surface.

$$Q_{HAP} = 0.014\ \frac{\text{kg}}{\text{m}^2 \cdot \text{year}} \quad \text{(source of HAP just under landfill cover)} \qquad (19)$$

Steady-state diffusion could also occur from a zone immediately below the cover, if the landfill material contained a source of benzene vapor at that location. Application of Equation (13) for this situation, through a cover 0.91 m (3 ft) thick, would result in:

$$Q_{HAP}(\text{maximum convection}) = v_{max}\, c_0 \qquad (20)$$

$$= \frac{146\,\text{m}}{\text{year}}\ (8.53 \times 10^{-5}\ \frac{\text{kg}}{\text{m}^3})$$

$$\therefore Q_{HAP}(\text{maximum convection}) = 0.012\ \frac{\text{kg}}{\text{m}^2 \cdot \text{year}}$$

Based on convection, during the period with maximum velocity (see Figure 1), the maximum benzene flux would be calculated as:

One can conclude that diffusion, particularly from a source near the cover, may be an important transport mechanism neglected by LAEEM.

Sensitivity analysis for biodegradation

The purpose of this section is to test the sensitivity of steady-state HAP emissions for the example landfill of Table 1 on the biodegradation rate, even when there is significant convection and diffusion. From the time scale criteria of Equation (17), it can be shown that the steady-state solution of Equation (19) should be appropriate during most of the active life of the landfill.

Figure 3 shows the predicted HAP emission rate as a function of the biodegradation rate, for a family of depths to the maximum benzene concentration, during the time when the maximum convection is occurring (see Figure 1; v_{max} = 146 m / year). A depth of 100 ft corresponds to a benzene source at the bottom of the landfill, and a depth of 3 ft corresponds to a source just beneath the landfill cover.

CONCLUSIONS

It has been shown that each of the following factors play a critical role with respect to the amount of HAPs that may be emitted from MSW landfills: the potential for biodegradation, and the depth of the source of the HAP with respect to the landfill surface. It the source of the HAP is deep within the landfill, and if there is the potential for biodegradation, the HAP releases may be insignificant when compared with LAEEM estimates.

Conversely, even during years after a landfill has been closed, if there are sources of HAPs within the MSW there will continue to be the potential for releases due to diffusion.

The techniques discussed within this paper allow for the relative assessment of the importance of these factors within any landfill under consideration, which should provide information complementary to the results from LAEEM.

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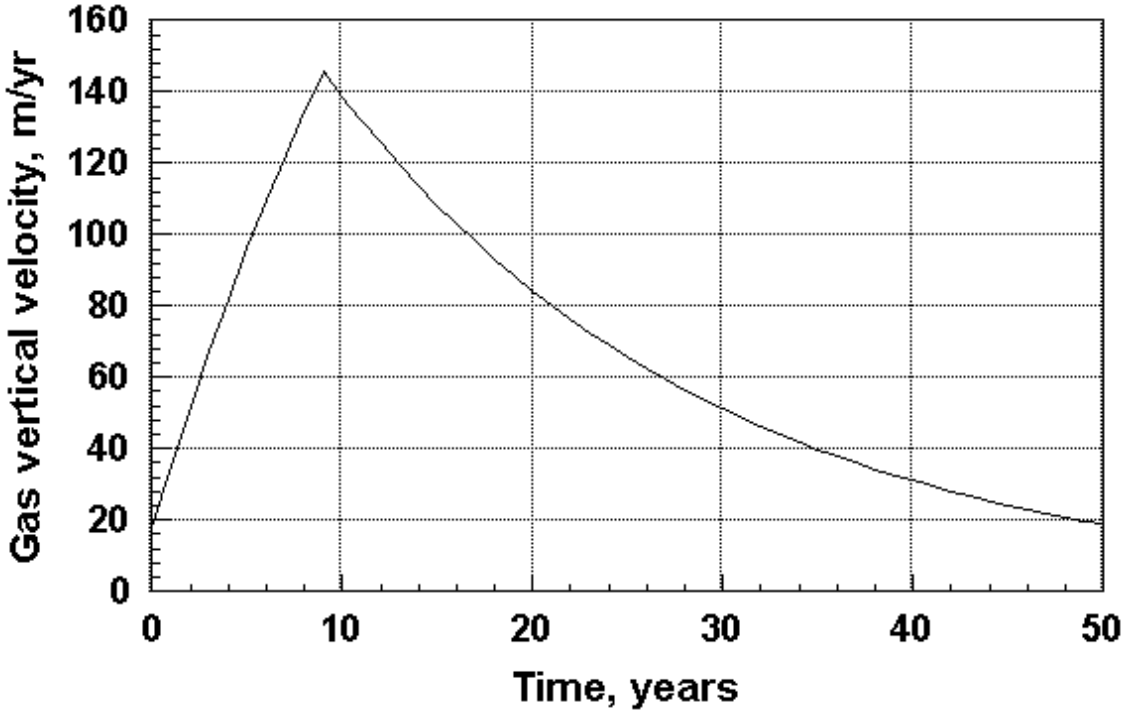

Figure 1

Vertical gas velocity for example landfill of Table 1,

calculated using LAEEM methodology

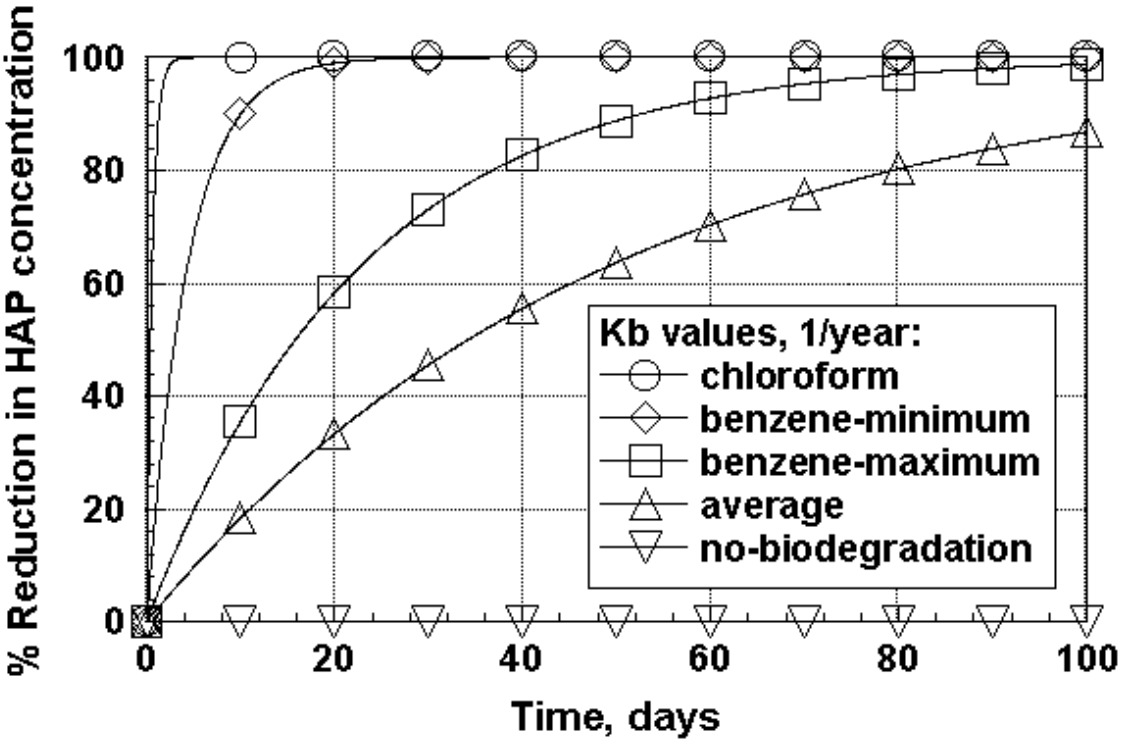

Figure 2

Effect of in-situ biodegradation on HAP concentration in landfill gas

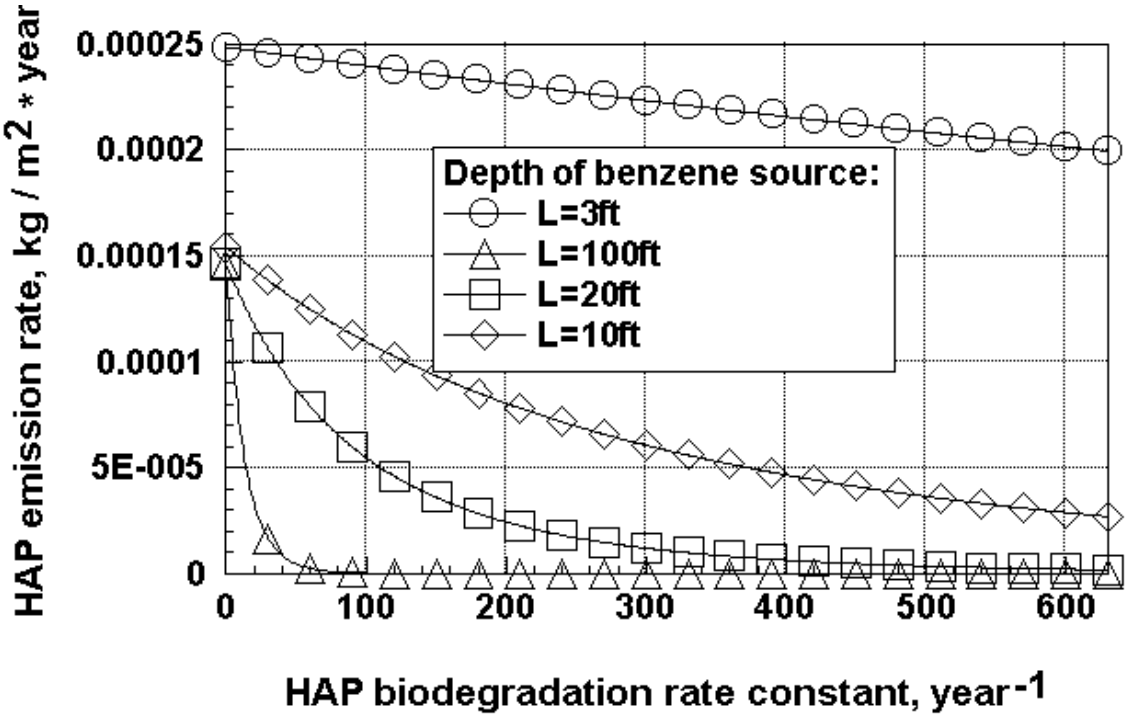

Figure 3

Effect of biodegradation on HAP emission

during time of highest convection for landfill of Table 1