



NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

**EVALUATION OF THE
EPA-RECOMMENDED APPROACH
TO PREDICTING AIR EMISSIONS FROM
PULP AND PAPER INDUSTRY LANDFILLS**

**TECHNICAL BULLETIN NO. 790
SEPTEMBER 1999**

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PRESIDENT'S NOTE

Although the pulp and paper industry's dependence on landfills for management of solid residuals has been declining for the past two decades, the industry still operates a significant number of such facilities and it owns others, which, while properly closed, may still have the potential to generate and emit landfill gas. With the advent of Title V of the Clean Air Act and emerging concerns about global climate change, gas emissions from all kinds of landfills have recently come under closer scrutiny. Because most studies of landfill gas have been done on municipal solid waste (MSW) landfills, default emission factors tend to be based on that type of landfill; however, application of these emission factors to the pulp and paper industry's landfills is problematic. The work reported in this technical bulletin demonstrates that current approaches mandated by EPA to estimate methane and HAP emissions from landfills almost certainly overestimate both from the industry's landfills, perhaps by orders of magnitude. These findings indicate a need to expand our knowledge of the mechanisms of gas formation in the industry's landfills, and the composition and emission rates for those landfill gases.

A handwritten signature in black ink, appearing to read "Ron Yeske", is positioned above the printed name.

Ronald A. Yeske

September 1999

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ABSTRACT

EPA used the Landfill Air Emissions Estimation Model (LAEEM) to calculate Clean Air Act (Title V) requirements for emissions of bulk gases and HAPs from landfills. LAEEM is a PC-based automated estimation tool developed and calibrated specifically for municipal solid waste (MSW) landfills. Field studies have shown that even for MSW, there is significant variation in the values of model parameters, and the user of LAEEM for MSW landfills would therefore be well advised to consider determining actual values through a field calibration study. Compared with MSW landfills, the contents of pulp and paper industry landfills are expected to decompose at lower rates, and ultimately to release lower amounts of methane and non-methane organic compounds, because they are either deficient in nutrients (especially nitrogen) or are inorganic, and because of their higher degree of saturation. Consequently, the extrapolation of MSW landfill emission data may not be appropriate for modeling emissions from pulp and paper industry landfills.

This technical bulletin examines the suitability of applying LAEEM and the AP-42 landfill emission factors to the prediction of bulk gas and HAP emissions from pulp and paper industry landfills, and explores alternative predictive approaches. It concludes that LAEEM, using the EPA-recommended default model parameters, would not provide an accurate representation of methane and HAP emissions from pulp and paper industry landfills. More realistic estimates of methane emissions could be obtained with modified parameter values, but would probably still not provide a realistic estimate of HAP emissions because LAEEM does not account for the attenuating effects of biodegradation and adsorption, nor does it account for the potentially slower migration of landfill gas through a fully saturated landfill zone.

Compositional analysis of gas collected from three pulp and paper industry landfills indicates a general absence of most of the HAP compounds, and suggests that the usage of LAEEM default HAP gas concentrations may lead to gross overestimation of HAP emissions from pulp and paper industry landfills. While a Windows™-based version of the LAEEM model has recently been released as LandGEM (Landfill Gas Emission Model), the modeling assumptions and the default values in the model remain the same.

KEYWORDS

uncontrolled landfill gas emissions, predictive models, methane, hazardous air pollutants, landfill composition, Title V, LAEEM, HAP, LandGEM

RELATED NCASI PUBLICATIONS

Technical Bulletin No. 431 (May 1984). *Landfill gas generation, migration, monitoring and control.*

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EVALUATION OF THE EPA-RECOMMENDED APPROACH TO PREDICTING AIR EMISSIONS FROM PULP AND PAPER INDUSTRY LANDFILLS

1.0 INTRODUCTION

1.1 Background

The U.S. Environmental Protection Agency (EPA) provides guidance for predicting air emissions from industrial and municipal installations through a series of models and emission factors. The models are based on mathematical interpretation of the mechanisms that are thought to be responsible for such emissions. Wherever possible, these models have been calibrated with laboratory and/or field emission data before publication. Where an inadequate understanding of the mechanisms controlling emissions exists, EPA has developed empirical emission factors that are based on wide-ranging field measurements. These emission factors are published in "Compilation of Air Pollutant Emission Factors" (referred to as AP-42) (EPA 1995a).

With respect to emissions from landfills, EPA has published a Landfill Air Emissions Estimation Model (LAEEM) in which the generation of methane is predicted from a simplified first order rate expression governing the degradation of organic matter by anaerobic microorganisms. It was developed as a quick method for screening potential methane and hazardous air pollutant (HAP) emissions from municipal solid waste (MSW) landfills. To compute the total quantity of emissions, a series of assumptions are made to estimate the volumes of carbon dioxide, non-methane organic carbon (NMOC) compounds, and toxic air pollutants or hazardous air pollutants (HAPs) and these are summed with the estimated methane volume. Collectively, these are referred to as uncontrolled landfill gas emissions. Site-specific data may be used to define model parameters or default values may be drawn from New Source Performance Standard (NSPS) emission guidelines or from AP-42. While a Windows™-based version of the LAEEM model has recently been released as LandGEM (Landfill Gas Emission Model), the modeling assumptions and the default values in the model remain the same. For simplicity, the remainder of this technical bulletin refers to the LAEEM model, although the issues discussed are valid for either model.

The pulp and paper industry will be required to comply with Clean Air Act (Title V) requirements to estimate emissions of bulk gases and HAPs from landfills. There is reason to question the applicability of LAEEM to estimate such emissions from industry landfills in view of the fact that it is based upon data gathered for MSW landfills. The physical and chemical nature of materials placed in industry landfills is sufficiently different from that of MSW landfills to generate lower emissions than might be predicted by the model. Similarly, the default landfill emission factors given by AP-42 are based largely on data from MSW landfills. Consequently, the extrapolation of MSW landfill emission data may not be appropriate to industry landfills. This technical bulletin examines the suitability of applying LAEEM and the AP-42 landfill emission factors to the prediction of bulk gas and HAP emissions from pulp and paper industry landfills and explores alternative predictive approaches. For perspective on typical paper industry landfill gaseous emissions, samples of landfill gas from three sites were collected and analyzed.

1.2 Scope of Work

The scope of this report is as follows:

- Review the EPA Landfill Air Emission Estimation Model (LAEEM) and comment on the assumptions upon which it is based and its limitations.
- Investigate the applicability of LAEEM to estimate bulk gas and HAP emissions from pulp and paper industry landfills.
- Evaluate an alternative approach for calculating HAP emissions which account for different HAP removal mechanisms such as volatilization, diffusion, adsorption, and biochemical transformation.
- Collect and analyze landfill gaseous emissions from three typical paper industry landfills.

2.0 BACKGROUND INFORMATION

2.1 Solid Waste Landfills

A modern landfill may be defined as a discrete area of land or an excavation that receives a range of solid waste. A sanitary landfill refers to an engineered facility for the disposal of municipal solid waste (MSW). In this report, the term "MSW landfill" refers to sanitary landfills regulated under Subtitle D of the Resource Conservation and Recovery Act. While pulp and paper industry landfills may also receive a range of solid residues, they more typically contain a much smaller variety of wastes, especially when compared to MSW landfills. In some cases, they receive only one type of waste such as wastewater treatment residuals, in which case, they are known as monofills.

A solid waste landfill can be regarded as a complex biochemical reactor, with solid waste and water as major inputs and landfill gas and leachate as the principal outputs. The solid wastes experience a range of simultaneous and interrelated biological, chemical, and physical changes (Krieth 1994). Landfill gases and leachates are created by the biologically induced conversion of organic materials. Dissolution and suspension of landfill materials and biological conversion products in the liquid percolating through the waste, dehalogenation and decomposition of organic compounds, and oxidation-reduction reactions affecting metals and the solubility of metals salts are important chemical reactions. Physical changes include settlement, evaporation and volatilization of water and other compounds into the vapor phase, and sorption of organic compounds on to the landfilled materials.

More detailed reviews regarding the operation and design of landfills are presented by NCASI (1984), EPA (1991), and others (Krieth 1994, Tchobanoglous et al. 1993).

2.2 Landfill Gas Generation

Landfill gases contain several constituents that are present in large amounts, i.e., the principal gases, and some in very small amounts, i.e., the trace gases. The principal gases, methane and carbon dioxide, are primarily produced by anaerobic decomposition of the biodegradable organic solid residues. Sources of trace gases may be brought to the landfill with the materials deposited there or the trace gases may be produced by biotic and abiotic conversion reactions in the landfill. Typical compositions of MSW landfill gases are shown in Table 1.

Table 1. Typical Constituents Found in MSW Landfill Gas (Krieth 1994; SAIC 1995)

Component	% (dry volume basis)
Methane	45-60
Carbon dioxide	34-60
Nitrogen	2-20
Oxygen	0.1-1.0
Ammonia	0.1-1.0
Sulfides, mercaptans	0-1.0
Hydrogen	0-0.3
Aromatic & Cyclic hydrocarbons	0.2
Paraffin hydrocarbons	0.1-0.2
Carbon monoxide	0-0.2
Other trace compounds	0.01-0.6

The generation of principal landfill gases is thought to occur in several sequential phases during the lifetime of a landfill (Krieth 1994; Pohland and Harper 1986). The first phase is aerobic, mitigated by the presence of oxygen remaining from the time of placement. Carbon dioxide is the major gas produced during this period, which continues until the oxygen is depleted. The remaining phases are anaerobic but follow distinct changes induced by changes in microbial population (Barlaz et al. 1990). Initially, gas production is dominated by carbon dioxide, significant amounts of hydrogen, and declining amounts of nitrogen. As methane production begins, there is a corresponding reduction in carbon dioxide production and a continuing reduction in nitrogen. Once established, methane production continues for many years in a pseudo-steady state condition. It is accompanied by approximately equivalent volumes of carbon dioxide and low levels of nitrogen.

For moderately decomposable wastes, the gas generation rate is thought to peak at the time of, or soon after, closure, and decline steadily afterwards. It is important to recognize that the duration of each phase, and therefore, the rate of landfill gas generation, will vary depending upon the distribution of organic components in a landfill, the availability of nutrients, the moisture content of the solids, moisture routing through the waste material, and the degree of initial compaction. For example, inclusion of nitrogen-limited solids will result in a nutrient imbalance and a retardation of landfill gas production. Insufficient moisture will also retard gas production as will increasing solid waste density. Practicing leachate recirculation through a landfill can substantially increase the total yield and rate of gas production (Pohland and Harper 1986).

From a regulatory perspective, prediction and control of emissions from landfills differs significantly from other emission source categories, such as manufacturing and transportation, because landfills can potentially generate air emissions long after closure.

2.3 Landfill Gas Modeling

Landfill gas simulation models can be classified as (1) models that predict gas generation only; (2) models that describe gas transport only; (3) models that combine gas generation and transport processes; and (4) models that include gas and heat generation and transport. These models have experienced limited success because of inherent complexities associated with the biological, chemical, and physical processes occurring in landfills. They become increasingly useful as field

data are obtained and used for calibration and verification. This report focuses upon gas generation models because LAEEM is based upon gas generation phenomena only. Further details on the other model types may be found in El-Fadel et al. (1997).

Because of the wide variety of biodegradable matter in MSW, no simple equation or rate constant can describe adequately the rate of biodegradation and the rate of gas generation in landfills (El-Fadel et al. 1997). While some substances such as sugars and starches are readily decomposable, other more complex materials such as cellulose require a longer time to degrade and lignins take even longer. The rate of gas generation can be predicted by considering the landfill as a batch reactor and invoking the Monod microbial growth model to express a relationship between substrate concentration and substrate utilization rate. Gas generation models with first or zero order kinetics are widely used models in engineering practice, with first order being the most common. In first order reactions, the rate of reaction is directly proportional to the concentration of substrate remaining; that is, they imply an environment capable of supporting biological activity in accordance with substrate availability. These models emphasize gas production for evaluating the potential benefit of gas recovery from MSW landfills and sizing landfill gas collection systems. Table 2 summarizes the most widely used models in addition to LAEEM. In using these models, there is an acceptance of inherent uncertainty in model predictions as a result of inadequate knowledge about the degradable refuse constituents, the model parameters such as lag, peak, and half-times, the parameters in the gas generation function, such as the first order decay rate, and refuse landfilling rates. For the most part, they are considered to be partially validated and therefore relatively site specific.

Table 2. Summary of Selected Gas Generation Models (El-Fadel et al. 1997)

Model	Description
EMCON Associates and Jacobs Engineering Co., 1976 (Scholl Canyon Model)	Single stage first order kinetic model. Tends to overestimate gas production. EPA LAEEM model uses similar logic.
Los Angeles Bureau of Sanitation, 1976 (Sheldon Arleta Model)	Two stage first order kinetic model. Two types of waste assumed: readily and slowly decomposable.
Los Angeles Municipal Environmental Research Laboratory, 1977 (Palos Verdes Model)	Two stage first order kinetic model. Three types of waste assumed: readily and moderately decomposable, and non-decomposable.
Halvadakis, 1983 (EMCON MGM)	Approximated gas generation rate with a triangular function. User must assign lag, peak, and conversion times.
Halvadakis, 1983 (MICROGEN)	Based on differential equations describing biological processes and biochemical reactions. No site-specific applications provided.
Hoeks, 1983	Exponential decay model based on first order degradation. No comparisons with field data.
Young, 1985, 1995	Model which uses sequential degradation. No comparisons with field data.
Marticorena, et al., 1992, 1993	First order model treating a landfill as layers deposited at different times. Used to simulate site-specific measurements at MSW landfills.
Gardener and Probert, 1993	Presented an exponential decay model based on first order reactions. Has been correlated with site-specific data. Records of type, composition, and dates of filling required for accuracy.

3.0 CURRENTLY APPROVED REGULATORY LANDFILL AIR EMISSIONS ESTIMATION MODEL AND EMISSION FACTORS

3.1 The EPA Landfill Air Emissions Estimation Model

The EPA Landfill Air Emissions Estimation Model (LAEEM) is a PC-based automated estimation tool, operating in a Windows™ environment, for calculating uncontrolled air emissions from municipal solid waste (MSW) landfills. LAEEM was developed for EPA by Radian Corporation (EPA 1996). It is public domain software available from the EPA Office of Air Quality Planning and Standards.

Model development was driven by the need to control air emissions from MSW landfills as required by Sections III(b) and III(d) of the Clean Air Act (CAA). Landfill emissions were regarded to exert adverse health and welfare impacts caused by the presence of non-methane organic compounds (NMOCs), toxic and hazardous air pollutants (HAPs), compounds that were explosive and odorous, and compounds that contributed to global warming effects (primarily methane).

The model was developed to serve as a quick method for screening potential methane and HAP emissions from MSW landfills to determine the applicability of the control requirements of the 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 generation from MSW landfills (Section 2). With the assumption that landfill gas acts as a carrier for NMOCs and HAPs, emission estimates of these compounds are made from the total landfill gas flow rate, based on the further assumption that landfill gas is an equal mixture of methane and carbon dioxide. The model was not intended to be used to estimate emissions for inventories or control equipment design. AP-42 emission factors were introduced in the model subsequently for this purpose as discussed later.

EPA's approach was to use the most simplified model available that was consistent with fundamental principles (EPA 1991). Kinetic rate coefficients were empirically adjusted to reflect changes in refuse moisture content and other landfill conditions. The Scholl Canyon model (Table 2), which is a first order, single stage model (EMCON Associates and Jacobs Engineering Co., 1976; EMCON Associates, 1980), was selected as the basis for LAEEM. The Scholl Canyon model makes two important simplifications that are contrary to reported observations (Section 2) in that it assumes that the gas production rate is at its peak upon initial waste placement and that anaerobic conditions are established immediately. Gas production is then assumed to decrease exponentially as a first order decay. The model allows for division of the landfill into modules (annual refuse accumulations) to account for different ages of the refuse accumulated over time. The total methane generation from the entire landfill (sum of each module's contribution) is at its peak upon landfill closure if a constant annual acceptance rate is assumed. Assuming that the refuse has been accepted at the same annual rate over time (i.e., all modules are the same), the following fundamental model equation is derived:

$$Q_{CH_4} = L_0 R (e^{-kc} - e^{-kt}) \quad (1)$$

where Q_{CH_4} is the methane generation rate at time t , $m^3/year$; L_0 is the potential methane generation capacity of the refuse, m^3/Mg ; R is the average annual refuse acceptance rate during active life, $Mg/year$; k is first order decay or methane generation rate coefficient, $year^{-1}$; c is the time since landfill closure, year; t is the time since the initial refuse placement, year.

The second model assumption can be accounted for by incorporating a lag time during which anaerobic conditions are established by substituting c and t with $(c + \text{lag time})$ and $(t + \text{lag time})$, respectively.

In addition to the assumption of first order kinetics and no other model mechanistic assumptions (discussed in subsequent sections), there are other limitations of LAEEM that may cause it to produce conservative (high) gas emission rates:

- It is assumed that nutrient availability is the only limiting factor on bacterial activity in a landfill (EMCON Associates 1980). Other environmental factors that limit gas production rates such as moisture content, temperature, pH, and nature of landfill contents are not considered.
- The model is based upon estimates of gas production measurements at several California landfills. These landfill covers were characterized by high permeability because they were made primarily from sand and gravel (reference 7 in Alberico et al. 1997). While this factor does not preclude a reasonable estimate of methane generation, the model will predict high *uncontrolled* methane gas emissions. Modern practice is to use landfill covers that are made predominately from dense clay that will not allow gas diffusion as readily as sand and gravel.
- The model does not allow for changes in landfill cover depth or biological and/or chemical reactions that might take place in the cover material, all of which can attenuate or reduce uncontrolled landfill gas emissions.
- The model assumes that maximum gas production occurs shortly after landfill closure. This may be true of California landfills, but in cold climate areas, maximum methane production rates may be greatly attenuated and/or delayed.
- The prediction of NMOC or HAP emissions is not based upon fate modeling approaches that are typically used in the wastewater treatment field. Rather, NMOC and HAP emissions are estimated assuming that the methane acts as a transport gas for the NMOCs and HAPs (EPA 1991).

3.2 Use of LAEEM

LAEEM is available in two formats, one for a Windows™ platform and the other for a DOS platform. The software is set up to model and store multiple landfill studies. Within a specific landfill study, reports and graphs of the estimated emissions can be produced for any particular air pollutant. The model provides the following features:

- Emission rate estimates for methane, NMOC, and HAPs emitted from solid waste landfills annually over the life of the landfill and for a specified number of years after the landfill has closed.
- Estimates of emissions based either on user-specified values for the parameters needed or on system default values. Two different sets of model default values are provided for calculating emissions. The first set, the CAA defaults, determine the applicability of the NSPS or emission guidelines for MSW landfills. These values were developed for national regulatory compliance purposes, that is, the maximum expected values with which to determine the applicability of the NSPS for new MSW landfills and the emission guidelines for existing MSW landfills (40 CFR 60 Subparts WWW and Cc). As a result, they are conservative in order to protect human health and to encompass a wide range of landfills. The second set, the AP-42 defaults, are based on emission factors from AP-42, which were derived from an EPA review of methane generation data from typical MSW landfills (EPA 1995b). The AP-42 default values are less conservative

than the CAA default values, and provide emission estimates that should reflect typical landfill emissions. They are suggested for use in developing estimates for state emission inventories. The most recent (November 1998) values of the CAA AP-42 defaults are less conservative than the previous values and are based on the results of a November 1997 MSW landfill litigation settlement. These values are used throughout this text.

A typical procedure for estimating emissions from a landfill would consist of five steps: (1) opening a landfill study; (2) defining the operating parameters of the landfill such as the area and waste deposition history of the landfill; (3) selecting model parameters for calculating emissions; (4) reporting emissions; and (5) saving the landfill study file. Detailed procedures for using the software are available in a user's manual, which is also available from the EPA Office of Air Quality Planning and Standards (EPA 1996).

3.3 Model Parameters

The solution of Equation 1 requires information for several parameters. Site-specific data are generally available for R, c, and t. When waste acceptance rate data are poor, R can be determined by dividing the wet mass of refuse in place by the landfill age. Also, non-degradable wastes should be subtracted from the accepted mass to prevent overestimation of methane generation.

The accuracy of methane (and, therefore, total gas) generation estimates depends greatly on the values assigned to the two landfill specific parameters, k, the first order decay rate coefficient, and L_0 , the potential methane generation capacity of the waste. EPA's estimation of these two key parameters was relatively controversial because of the limited database upon which recommended default values were initially based and because, in the preliminary development round, the data were drawn primarily from southern California landfills. Values for k and L_0 are preferably estimated from site-specific gas generation data but these are unlikely to be available over the requisite long periods of time. In the absence of site-specific data, EPA recommended that default values be used.

The concentrations of principal and trace gases must be specified. In the absence of site-specific data based upon landfill gas analysis, default concentration values are recommended by EPA for methane, carbon dioxide, NMOCs, and HAPs.

This section discusses the assignment of values to the principal parameters in LAEEM, the default values for these parameters, and the rationale for selection of the default values.

3.3.1 *The First Order Decay Rate Coefficient, k*

The first order decay rate, k, is an estimate of the methane generation rate in a specific landfill. The higher the value of k, the faster the methane generation rate from each module decreases with time. Although the value of k is known to be a function of solid waste moisture content, nutrient availability, pH, and temperature, there is no mechanistic attempt to express the sensitivity of k to these variables in the model. Estimates of k are empirical.

The k values obtained from the data collected for the NSPS and emission guideline development ranged from 0.003 to 0.21 year⁻¹ (EPA 1991). While sources of these data included the literature, laboratory simulators, model simulations following calibration with field test data, and field measurements, all of the data sources were related to MSW landfills. (The following discussion is relevant to the other model parameters discussed in the following sub-sections.) There were no long-term landfill gas generation data available to estimate k values by regression. Instead, a limited number of gas flow measurements were collected at 58 landfills using EPA Method 2E (EPA 1991), a procedure developed during the guideline investigations. These measurements could be regarded only as single point estimates of gas generation rate and were used to back calculate estimates of k

using the Scholl Canyon model for three assumed values of L_0 to test the suitability of paired values of k and L_0 . These values represented the 20th, 50th, and 80th percentile values available in the literature (Pelt 1991). After receiving criticism for the model and model parameter values that were selected on the basis of the above analysis, the EPA collected new data and revised the procedures to estimate default model parameters (Pelt 1993). Data from 44 landfills in different parts of the U.S. were used in this analysis. Table 3 presents CAA and AP-42 default values for k and L_0 .

Table 3. EPA Default Values for k and L_0 (EPA 1998)

Source	k (year ⁻¹)	L_0 (m ³ CH ₄ /Mg waste)
EPA AP-42	0.04	100
EPA CAA	0.05 (0.02)*	170

* for arid regions (rainfall < 25 in per year)

An EPA-sponsored pilot investigation of landfill gas recovery systems at six MSW landfills evaluated the effects of climate on methane production rates (Campbell et al. undated). It could not demonstrate a relationship between methane generated per ton of solid waste, the climate, or landfill age because the sample size was too small. It was observed that data on landfill composition were very limited. This made it difficult to account for differences in landfill characteristics. A further study by the same investigators (Peer et al. undated) on 21 MSW landfills from all parts of the U.S. showed that methane generation was relatively poorly correlated to landfill depth and solid waste mass. None of the climate variables (rainfall, temperature, dewpoint) could be correlated to methane generation rate.

3.3.2 Methane Generation Potential, L_0

The theoretical value of L_0 depends on the type of solid waste only and is based upon an empirical formula representing the chemical composition of the solid waste components. The higher the cellulose content, the greater the value of L_0 . The obtainable value of L_0 accounts for nutrient availability and moisture content. It is estimated from overall biodegradability of the waste components and is regarded to be lower than the theoretical L_0 . Even if a waste has a high cellulose content, if the landfill conditions are not conducive to anaerobic microorganisms, the methane generation potential may never be reached. Values of theoretical and obtainable L_0 ranged from 220 to 9540 ft³ (6.2 to 270 m³) CH₄/Mg of waste (EPA 1991). In the follow-up investigation of 44 landfills, it was concluded that 2,000 to 7,000 ft³ (57 to 198 m³) CH₄/Mg of waste was the range that most probably represented the actual methane generation potential from material in MSW landfills (Pelt 1993).

In the absence of landfill-specific data, EPA recommends the use of default L_0 values. The most recent (November 1998) CAA default value is 6,000 ft³ (170 m³)/Mg of waste (Table 3). The lower AP-42 default value of 3,530 ft³ (100 m³)/Mg of waste is recommended for emission inventory purposes.

Recently, an opportunity to test the validity of the default values for k and L_0 arose at MSW landfills operated by the Los Angeles County Sanitation Districts. These landfills were among the first in the U.S. to install landfill gas recovery systems and now have available over 20 years of gas generation

data. Site specific k and L_0 parameters were estimated using a simple spreadsheet first order model virtually identical to LAEEM (Huitric and Soni 1997). As shown in Table 4, the k and L_0 values were similar to the AP-42 default values. However, at the time of publication of their paper, the AP-42 default value for L_0 was 125 m^3/Mg , suggesting a more conservative default value. EPA has recognized this and, as of November 1998, has been recommending the lower value of 100 m^3/Mg . Since long-term landfill gas generation data are not available for pulp and paper industry landfills, this technique for determining site-specific k and L_0 values is probably not applicable by the industry.

Table 4. Comparison of Measured and Default k and L_0 Values

Source	$k(\text{year}^{-1})$	L_0 ($m^3 \text{ CH}_4/\text{Mg waste}$)
EPA AP-42 (1995a)	0.04	125
EPA AP-42 (1998)	0.04	100
Huitric & Soni (1997)	0.03 – 0.04	39.9 – 125.7

An example calculation in Appendix C (Example 1) illustrates the application of AP-42 default values for k and L_0 in LAEEM for the case of a typical pulp and paper industry landfill using landfill dimensions given later in Table 11.

3.3.3 *Non-Methane Organic Compounds (NMOCs)*

The level of NMOCs found in landfill gases depends upon the constituents of the waste materials in the landfill. LAEEM contains no mechanistic fate models (similar to those used in the wastewater treatment field) that account for the emission of individual air pollutants. Instead, the model uses a selection of emission factors in concert with the total gas flow rate to estimate the mass of NMOC emissions.

In order to generate the emission factors, data from responses to Section 114 questionnaires, from a national landfill management company, and from South Coast Air Quality Management District (SCAQMD) emission test results were reviewed to formulate generic default values for total NMOC emission factors (EPA 1991; Pelt 1993). In all, data from 23 landfills were reviewed, including six that were regarded as co-disposal sites; that is, they received hazardous waste as well as municipal solid wastes (EPA 1991). To simplify the basis of comparison, EPA normalized the NMOC data with respect to hexane. The concentrations of total NMOCs ranged from 237 to 14,294 parts per million by volume (ppmv) as hexane. In the revised database evaluated in 1993, total NMOC concentrations ranged from 186 to 9,437 ppmv as hexane.

The concentrations for methane and carbon dioxide must be specified before setting values for total NMOCs. The default values for methane and carbon dioxide assume equal volumes of both gases. These values can be changed when site-specific data are available. Total NMOC concentrations are related to the system defaults, so selecting CAA or AP-42 defaults for k or L_0 will invoke the corresponding defaults for total NMOC concentrations. As of this writing, EPA recommends three default total NMOC concentrations for use in the model (EPA 1996): one for the CAA default option and two for the AP42 default option (one for co-disposal and one for non co-disposal as shown in Table 5).

Table 5. Comparison of Default Values for Total NMOC Concentrations

Default	Total NMOCs as Hexane equivalents (ppmv)	
CAA	4,000	
	Co-disposal with hazardous wastes	
	<i>Yes</i>	<i>No</i>
AP-42	2,420	595

These default emission factors were developed from gas concentrations at MSW landfills, and are unlikely to reflect NMOC emissions from pulp and paper industry landfills in view of the difference in make up of the two types of landfills. However, the EPA encourages the collection of site-specific data (using the recommended Method 25C [EPA 1991] for sample analysis) but the total NMOC data must be corrected for air infiltration into the collected landfill gas as shown in AP-42 (EPA 1998, 1995a). Example 2 in Appendix C demonstrates the use of LAEEM to calculate total NMOC emissions.

To derive recommended default values of *individual* NMOCs, the review of NMOC data also focused upon the concentrations of individual NMOCs in landfill gases. Responses to Section 114 letters and SCAQMD test results from the 46 landfills survey indicated that after carbon dioxide, ethane, toluene, and methylene chloride were the major NMOC constituents, with average concentrations of 143, 52, and 20 ppmv, respectively. The most frequently detected compounds were trichloroethylene, benzene, and vinyl chloride (EPA 1991). A disproportionate amount of data in this review were from California so that site-specific variables such as climatic conditions, soil structure, waste composition, and landfill size were not accounted for (EPA 1993).

Based upon the above review, the recommended individual NMOC (and some inorganic compound) concentrations (corrected for air infiltration) that may be used in LAEEM when site-specific data are not available, are listed in Table 6 for non co-disposal landfills (EPA, 1998). An extensive statistical analysis demonstrated that the only statistically significant differences of individual emissions between the co-disposal and the non co-disposal scenarios were for benzene and toluene. For the co-disposal scenario, the default concentration for those compounds are 11.1 and 165 ppmv, respectively.

Table 6. Default Concentrations for Air Pollutants Listed in LAEEM (EPA 1998)

Chemical	Concentration (ppmv hexane equivalents) <i>Non Co-disposal</i>
1,1,1-Trichloroethane (Methyl Chloroform)*	0.48
1,1,2,2-Tetrachloroethane*	1.11
1,1-Dichloroethane (Ethylidene Chloride)*	2.35
1,1-Dichloroethene (Vinylidene Chloride)*	0.20
1,2-Dichloroethane (Ethylene Dichloride)*	0.41
1,2-Dichloropropane (Propylene Dichloride)*	0.18
2-Propanol	50.1
Acetone	7.01
Acrylonitrile*	6.33
Benzene*	1.91
Bromodichloromethane	3.13
Butane	5.03
Carbon Disulfide*	0.58
Carbon Monoxide	141
Carbon Tetrachloride*	0.004
Carbonyl Sulfide*	0.49
Chlorobenzene*	0.25
Chlorodifluoromethane	1.30
Chloroethane (Ethyl Chloride)*	1.25
Chloroform*	0.03
Chloromethane	1.21
Dichlorobenzene (p)*	0.21
Dichlorodifluoromethane	15.7
Dichlorofluoromethane	2.26
Dichloromethane (Methylene Chloride)*	14.3
Dimethyl Sulfide (Methyl Sulfide)	7.82
Ethane	889
Ethanol	27.2
Ethylbenzene*	4.61
Ethyl Mercaptan	2.28
Ethylene Dibromide	0.001
Fluorotrichloromethane	0.76
Hexane*	6.57
Hydrogen Sulfide	35.5
Mercury (total)*	2.92×10^{-4}
Methyl Ethyl Ketone*	7.09
Methyl Isobutyl Ketone*	1.87
Methyl Mercaptan	2.49
Pentane	3.29
Perchloroethylene (Tetrachloroethylene)*	3.73
Propane	11.1
Toluene*	39.3
Trichloroethene (Trichloroethylene)*	2.82
t-1,2-Dichloroethene	2.84
Vinyl Chloride*	7.34
Xylenes*	12.1

*HAPs as defined in the Clean Air Act

3.3.4 Hazardous Air Pollutants (HAPs)

In the absence of site-specific data, default HAP concentrations that are recommended for use with LAEEM are given in Table 6 (asterisked items). Landfill sites that have hazardous waste co-disposal or Superfund sites should use the co-disposal option for estimating HAP emissions. In cases where it is not known whether a landfill has ever been used for hazardous waste, the co-disposal option should be invoked. However, in all cases, EPA recommends that test data be collected for HAPs (using Method 18) to obtain more accurate estimates of HAP emissions. Example 3 in Appendix C demonstrates the use of LAEEM to calculate HAP emissions.

Recently, Alberico, et al. (1997) measured in-situ ambient air concentrations of a critical HAP, vinyl chloride, at two MSW landfills in Ontario, Canada. The Ontario Ministry of Environment uses LAEEM with the AP-42 default parameters to determine if landfill gas control systems are required at landfills. The Alberico study found measured ambient air concentrations of vinyl chloride to be 1% to 16% of those predicted by the model. Key results are summarized in Table 7. This study casts doubt on the ability of LAEEM to accurately calculate HAP emissions using the AP-42 default HAP values.

Table 7. Comparison of LAEEM-Predicted Vinyl Chloride Emissions to Measured Values at Two Canadian Landfills (Alberico, et al. 1997)

Landfill	Predicted Average Concentration ($\mu\text{g}/\text{m}^3$)	Measured Average Concentration ($\mu\text{g}/\text{m}^3$)
Eastview (Guelph, Ontario)	0.260	0.041
Britannia (Mississauga, Ontario)	4.860	0.045

3.4 LAEEM and Emission Factors - Summary

The EPA Landfill Air Emissions Estimation Model (LAEEM) is a PC-based automated estimation tool, operating in a Windows™ environment, for calculating uncontrolled air emissions from landfills. It was developed and calibrated specifically for municipal solid waste (MSW) landfills. It is based upon a simple first order decay model that predicts the rate of methane generation as a function of the biodegradation of organic matter in the landfill. It assumes equal volumes of carbon dioxide production to predict overall landfill gas flow rates. The accuracy of prediction hinges upon the values selected for k , the first order decay rate and L_0 , the methane generation potential. The model incorporates k and L_0 default values, which were based upon a limited data set. Recent data presented in this bulletin suggest that lower values, especially for L_0 , might be more appropriate even for MSW landfills.

Prediction of NMOCs and HAPs is based upon the assumption that the landfill gas acts as carrier gas, stripping and transporting trace volatile compounds from the landfill. EPA provides default values for 46 air pollutants for use in computing mass emissions when site-specific data are lacking. Default concentration values are provided in the model for 46 air pollutants. The derivation of these default values was based upon a limited data set, that may not be representative of landfill characteristics on a nation-wide basis. Recent data presented in this bulletin for one HAP compound in landfill gases measured at two landfills suggest there may be a high level of conservatism in the default air pollutant concentrations.

4.0 IMPLICATIONS OF USING THE EPA LANDFILL AIR EMISSIONS ESTIMATION MODEL IN THE PULP AND PAPER INDUSTRY

In order to facilitate a better understanding of the limitations associated with the application of LAEEM to pulp and paper industry landfills, the following is a comparison of the physical and chemical attributes of municipal and pulp and paper industry landfills.

4.1 Characteristics of Municipal Solid Waste Landfills

Municipal solid waste (MSW) landfills have evolved from the open dumps of the fifties into the highly engineered and regulated sanitary landfills of the nineties. The passage of the 1993 Subtitle D Municipal Waste Regulations of the Resource Recovery and Conservation Act has significantly upgraded design standards for municipal solid waste landfills. Modern landfill designs include a composite liner and leachate control system, and landfill gas recovery and utilization systems.

The typical composition and moisture content of MSW landfilled in the U.S. has been reported by Tchobanoglous et al. (1993) as shown in Table 8. Using these data, a composite moisture content of about 21% can be calculated.

Table 8. Typical Composition and Moisture Content of U.S. MSW (Tchobanoglous, et al 1993)

Component	Percent by Dry Weight	Percent Moisture
<i>Organics</i>		
Paper	34.0	6
Yard waste	18.5	60
Food wastes	9.0	70
Plastics	7.0	2
Cardboard	6.0	5
Textiles	2.0	10
Wood	2.0	20
Leather	0.5	10
Rubber	0.5	2
<i>Total</i>	<u>79.5</u>	-
<i>Inorganics</i>		
Glass	8.0	2
Tin cans	6.0	3
Other metals	3.0	3
Dirt, ash	3.0	-
Aluminum	0.5	2
<i>Total</i>	<u>20.5</u>	-

MSW landfills are designed and operated to exclude external water from precipitation and runoff. They are also operated to achieve high in-place densities, typically in the range of 37 to 44 lb/ft³. MSW landfills are unsaturated, with void space that facilitates gas flow.

4.2 Characteristics of Solid Wastes Placed in Pulp and Paper Industry Landfills

NCASI has collected data that characterize pulp and paper industry landfills and the materials placed in them. Figure 1 and Tables 9 through 11 summarize some of this information. Table 9 indicates the type and proportions of treatment residuals currently being placed in company landfills. Figure 1 and Table 9 present industry-wide statistics regarding the types and proportions of materials placed in industry landfills. Table 10 presents wastewater treatment residuals properties prior to landfilling. The properties of landfilled residuals may change over time in response to precipitation, landfill design, consolidation, biological activity, etc. Table 11 presents some statistics on overall amounts of material landfilled by the industry nationally, but inferences as to the makeup of a “typical” or “representative” landfill cannot be drawn from the tables.

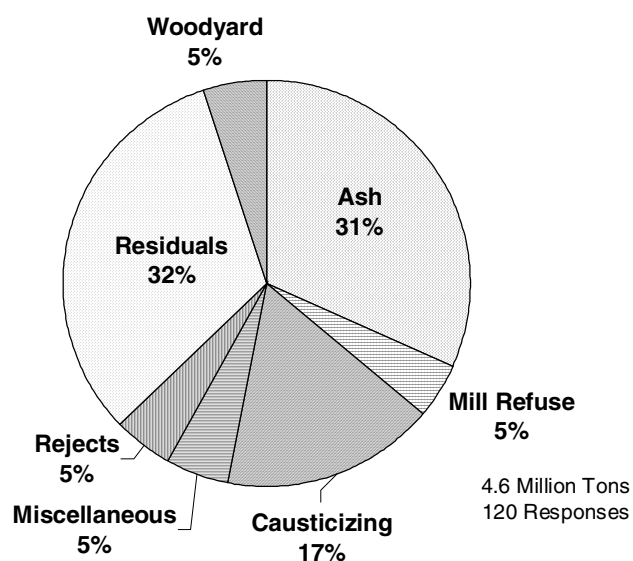


Figure 1. Materials Placed in Company-Owned Landfills Industry-Wide

While the tables and figure present data on the characteristics of pulp and paper industry solid wastes managed by landfilling and of the landfills themselves, a review of data on the specific contents of a limited number of landfills (NCASI 1992) indicates that differences between facilities in amount and type of production, power generation and energy recovery operations, regulatory requirements, and beneficial use opportunities, etc. yield wide variations in landfill characteristics with regard to design, type of materials contained, and relative quantities of each type of material present in any particular industry landfill.

MSW landfills probably have much more heterogeneous content than pulp and paper industry landfills, but ironically, there may well be less variation in composition between MSW landfills than there is between pulp and paper industry landfills.

Table 9. Wastewater Treatment Residual Types Sent to Pulp and Paper Industry Landfills (NCASI 1999)

Residual Type	Percent by Dry Weight
Primary	38
Secondary	1
Combined	56
Dredged	5

Table 10. Properties of Wastewater Treatment Residuals Sent to Pulp and Paper Industry Landfills (NCASI 1989, 1998)

Property	Range	Median Value
Solids Concentration (percent)	8-75	35
Porosity (percent)	73-86	80
Density - wet basis (lb/ft ³)	48-72	69
Ash Content (percent)	10-75	53

Table 11. Pulp and Paper Industry Landfill Characteristics (NCASI 1992)

Landfill Characteristic	Range	Median Value
Capacity (acre)	1.5-500	28
Current use (acre)	0.4-200	11
Final Depth (ft)	5-180	30
Final Volume (yd ³)	1,000-1,300,000	12,000

It is thus difficult to make specific and direct comparisons of pulp and paper industry landfills to MSW landfills. It is possible, however, to make general statements about how differences between the types of materials in MSW landfills and those in pulp and paper industry landfills would lead to differences in the ways in which landfill gas and associated compounds are generated and emitted. The behavior of any specific pulp and paper industry landfill would, of course, depend on the particular characteristics of that landfill.

4.3 Landfill Gas Generation Potential – Estimation of k and L₀

MSW landfills contain a high proportion of yard wastes (18.5 percent, Table 8), which are rich in nitrogen. This and other nitrogen-rich material in MSW provide sufficient nutrients, at least in parts of the landfill, to support vigorous anaerobic biodegradation of the organics present in the landfill. Pulp and paper industry landfills do not normally contain these materials. While secondary wastewater treatment residuals from pulp and paper mills may have carbon to nitrogen ratios that

favor biodegradation of organic material, only 1% of the residuals sent to company landfills are such biosolids. Table 9 indicates that 56% of landfilled wastewater treatment residuals are a combination of residuals from primary and secondary wastewater treatment with the majority of the combination usually being from primary treatment; 38% of landfilled residuals are primary residuals alone. Primary residuals contain only 0.27% nitrogen and even combined primary and secondary residuals contain only 0.85% nitrogen (median values – NCASI 1984a). These data show that wastewater treatment residuals placed in pulp and paper industry landfills tend to be deficient in the nitrogen needed to support anaerobic degradation.

The contention that nitrogen deficiency suppresses gas generation is supported by results of laboratory anaerobic digestion tests on pulp and paper wastewater treatment residuals. Digester gas generation rates were observed to be 0.4 to 0.55 m³/kg volatile solids destroyed (NCASI 1984b). This is about half the value for typical municipal wastewater sludge. For a median residual solids content of 35% (Table 10), L₀ can be calculated from these data to range from 44 to 88 m³/Mg wet residuals. This is one-third to two-thirds of the AP-42 default value for L₀ derived by EPA for MSW landfills.

Some landfills may contain only combustion ash residues (coal ash, wood ash, and treatment residuals ash) which constitute over 30% of the materials placed in industry landfills (Figure 1), or mixtures of ash and causticizing materials (lime mud, green liquor dregs, and lime slaker grits). These materials are predominantly inorganic and therefore unlikely to biodegrade and produce significant quantities of landfill gas. Additionally, these materials have pHs which typically are outside those required for biological activity and well outside those amenable to methanogenic activity. The remaining “Miscellaneous” shown in Figure 1 which are sometimes placed in industry landfills contain varying amounts of organic material, but most of the organic content is cellulose or bark both of which are deficient in nitrogen and other nutrients.

Thus, materials placed in pulp and paper industry landfills are either deficient in nutrients (especially nitrogen) to support anaerobic decomposition or they are inorganic and not subject to anaerobic decomposition to produce landfill gas. These observations taken together indicate that the potential for pulp and paper industry landfills to produce gas is lower than it is for MSW landfills. This conclusion is corroborated by the observation that as of this writing there are no commercial (i.e., for profit) landfill gas collection systems installed at any U.S. pulp and paper industry landfills whereas such systems are frequently found at MSW landfills.

Using the default MSW landfill-based values for k and L₀ in LAEEM will very likely lead to overestimation of landfill gas generation rates from industry landfills. Field and laboratory experiments could be done to confirm this conclusion. NCASI plans to initiate laboratory studies in 1999.

4.3.1 Loss of Methane by Oxidation in Landfill Covers

Recent work on modeling kinetics of methane oxidation in MSW landfill covers suggests that much of the methane passing from a landfill into the cover can be completely oxidized (Bogner et al. 1997). Methanotrophic bacteria oxidize methane to carbon dioxide by using the methane monooxygenase (MMO) enzyme system. Work by other investigators (references 2-7 in Bogner et al. 1997) has shown that methanotrophic methane oxidation in aerated cover soils can be a major natural control on methane emissions. A PC-based three-dimensional finite difference model, the Landfill Methane Emissions Model (LMEM), developed by Bogner et al. (1997), simulates gas mass transfer through the cover and microbial methane oxidation. LMEM predictions were shown to mimic methane oxidation measured in laboratory and full scale landfills.

For industry landfills, where landfill gas is generally not recovered but is allowed to migrate through the cover as uncontrolled emissions, it is likely that a large portion of the methane and perhaps other gases are oxidized within the cover. This would reduce the amount of methane in the landfill gas emitted. The default values for k and L_0 used in LAEEM do not account for methane oxidation since they are based on data from gas collection systems, not measurements of emissions through landfill covers. Therefore, the default values may be overpredictive of emissions from industry landfills for this reason alone.

4.4 Estimates of HAP Emissions

Much of the information on NMOCs and HAPs that was used to derive default parameters in LAEEM was based upon a limited database collected primarily at California landfills. These landfills were nearly all MSW landfills with a few co-disposal landfills included in the database. There were sufficient air pollutants present in these test sites to warrant the inclusion of default emission factors for 46 air pollutants in LAEEM. Table 12 lists concentrations of HAPs that were measured in 22 pulp and paper industry landfill leachates (NCASI 1992). More than 30 HAPs were found but only 13 HAPs were detected in one or more leachates. Ten of the 30 HAPs were detected only once, suggesting that their presence is not common in industry leachates. Of the 13 HAPs in Table 12, only toluene was detected frequently. From Henry's Law, the very low HAP concentrations in the leachates correspond to low levels in landfill gas that might be in equilibrium with the leachate. Although no direct inference is possible regarding the concentration of HAPs in landfill gas from leachate data, the data do strongly suggest that HAPs in industry landfill gases should be present only at very low concentrations if they are present at all. They would almost certainly be much lower than the default concentrations used in LAEEM. Therefore, use of the default HAP concentrations in LAEEM will likely predict overly high emissions of HAPs from industry landfills. Measurement of HAPs in industry landfill gases would help verify this supposition.

Table 12. Typical HAP Concentrations in Pulp and Paper Industry Landfill Leachates (NCASI 1992)

HAPs in one or more leachates	No. of Samples	No. of non-detects	HAP Concentration ($\mu\text{g/L}$)	
			Median (MDL)	Maximum
Benzene	18	17	ND(10)	1.6
Chlorobenzene	18	17	ND(5)	5.4
Chloroform	18	17	ND(5)	24
1,1-Dichloroethane	13	12	ND(3)	9.2
1,2-Dichloroethane	18	17	ND(5)	5.9
t-1,2-Dichloroethylene	13	12	ND(3)	19
Ethylbenzene	13	11	ND(3)	2.1
Methyl ethyl ketone	13	11	ND(100)	2917
Tetrachloroethylene	13	12	ND(3)	3.4
Toluene	18	7	35	820
Trichloroethylene	18	17	ND(5)	2600
Trichlorofluoromethane	12	11	ND(3)	6.6
Xylene	12	11	ND(3)	23

ND – nondetect

MDL – method detection limit

4.4.1 Industry Landfill Gas Characterization Study

For perspective on typical industry landfill gaseous emissions, NCASI had a contractor (EMCON, Inc.) collect and analyze landfill gas at three U.S. pulp and paper industry landfills. The sites were chosen because they are among the few in the industry with gas collections systems. Landfill gas samples were acquired in May 1998 from the three industry landfills identified as Sites A-1, A-2 and A-3. General characteristics of these sites are presented in Table 13.

Table 13. Characteristics of Sampling Sites

Site	Location	Mill Type	Landfill Operating Status	Gas Extraction System Type
A-1	Northeastern U.S.	Tissue & Coarse Paper	Closed	Passive Venting
A-2	Northeastern U.S.	Bleached Kraft Pulp & Fine Paper	Closed	Passive Venting
A-3	North Central U.S.	Bleached Kraft Pulp & Fine Paper	Active	Active Extraction

Samples from each facility were collected in an evacuated 6-L Summa® canister and forwarded directly to a contract laboratory for EPA TO-14 (Volatile Organic Compounds), ASTM D1945 (Natural Gas) and EPA Method 15/16 (Sulfur Compounds) analyses. Samples from Site A-1 were acquired from two of seven existing passive vents along the crest of the disposal area, and composited into a single Summa® canister for analyses. The sample from Site A-2 was acquired from the lone passive vent located approximately in the center of the site. The passive venting systems at site A-1 and A-2 consist of shallow trenches and/or wells, installed as part of the final cap construction. The passive vents were sealed prior to sampling and sample collection was carefully monitored to prevent air intrusion during sampling. The sample from Site A-3 was taken from the gas stream flowing to the enclosed flare system; and thus represents an average composition from the entire active collection system. Review of previous flow and gas quality data collected from Site A-3 indicates that the sample was obtained under conditions that represent typical daily extraction conditions.

Analytical results from the landfill gas samples are presented in Tables 14, 15, and 16. Included in each table are the AP-42 default concentrations for MSW landfills (EPA 1998). Table 14 presents concentrations of bulk gases and values for Btu and specific gravity. Table 15 presents analysis results of sulfur compounds. Table 16 presents concentrations of volatile organic carbon (VOC) compounds. HAPs are denoted in Table 16 and comprise approximately half of the compounds reported.

Examination of Table 14 show that methane (CH₄) and carbon dioxide (CO₂) concentrations from the passive (static) venting systems generally agree with the AP-42 defaults. However, the CH₄ and CO₂ concentrations for the actively vented Site A-3 sample are much lower. This is probably due to the fact that the system is primarily operated to minimize escape of odorous gases from the landfill. System flows are kept quite high, probably resulting in more air infiltration than would occur in a passive system. The elevated oxygen and nitrogen concentrations for Site A-3 are in accord with this scenario.

Table 14. Natural Gas Analysis (ASTM D1945)

Analyte ^a	AP-42 Default Concentration Static Conditions (%)	AP-42 Default Concentration Active Conditions (%)	MDL (%)	Site A-1 (Static Conditions) (%)	Site A-2 (Static Conditions) (%)	Site A-3 (Active Conditions) (%)
Methane	54	50	0.010	51	57	14
Ethane	ND	ND	0.010	ND	ND	ND
Propane	ND	ND	0.010	ND	ND	ND
Neopentane	ND	ND	0.010	ND	ND	ND
Isobutane	ND	ND	0.010	ND	ND	ND
n-Butane	ND	ND	0.010	ND	ND	ND
Isopentane	ND	ND	0.010	ND	ND	ND
n-Pentane	ND	ND	0.010	ND	ND	ND
n-Hexane	ND	ND	0.010	ND	ND	ND
n-Heptane	ND	ND	0.010	ND	ND	ND
Oxygen	ND	1	0.100	1.2	ND	6
Carbon Dioxide	46	44	0.010	40	43	15
Nitrogen	ND	5	1.000	8.1	ND	65
BTU (Btu/ft ³)	550.0	505.0		511.9	576.1	142.5
Specific Gravity	0.980	0.985		0.985	0.974	0.997

^a Typical default concentrations present general MSW landfill gas characteristics (EMCON 1982).

The system operator at Site A-3 reports that the CH₄ concentration does exceed 50% if the system is allowed to return to static conditions. The slightly elevated levels of oxygen and nitrogen in the sample for Site A-1 probably indicate either air infiltration into the system or contamination of the sample with atmospheric air.

Analytical results for reduced sulfur compounds are presented in Table 15. None of these compounds are considered HAPs. The sample from Site A-1 had no detectable reduced sulfur gases and is thus in agreement with all the AP-42 defaults except that it is lower in hydrogen sulfide (H₂S) than the default value. Samples from Sites A-2 and A-3 had no detectable reduced sulfur gases except H₂S. Thus, they are also in agreement with the AP-42 defaults except they are considerably higher in H₂S. Differences in the H₂S contents are likely due to production of kraft pulp at the mills associated with Sites A-1 and A-2.

The analytical results for VOCs (including several HAPs) are presented in Table 16. Most notable is that very few VOCs were detected in any of the samples. Of the 46 compounds analyzed, only six compounds, all of which are HAPs, were detected. Only one, toluene, was detected in more than one sample. The other five compounds were detected only in the sample from Site A-3. None of the detected compounds exceeded even half of the AP-42 default concentration, though method detection limits (MDL) for 12 of the 24 HAPs analyzed did exceed the AP-42 default concentrations. The facility with the largest volume of VOCs (Site A-3) had an aggregate concentration of 10.45 ppmv VOCs compared to the aggregate AP-42 default VOC concentration of 1,717 ppmv, or less than 1% of the default value. The three samples had aggregate detected HAP concentrations ranging from less than 0.1% to about 2.5% of the aggregate AP-42 default HAP concentration of 412.12 ppmv. Even if all twelve of the nondetected HAPs with MDLs exceeding the default are assumed to have

been present at a concentration just below the reported MDL (a highly unlikely scenario), the sample with the highest aggregate HAP concentration (Site A-3) still would have contained HAPs at a concentration of less than 6% of the aggregate AP-42 default value.

Table 15. Sulfur Compounds (EPA 15/16)

Analyte ^a	Default MSW LFG Concentration (ppmv)	MDL (ppmv)	Site A-1 (ppmv)	Site A-2 (ppmv)	Site A-3 (ppmv)
Hydrogen sulfide	35.5	1.0	ND	120	140
Carbonyl sulfide	ND	1.0	ND	ND	ND
Carbon disulfide	ND	1.0	ND	ND	ND
Dimethyl sulfide	ND	1.0	ND	ND	ND
Dimethyl disulfide	ND	1.0	ND	ND	ND
Methyl mercaptan	ND	1.0	ND	ND	ND

^a Typical default concentrations from November 1997 AP-42 Standards for Municipal Solid Waste Landfills, Table 2.4-1 Uncontrolled Landfill Gas Concentrations and Table 2.4-2, Default Concentrations of Benzene, NMOC and Toluene Based on Waste Disposal History.

In summary, the CH₄, CO₂, and reduced sulfur gas concentrations in the three industry landfill gas samples are in general agreement with the AP-42 default values for MSW landfills except that H₂S concentrations show some deviation. The data indicate that VOC and HAP content of industry landfill gas should be expected to be only a small fraction of the content predicted using AP-42 defaults.

Table 16. VOC Compounds (EPA TO-14)

Analyte ^a	Default MSW LFG				
	Concentration (ppmv)	MDL (ppmv)	Site A-1 (ppmv)	Site A-2 (ppmv)	Site A-3 (ppmv)
1,1,1-Trichloroethane (methyl chloroform)	0.48	0.001	ND	ND	ND
1,1,2,2-Tetrachloroethane	1.11	0.002	ND	ND	ND
1,1,2-Trichloroethane	0.1	0.001	ND	ND	ND
1,1-Dichloroethane (ethylidene dichloride) ^c	2.35	0.001	ND	ND	ND
1,2-Dichloroethene (vinylidene chloride) ^c	0.201	0.001	ND	ND	ND
1,2-Dichloroethane (ethylene dichloride) ^c	0.407	0.001	ND	ND	ND
1,2-Dichloropropane (propylene dichloride) ^c	0.171	0.001	ND	ND	ND
2-Propanol (isopropyl alcohol)	50.06	0.001	ND	ND	ND
Acetone	7.01	0.001	ND	ND	ND
Acrylonitrile ^c	11.5	0.001	ND	ND	ND
Bromodichloromethane	3.13	0.001	ND	ND	ND
Butane	5.03	0.001	ND	ND	ND
Carbon Disulfide ^c	0.583	0.001	ND	ND	ND
Carbon Monoxide	309	0.001	ND	ND	ND
Carbon tetrachloride ^c	0.004	0.001	ND	ND	ND
Carbonyl sulfide ^c	0.49	0.001	ND	ND	ND
Chlorobenzene ^c	0.254	0.001	ND	ND	ND
Chlorodifluoromethane	1.21	0.001	ND	ND	ND
Chloroethane (ethyl chloride)	1.37	0.001	ND	ND	ND
Chloroform ^c	0.019	0.001	ND	ND	ND
Chloromethane	1.21	0.002	ND	ND	ND
Dichlorobenzene ^d	0.213	0.001	ND	ND	ND
Dichlorodifluoromethane	15.7	0.001	ND	ND	ND
Dichlorofluoromethane	4.4	0.001	ND	ND	ND
Dichloromethane (methylene chloride) ^c	14.3	0.001	ND	ND	ND
Dimethyl sulfide (methyl sulfide)	7.82	0.001	ND	ND	ND
Ethane	1105	0.001	ND	ND	ND
Ethanol	27.2	0.001	ND	ND	ND
Ethyl mercaptan	2.28	0.001	ND	ND	ND
Ethylbenzene ^c	4.61	0.001	ND	ND	0.38
Fluorotrichloromethane	0.756	0.001	ND	ND	ND
Hexane ^c	6.57	0.001	ND	ND	ND
Methyl ethyl ketone	7.09	0.001	ND	ND	ND
Methyl isobutyl ketone	1.21	0.001	ND	ND	ND
Methyl mercaptan	4.33	0.001	ND	ND	ND

continued on next page

Analyte ^a	Default MSW LFG				
	Concentration (ppmv)	MDL (ppmv)	Site A-1 (pmmv)	Site A-2 (pmmv)	Site A-3 (pmmv)
Pentane	3.29	0.001	ND	ND	ND
Perchloroethylene (tetrachloroethene)	3.73	0.001	ND	ND	ND
Propane	11.1	0.001	ND	ND	ND
Trichloroethylene (trichloroethene) ^c	2.82	0.001	ND	ND	ND
t-1,2-dichloroethene	2.84	0.001	ND	ND	ND
Vinyl chloride ^c	7.34	0.001	ND	ND	ND
Xylenesc	12.1	0.001	ND	ND	1.42
Benzene (Unknown Co-Disposal) ^c	1.91	0.001	ND	ND	0.91
Toluene (Unknown Co-Disposal) ^c	39.3	0.001	0.14	0.22	7
1,3,5-Trimethylbenzene ^c	N.A. ^b	0.001	ND	ND	0.19
1,2,4-Trimethylbenzene ^c	N.A. ^b	0.001	ND	ND	0.55

^a Typical default concentrations from November 1997 AP-42 Standards for Municipal Solid Waste Landfills, Table 2.4-1 Uncontrolled Landfill Gas Concentrations and Table 2.4-2, Default Concentrations of Benzene, NMOC and Toluene Based on Waste Disposal History.

^b Compounds not referenced in AP-42, but analyzed as part of EPA Method TO-14.

^c Hazardous Air Pollutants (HAPs) listed in Title III of the 1990 Clean Air Act Amendments.

^d EPA source tests did not indicate whether this compound was the para- or ortho- isomer. The para isomer is a Title III listed HAP.

5.0 ALTERNATIVE MODELS FOR HAP EMISSIONS

HAP emissions from landfills are influenced by the following factors, each of which has the potential to affect significantly the rate of emission:

- the rate of volatilization from liquid into gas
- the rate of methane and carbon dioxide gas convection, measured as vertical velocity
- the rate of molecular diffusion of gas constituents from high concentration areas within the landfill into the atmosphere
- the rates of adsorption of HAPs onto solid materials within the landfill
- the microbial transformation of HAPs within the landfill into other chemical compounds.

The EPA LAEEM model takes into account only one of these factors, the convection resulting from landfill decomposition.

As discussed in Section 4, it is expected that paper industry landfills will have a lower lifetime potential for gas emission, as well as a lower rate of decomposition, both of which would result in significantly lower HAP emissions. The assessment of the importance of each of the other factors in predicting HAP emissions is a fairly involved task, but the results of a detailed analysis of these factors are included in Appendices B and C and presented in summary form in Table 17. The following subsections qualitatively discuss each of the factors influencing HAP emissions.

Table 17. Significance of Factors Affecting HAP Movement

Factor affecting HAP movement	Included in LAEEM	Significance for pulp and paper industry landfills	Reference for more detail
Volatilization	No	<ul style="list-style-type: none"> Generates HAPs from liquid phase Data are generally unavailable, except for leachate 	<ul style="list-style-type: none"> App. A, Table A1 Table 4.6
Convection	Yes	<ul style="list-style-type: none"> Results from landfill decomposition Sweeps HAPs from landfill into atmosphere 	<ul style="list-style-type: none"> App. C, Examples 1-4, 6
Diffusion	No	<ul style="list-style-type: none"> Causes HAP releases even from non-decomposing landfills 	<ul style="list-style-type: none"> App. C, Examples 6, 7, 9
Adsorption	No	<ul style="list-style-type: none"> The organic content of industry landfill materials may provide a significant retardant to HAP releases 	<ul style="list-style-type: none"> App. C, Examples 6, 8
Biochemical transformation	No	<ul style="list-style-type: none"> Microbial degradation can greatly reduce HAP emissions 	<ul style="list-style-type: none"> App. A, Table A1 App. C, Example 8

5.1 Volatilization

Volatilization is the process by which compounds change from the liquid to the gas phase within the landfill, and then become available for transport either by convection with the bulk gas mixture, or by diffusion even in the absence of bulk gas movement resulting from landfill decomposition. In the absence of volatilization, HAP emissions would not occur.

Table 12 contains a listing of typical pulp and paper industry landfill leachate HAP concentrations. Although no direct inference is possible regarding the concentration of HAP in landfill gas from leachate data, the absence of many of the AP-42 HAPs in pulp and paper industry leachate suggests that the AP-42 default values may be too high for industry landfills.

Generally, the effect of volatilization is either ignored for lack of data, or incorporated through the use of concentration boundary conditions at the lower edge of the landfill.

5.2 Convection

Convection is the process by which compounds are swept along with the principal gas mixture. The convection through the surface of the landfill of any gas can be calculated as follows:

$$Q_p = vcA \quad (2)$$

where Q_p is the convective flux of pollutant, P, Mg/year; v is the principal gas velocity, m/year; c is the mass concentration of P, Mg/m³, A is the surface area of landfill, m².

A median solids concentration in industry residuals of 35% (Table 9) equates to a median moisture content of 65% as compared to a typical MSW landfill moisture content of only about 21% (Table 8).

Given the typically small grain size of mill wastewater treatment residuals, it is likely that many residuals are completely or nearly completely saturated with water when they are placed in landfills (i.e., pore spaces are full of water). Monofills containing these materials would therefore be essentially saturated. The heterogeneous nature of MSW landfills (resulting in larger pore sizes) and the lower moisture content indicate that they would not tend to be completely saturated. This difference in saturation can have a profound effect on gas flow by convection within the landfill. Pores filled with water will obviously not be available for convective movement of gases so the more saturated the landfill contents are, the less convective transport of gases there can be to the surface or other emission points.

This difference between MSW landfills and pulp and paper industry landfills is potentially very significant in terms of predictions of HAP emissions using the LAEEM because convection is the only mechanism included in LAEEM for describing HAP movement.

The application of LAEEM in Appendix C, Examples 1–5 illustrates the effect of convection.

5.3 Diffusion

Diffusion is the process by which HAP compounds move from areas of high concentration to areas of low concentration, and is generally described by Fick's Law (Bird et al., 1960). For the case of a landfill in which vertical flow is the main consideration,

$$Q_{Pdiff} = -D_{eff} \frac{\delta c}{\delta z} \quad (3)$$

where Q_{Pdiff} is the diffusive flux of pollutant P, Mg/m²-year; D_{eff} is the effective diffusion coefficient, m²/year; c is the concentration of pollutant, P, Mg/m³, and z is the vertical distance, m.

The diffusion coefficient varies for each particular pollutant, and can be estimated using standard methods (Lyman et al., 1982). The effective diffusion coefficient within a porous medium is calculated as the diffusion coefficient divided by a factor known as the tortuosity, which generally varies between 2 and 6, with an average value of 3 (Cussler 1985).

Typical values of the effective diffusivity within a porous material are on the order of 0.01–0.02 m²/yr, and 100–200 m²/yr, for liquid and gas phases, respectively. The implication of the several orders of magnitude higher gas phase effective diffusion coefficient is that gas movement via diffusion within the unsaturated zone is expected to be a relatively rapid phenomenon. As discussed above, pulp and paper industry landfills could reasonably be expected to be more saturated than MSW landfills, so diffusion within them could be a much slower process than it would be within MWS landfills.

LAEEM ignores the effect of diffusion, which for slowly decomposing landfills may be the predominant transport mechanism. To determine whether diffusion is important for a particular landfill, the method of time scale analysis, explored in Appendix B and Appendix C Example 6, may be used. The methods of Examples 7 and 9 can be used to predict the diffusion driven emission from a slowly decomposing landfill, which may be the case for many industry landfills.

5.4 Adsorption

Adsorption is the process by which HAPs are bonded on to the solid matrix of materials within the landfill. The net expected effect of adsorption on HAPs is to slow down their rate of release, although data on the adsorption of HAPs onto solid waste material are not readily available.

Because of this lack of data, the following method is used to estimate the adsorption of pesticides on to soils (Lyman et al., 1982):

$$K_{OC} = \frac{\mu\text{g adsorbed} / \text{g organic carbon}}{\mu\text{g} / \text{mL solution}} \quad (4)$$

and

$$\log_{10} K_{OC} = 1.029 \log_{10} K_{OW} - 0.18 \quad (5)$$

where K_{OW} is the octanol/water partition coefficient.

Values of $\log_{10}K_{OC}$ are known to vary between 0 and 7, expressed in the above units (Lyman et al., 1982). This method can be used to express the adsorption of other organic compounds, such as HAPs, onto the soil/solid waste matrix within a landfill.

5.5 Biochemical Transformations

Because the solid waste within the landfill contains active microbial cultures, which are decomposing the solids primarily into methane, carbon dioxide, and water, it is probable that decomposition of some of the HAPs can also be occurring, in a manner similar to that of degradation of pollutants in an aquifer. This biodegradation is often assumed to be a first order process, described by the following equation:

$$R_p = -k_b c \quad (6)$$

where R_p is the rate of biodegradation of P, $\text{Mg}/\text{m}^3\text{-year}$; c is the concentration of P, Mg/m^3 ; and k_b is the first order decay coefficient, year^{-1} .

Table A.1 in Appendix A contains a list of typical first order decay rates for selected HAP compounds contained in AP-42 (EPA, 1995a). The actual decay rate would be a function of the organic substrate within the landfill, as well as environmental conditions such as pH and oxygen level, but for estimation purposes, the values in Table A.1 indicate the potential significance of biodegradation for a particular compound.

Example 8 in Appendix C can be used to assess the influence of biodegradation, and to show that HAP compounds with a sufficiently high degradation rate may have low emission rates, even if present in high concentrations within the landfill.

5.6 Concluding Remarks – Alternative Models

The EPA LAEEM model provides a simple method to estimate HAP emissions from MSW landfills, but probably overestimates gas emissions from pulp and paper industry landfills, as discussed in Section 4.3. The basis for the LAEEM calculation of HAP emissions from landfills is explored in Appendix C, Examples 1 – 4.

Use of the LAEEM method in Example 5 suggests that perhaps a 50% reduction in estimated HAP emission rates may result from the adjustment of k and L_0 values.

It is difficult to generalize on the importance of those additional factors affecting HAP emissions, namely diffusion, adsorption, and biodegradation, in the absence of specific characteristics for a particular landfill. The method of time scale analysis presented in Example 6 suggests a very simple method for determining which of these factors may be important, based on the depth of the landfill, degree and location of a saturated zone, and the biodegradation rates for particular HAP compounds of interest. It may turn out, for example, that although LAEEM would predict a high emission rate for a given HAP, the time scale for biodegradation may be relatively quick, allowing for in-situ conversion of that compound to an innocuous form prior to its release into the atmosphere.

Many of the pulp and paper industry landfills may be decomposing at such a slow rate that the usage of LAEEM may be completely inappropriate. HAP emissions could still be occurring, albeit at very slow rates, through gas-phase molecular diffusion, and the alternative method for HAP emission estimation shown in Example 7 could be used to demonstrate this. Example 8 suggests how a sensitivity analysis can be used on the HAP emissions predicted in Example 7, and in particular shows in Figure C.6 the dramatic reductions in emissions that are possible when biodegradation rates are high. As shown in Appendix A, Table A.1, many of the listed HAP compounds are known to have high biodegradation rates, which could prove very advantageous in reducing HAP emissions from pulp and paper industry landfills.

Finally, the method of Example 9 shows how to estimate the rate of attenuation of HAPs that can be expected to occur over time from the diffusion-driven release into the atmosphere. One can conclude that the gas phase emission from the unsaturated zone is relatively rapid, but the release from the liquid phase is a rather slow process. One would expect, then, that the absence of many of the HAPs from pulp and paper industry landfill leachate, as shown in Table 12, would suggest their absence in the gases emitted into the atmosphere.

6.0 SUMMARY AND CONCLUSIONS

6.1 Summary

LAEEM is derived from a simplified empirical first order decomposition model, using default decomposition rates, methane generation potential, and HAP gas concentrations obtained from studies of municipal solid waste landfills. Field studies have shown that even for municipal solid waste, there is significant variation in the values of these parameters, and the user of LAEEM for MSW landfills would therefore be well advised to consider determining actual values through a field calibration study.

Compared with MSW landfills, pulp and paper industry landfills are expected to decompose at lower rates, and ultimately to release lower amounts of methane and non-methane organic compounds per unit volume of solid waste, because of the different composition of the landfilled materials (including nutrient deficiency and inorganic content) and higher moisture content.

The absence of a number of HAP compounds in industry landfill leachates suggests that the usage of LAEEM default HAP gas concentrations overestimates HAP emissions from industry landfills even if landfill gas emission estimates were accurate. Actual measurements of HAP concentrations in three pulp and paper industry landfill gas samples confirm that HAP (and other VOC) concentrations are only a small fraction of the AP-42 default concentrations that are based on MSW landfill gas measurements.

The slower rate of decomposition expected in industry landfills and likely saturation conditions would tend to downplay the predominance of convection as a transport mechanism for the HAP gas compounds which are present. Although diffusion can still serve as a means to release the HAP gases, the saturated conditions present in many industry landfills would greatly retard gas emission. The combined effects of adsorption and biodegradation could also serve to reduce the HAP gas emissions.

6.2 Conclusions

The following conclusions may be drawn:

- Based on the above analyses, the EPA Landfill Air Estimation Model (LAEEM), using the default AP-42 constants for k and L_0 , and HAP concentrations, almost certainly overestimates both methane and HAP emissions from most pulp and paper industry landfills.
- The EPA LAEEM, with adjusted k and L_0 values, based on industry-specific studies, would provide more realistic estimates of methane and carbon dioxide emissions from pulp and paper industry landfills.
- Observation of leachate concentrations in conjunction with a limited number of actual landfill gas measurements makes it clear that the AP-42 default concentrations for HAPs and VOCs are far too high for use in estimating pulp and paper industry landfill emissions.
- The EPA LAEEM, even with adjusted k and L_0 values and corrected HAP/VOC values, may still overestimate HAP emissions from pulp and paper industry landfills. LAEEM does not account for the attenuating effects of biodegradation and adsorption, nor does it account for the potentially slower migration of landfill gas through a fully saturated landfill zone.

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APPENDIX A

SELECTED PROPERTIES OF AP-42 HAZARDOUS AIR POLLUTANTS

Table A.1. Selected Properties of AP-42 Hazardous Air Pollutants^{a,b,c}

Compound	Molecular Weight	Henry's Law Constant (atm·m ³ /mole)	Log Octanol/Water Partition Coefficient	Half-Life (days)	Vapor Pressure (mm Hg at 25°C)
1,1,1-Trichloroethane	133.41	8.00 E-03	2.49	1.1	123.7
1,1,2,2-Tetrachloroethane	167.85	4.55 E-04	2.39	8 – 11	6.1
1,1,2-Trichloroethane	133.41	1.20 E-03	2.07	nil	30.3
1,1-Dichloroethane	98.96	5.87 E-03	1.79	18 - 36	227
1,1-Dichloroethene	96.94	NA	NA	NA	NA
1,2-Dichloroethane	98.96	9.77 E-04	1.48	nil	78.7
1,2-Dichloropropane	112.99	2.07 E-03	1.99	20	49.67
2-Propanol	60.01	6.85 E-06	0.25	25 - 75	20.99
Acetone	58.08	3.67 E-05	-0.24	34 - 253	231
Acrylonitrile	53.06	1.10 E-04	0.25	9 - 52	107.8
Benzene	78.12	5.43 E-03	2.13	3 - 16	95.19
Bromodichloromethane	163.83	1.63 E-03	2.10	4.5	50
Butane	58.12	NA	NA	NA	NA
Carbon Disulfide	76.14	1.40 E-03	1.70 – 4.16	nil	297
Carbon Monoxide	28.01	NA	NA	NA	NA
Carbon Tetrachloride	153.84	3.04 E-02	2.83	16	113.8
Carbonyl Sulfide	60.07	NA	NA	NA	NA
Chlorobenzene	112.56	3.45 E-03	2.84	1.7 – 3.4	11.9
Chlorodifluoromethane	86.47	2.94 E-02	1.08	nil	4279
Chloroethane	64.52	NA	NA	NA	NA
Chloroform	119.38	4.35 E-03	1.97	0.4	246
Chloromethane	50.49	2.40 E-02	0.91	51	4309.7
1, 4 Dichlorobenzene	147.01	1.50 E-03	3.52	nil	1.76
Dichlorodifluoromethane	120.91	NA	NA	NA	NA
Dichlorofluoromethane	102.92	2.50 E-02	1.55	nil	1216
Dichloromethane	84.93	2.68 E-03	1.25	70	434.9
Dimethyl Sulfide	62.13	NA	NA	NA	NA
Ethane	30.07	NA	NA	NA	NA
Ethanol	46.08	6.29 E-06	-0.31	98	59.03
Ethylbenzene	106.17	8.44 E-03	3.15	32	9.53

continued on next page

Compound	Molecular Weight	Henry's Law Constant (atm-m ³ /mole)	Log Octanol/Water Partition Coefficient	Half-Life (days)	Vapor Pressure (mm Hg at 25°C)
Ethyl Mercaptan	62.13	NA	NA	NA	NA
Fluorotrichloromethane	137.37	NA	NA	NA	NA
Hexane	86.18	NA	NA	NA	NA
Hydrogen Sulfide	34.08	NA	NA	NA	NA
Mercury	200.61	NA	NA	NA	NA
Methyl Ethyl Ketone	72.11	1.05 E-05	0.29	104 - 155	90.6
Methyl Isobutyl Ketone	100.16	9.40 E-05	1.19	10 - 25	14.5
Methyl Mercaptan	48.11	NA	NA	NA	NA
Pentane	72.15	1.26	3.39	13	513
Perchloroethylene	165.83	NA	NA	NA	NA
Propane	44.1	NA	NA	NA	NA
Toluene	92.14	5.94 E-03	2.73	3 - 21	28.4
Trichloroethene	131.29	1.03 E-02	2.42	3	69
t-1,2-Dichloroethene	96.94	6.72 E-03	2.06	2.4	340
Vinyl Chloride	62.5	1.07 E-02	1.38	4 - 9	2660
1,2 Xylene	106.16	5.10 E-03	3.12	2	6.6
1,3 Xylene	106.17	7.68 E-03	3.20	51	8.3
1,4 Xylene	106.17	7.68 E-03	3.15	51	8.7

^a Howard, P.H. (Ed.). 1989. *Handbook of environmental fate and exposure data for organic chemicals, Volume I - Large production and priority pollutants*. Chelsea, Michigan: Lewis Publishers.

^b Howard, P.H. (Ed.). 1990. *Handbook of environmental fate and exposure data for organic chemicals, Volume II - Solvents*. Chelsea, Michigan: Lewis Publishers.

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APPENDIX B

ALTERNATE MODELING APPROACHES

1.0 INTRODUCTION

A variety of alternative modeling approaches are possible that allow for the incorporation of effects such as diffusion, adsorption, and biodegradation, in addition to the convective effect included in LAEEM, to predict HAP emissions. This Appendix begins with a derivation of the general equations used to describe HAP movement, and then presents solutions to several important special cases. The application of these solutions to example problems is explored in Appendix C.

1.1 Development of HAP Movement Equations

To estimate HAP emissions from pulp and paper industry landfills where lateral subsurface movement beyond the boundaries of the landfill is not of primary concern, the simplest approach is to consider only the vertical movement of gases. Consider the schematic control section through the landfill, shown in Figure B.1.

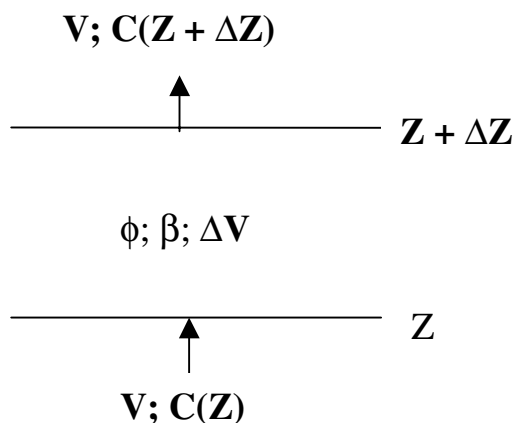


Figure B.1. Control section in landfill for vertical movement

Let	ϕ	= porosity of landfill = (volume through which gas moves) / total volume
	β	= linear adsorption coefficient
	c	= HAP concentration in gas phase ; Mg/m^3
	D	= effective diffusion coefficient; m^2/yr
	k_b	= first-order decay coefficient; $1/\text{yr}$
	S	= source term for HAPs from volatilization within control volume; $\text{Mg}/\text{m}^3/\text{yr}$
	v	= convective velocity of principal gases; m/yr
	ΔV	= volume of control volume; m^3
	z	= vertical distance; m
	t	= time; yr

Then the principle of mass balance can be applied to the control volume by stating that the time rate of accumulation of mass must equal the time rate of (inflow – outflow + volatilization – decay) within the control volume:

$$\text{Accumulation within pore volume} = (\Delta V) \frac{\partial c}{\partial t} \dots\dots\dots (\text{B.1})$$

$$\text{Accumulation by adsorption} = (\Delta V) \phi \beta \frac{\partial c}{\partial t}$$

$$\text{In by convection} = vc(z)$$

$$\text{In by diffusion} = -D \frac{\partial c}{\partial z}$$

$$\text{Out by convection} = vc(z + \Delta z)$$

$$\text{Out by diffusion} = -D \frac{\partial c(z + \Delta z)}{\partial z}$$

$$\text{Volatile source} = (\Delta V)S \text{ (typically } S \text{ is assumed to be zero)}$$

$$\text{Decay} = (\Delta V \phi)(-k_b c)$$

Applying the mass balance principle to the terms identified within Equation (B.1), assuming no sources, and taking the limit as Δz approaches zero, results in Equation (B.2):

$$\phi(1 + \beta) \frac{\partial c}{\partial t} = -v \frac{\partial c}{\partial z} + D \frac{\partial^2 c}{\partial z^2} - k_b \phi c \dots\dots\dots (\text{B.2})$$

To determine a unique solution to Equation (B2), initial conditions (IC) and boundary conditions (BC) must be specified, as follows:

$$\text{IC: At time } t = 0, c = c_i \dots\dots\dots (\text{B.2a})$$

$$\text{BC 1a: At } z = 0, \frac{\partial c}{\partial z} = 0 \text{ (no HAP flux through bottom of landfill).. (B.2b)}$$

$$\text{or BC 1b: At } z = 0, c = c_0 \dots\dots\dots (\text{B.2c})$$

$$\text{BC 2: At } z = H \text{ (top of landfill), } c = 0 \dots\dots\dots (\text{B.2d})$$

The mass flow rate of HAP through the landfill surface is then found through the application of the following Equation:

$$Q_{\text{HAP}} = vc - D \left(\frac{\partial c}{\partial z} \right) A \dots\dots\dots (\text{B.3})$$

evaluated at the top of landfill ($z = H$)

2.0 Solution of HAP Movement Equation

Solutions to Equations (B.2) and (B.3) allow for the more advanced characterization of the distribution of HAPs within the landfill, and provide insight into the relative importance of each of the landfill parameters in the mass balance equations. Solutions to the most important cases are provided in the current section, and their application to pulp and paper industry landfills are provided in the Appendix C.

2.1 *Steady-State Solutions*

Because of the complexity involved in solving the partial differential convection-diffusion Equation (B.2), it is appealing to consider the possible “steady-state” solutions (those in which the time-varying term, dc/dt , is set = 0) describing HAP concentrations which are expected to remain relatively constant over time. Conceptually, the only steady-state solution is $c = 0$, because eventually all the HAPs must either migrate from the landfill or be converted into other forms, and the principal gas velocity, v , is generally expected to be a function of time. Nevertheless, steady-state solutions are very useful for estimation purposes and, in many cases, it is questionable whether the input data are sufficiently defined to warrant more rigorous solutions.

Three important steady-state solutions are presented: first, the basis for EPA’s LAEEM; second, a more advanced solution that also incorporates the effects of diffusion and biodegradation; and third, a solution for the case in which diffusion is the only transport mechanism.

2.1.1. LAEEM

LAEEM starts with Equation (B.2), and sets $dc/dt = D = k = S = 0$, that is to say it begins with the following equation:

$$v \frac{dc}{dz} = 0 \dots \dots \dots (B.4)$$

Clearly, the only solution to this is that $c = \text{constant}$ and in the case of LAEEM, the constant defaults to the AP-42 or Clean Air Act (CAA) parameters.

A modified form of Equation (B.3), in which the effect of diffusion is omitted, is then used to describe the HAP emission:

$$Q_{\text{HAP}} = vc \dots \dots \dots (B.5)$$

2.1.2. Convection-Diffusion-Biodegradation Equation

Consider the equation resulting from the steady-state version of Equation (B.2):

$$D \frac{d^2c}{dz^2} - v \frac{dc}{dz} - \phi k_b c = 0 \dots \dots \dots (B.6)$$

$$\text{BC 1: At } z = 0, c = c_0$$

$$\text{BC 2: At } z = H, c = 0$$

Through the method of ordinary differential equations (Rabenstein 1972), the following solution for the concentration profile can be derived:

$$c = a_1 e^{R_1 z} + a_2 e^{R_2 z} \dots \dots \dots (B.7)$$

$$\text{where } R_1 = \frac{v + \sqrt{v^2 + 4\phi k_b D}}{2D}; R_2 = \frac{v - \sqrt{v^2 + 4\phi k_b D}}{2D}$$

$$a_1 = \frac{c_0 e^{R_2 H}}{e^{R_2 H} - e^{R_1 H}}; a_2 = c_0 - a_1$$

Similarly the emission of HAP through the landfill surface can be shown to be the following expression:

$$Q_{\text{HAP}} = -DA(a_1 R_1 e^{R_1 H} + a_2 R_2 e^{R_2 H}) \dots \dots \dots (B.8)$$

where A = surface area of landfill; m²

It can be seen that the steady-state HAP emission is proportional to the effective diffusivity, the concentration of HAP at the lower boundary condition, and the landfill surface area.

From the methods of ordinary differential equation solution, it can be shown that the solution, Equations (B.7) and (B.8), are strictly valid only when k_b and v are non-zero. As a practical matter, the solution provided can still be used even in cases when k_b and/or v equal zero, by using numerically small values.

The short term effect of convection is to increase the emission rate, and to decrease the long term emission. Biodegradation decreases both short and long term emissions (although there is always the possibility that HAPs are formed as breakdown products). Example 8 explores the effects of convection and biodegradation on diffusion in Example 7.

2.1.3 Diffusion Equation

As described in an earlier section, it is quite conceivable that the rate of decomposition of the bulk organic materials within pulp and paper industry landfills may be very slow compared to decomposition rates in municipal landfills. To estimate the steady-state diffusion driven transport that would occur through the unsaturated zone of the landfill (see Figure B.1), the following equation could be used:

$$D \frac{d^2 c}{dz^2} = 0 \dots \dots \dots (B.9)$$

$$\text{BC 1 : At } z = 0, c = c_0$$

$$\text{BC 2 : At } z = H, c = 0$$

The solution of Equations (B.9) and (B.3) yields both the concentration profile, and the steady-state mass flowrate of HAP through the landfill surface:

$$c = c_0 \left(1 - \frac{z}{H}\right) \dots \dots \dots (B.10)$$

$$Q_{\text{HAP}} = \frac{Dc_0 A}{H} \dots \dots \dots (B.11)$$

The application of these steady-state solutions is shown in Example 7.

2.2 *Unsteady-State Solutions*

Unsteady-state solutions to the HAP movement Equation (B.2) may be required, and involve either the use of analytical or numerical solution techniques. General analytical solutions are available only for specialized cases, one of which is presented here. The finite-element numerical solution technique is available, and is briefly discussed in this section.

2.2.1 Unsteady-State Diffusion: Analytical Solution

A non-decomposing landfill could still be emitting HAPs for some period of time. Equation (B.2) can be adapted to describe this situation as follows:

$$\phi(1 + \beta) \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \dots\dots\dots(B.12)$$

IC: At t = 0, c = c₀

BC 1: At z = 0 (bottom of landfill), $\frac{\partial c}{\partial z} = 0$ (no flux)

BC 2: At z = H (top of landfill), c = 0

By the separation of variables technique (Haberman 1983) it can be shown that the following equation provides the exact solution:

$$c = \sum_{i=0}^{\infty} K_i e^{-\lambda_i^2 \tau} \cos(\lambda_i Z) \dots\dots\dots(B.13)$$

$$Q_{HAP} = \frac{Dc_0 A}{H} \sum_{i=0}^{\infty} K_i \lambda_i e^{-\lambda_i^2 \tau} \sin \lambda_i$$

where $\lambda_i = (2i + 1) \frac{\pi}{2}$

$$K_i = \frac{4 \sin \lambda_i}{\sin(2\lambda_i) + 2\lambda_i}$$

$$\tau = \frac{t}{\frac{H^2 (\phi(1 + \beta))}{D}}$$

$$Z = \frac{z}{H}$$

One useful result from the above solution is that it provides a natural way to determine the time-scale for diffusion, $\phi(1+\beta)L^2/D$. Time scales for each of the factors affecting HAP movement can similarly be defined, as summarized in Table B.1, and illustrated in Example 6, Appendix C. Time varying emissions are illustrated in Example 9.

Table B.1: Time Scales for HAP Fate and Transport Mechanisms

Factor	Time Scale
Convection	$\phi(1 + \beta) L / v$
Diffusion	$\phi(1 + \beta) L^2 / D$
Biodegradation	$(1 + \beta) / k$

(Where L = characteristic length; D = characteristic diffusivity)

2.2.2 General Unsteady-State: Finite-Element Solution

Finite-element solutions to equations of the form of Equation (B.2) are commonly used in the solution of groundwater contaminant transport problems (Bear, 1979). However, whenever the time scales for more than one of the fate and transport mechanisms are sufficiently close, numerical solutions obtained by any method are likely to exhibit inaccuracies (Carey and Oden., 1986), and hence must be used with caution.

The finite-element methodology (FEM) can be utilized for one, two, or three dimensions of the full set of equations describing both principal and trace gases. However, no general purpose FEM modeling tool is currently available with an interface appropriate for landfills. Customized models could be implemented, but would likely require extensive field calibration to make their predictions reasonably accurate.

In the absence of the convective effect from principal gas velocity movement, and other effects such as “barometric pumping” resulting from changes in atmospheric pressure, HAPs which are found in the unsaturated zone of the landfill can still be expected to be emitted as the result of the high values of gas diffusion coefficients. The solution technique of equation B.13 allows for the presentation of the concentration profiles and emission time trace to be plotted in the non-dimensionalized form of Figures C.6 and C.7 in Appendix C.

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APPENDIX C

EXAMPLE CALCULATIONS OF HAP EMISSIONS

Example 1: LAEEM methodology for calculating methane emissions

A 100 acre, 30 ft deep landfill is filled with pulp and paper industry waste with a density of 69 lbs/ft³ over the ten year period 1988 – 1997. Use the LAEEM methodology to predict emissions of methane during the time period 1988 - 2050.

Solution:

- Calculate the total volume of material within the landfill:

$$V = 100 \text{ acres} \times \frac{43,560 \text{ ft}^2}{\text{acre}} \times 30 \text{ ft} = 130,680,000 \text{ ft}^3$$

- Calculate the mass per layer:

$$M_{\text{total}} = 130,680,000 \text{ ft}^3 \times 69 \frac{\text{lbs}}{\text{ft}^3} \times 454 \frac{\text{g}}{\text{lb}} \times \frac{\text{Mg}}{10^6 \text{ g}} = 4,093,682 \text{ Mg}$$

$$M_{\text{layer}} = \frac{M_{\text{total}}}{10} = 409368.2 \text{ Mg}$$

- Calculate the lifetime methane generation potential per layer:

Assuming LAEEM's default L_0 value of 124.9056 m³ CH₄ / Mg refuse:

$$409368.2 \frac{\text{Mg}}{\text{layer}} \times 124.9056 \frac{\text{m}^3 \text{ CH}_4}{\text{Mg}} = 51,132,377 \frac{\text{m}^3 \text{ CH}_4}{\text{layer}}$$

- Calculate the rate of methane generation at any time t , since the placement of the layer:

From Equation (3.1), for an open landfill ($c = 0$), $\frac{dQ_{CH_4}}{dt} = kL_0 e^{-kt}$

From LAEEM's default k value of 0.04 /year :

$$\begin{aligned} \text{Methane generation in layer} &= \frac{0.04}{\text{yr}} \times 51,132,377 \text{ m}^3 \text{ CH}_4 \times e^{-kt} \\ &= 2,045,295 e^{-0.04t} \frac{\text{m}^3 \text{ CH}_4}{\text{yr}} \times \frac{1000 \text{ L}}{\text{m}^3} \times \frac{22.414 \text{ L}}{\text{mol CH}_4} \times 16.0426 \frac{\text{g CH}_4}{\text{mol CH}_4} \times \frac{\text{Mg CH}_4}{106 \text{ g CH}_4} \\ &= 1464 e^{-0.04t} \frac{\text{Mg CH}_4}{\text{yr}} \end{aligned}$$

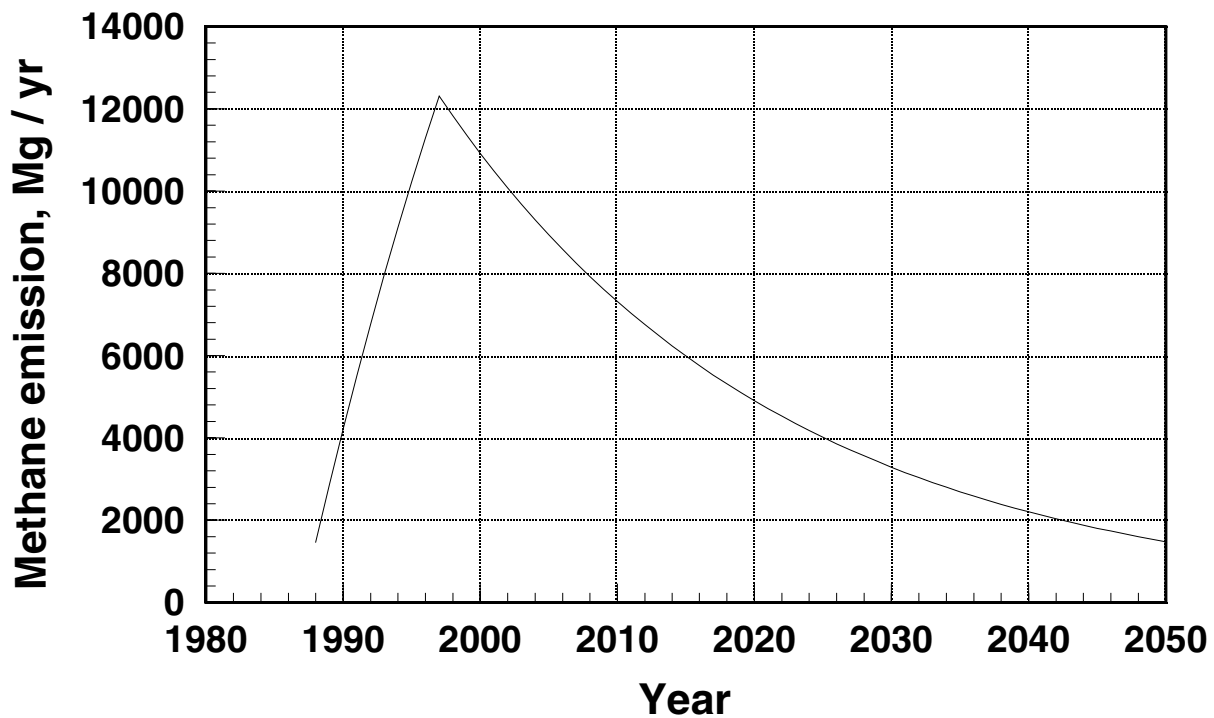


Figure C.1. Methane Emission Plot for the Landfill in Example 1

HAP emissions for any constituent can be estimated based on the emissions of methane and carbon dioxide, as explored in Example 2.

Example 2: LAEEM methodology for calculating non-methane organic compound emissions

Estimate the emission of non-methane organic compounds (NMOC) from the landfill in Example 1, using the LAEEM default assumptions of equimolar methane – carbon dioxide concentrations, and an NMOC concentration of 595 ppmV.

Solution:

- Calculate the rate of carbon dioxide generation at any time t since the placement of the layer:

Assuming LAEEM's default 50%-50% CH₄-CO₂ composition,

$$\begin{aligned} \text{Carbon dioxide generation in layer} &= 2,045,295 e^{-0.04t} \frac{\text{m}^3 \text{CO}_2}{\text{yr}} \times \frac{1000 \text{ L}}{\text{m}^3} \\ &\times \frac{\text{mol CO}_2}{22.414 \text{ L}} \times 44.0098 \frac{\text{g CO}_2}{\text{mol CO}_2} \times \frac{\text{Mg CO}_2}{106 \text{ g CO}_2} \\ &= 4016 e^{-0.04t} \frac{\text{Mg CO}_2}{\text{yr}} \end{aligned}$$

- Calculate the rate of principal gas production generation at any time t in a typical layer:

Total gas generation = rate of CH₄ generation + rate of CO₂ generation

$$= 4,090,590 e^{-0.04t} \frac{\text{m}^3}{\text{yr}}$$

- Calculate the rate of non-methane organic compound using the AP-42 default partial pressure of 595 ppmV:

$$\text{NMOC generation} = 595 \times 10^{-6} \times 4,090,590 e^{-0.04t} = 2433 e^{-0.04t} \frac{\text{m}^3}{\text{yr}}$$

- Results of spreadsheet implementation of the above equations are shown in Figure C.2.

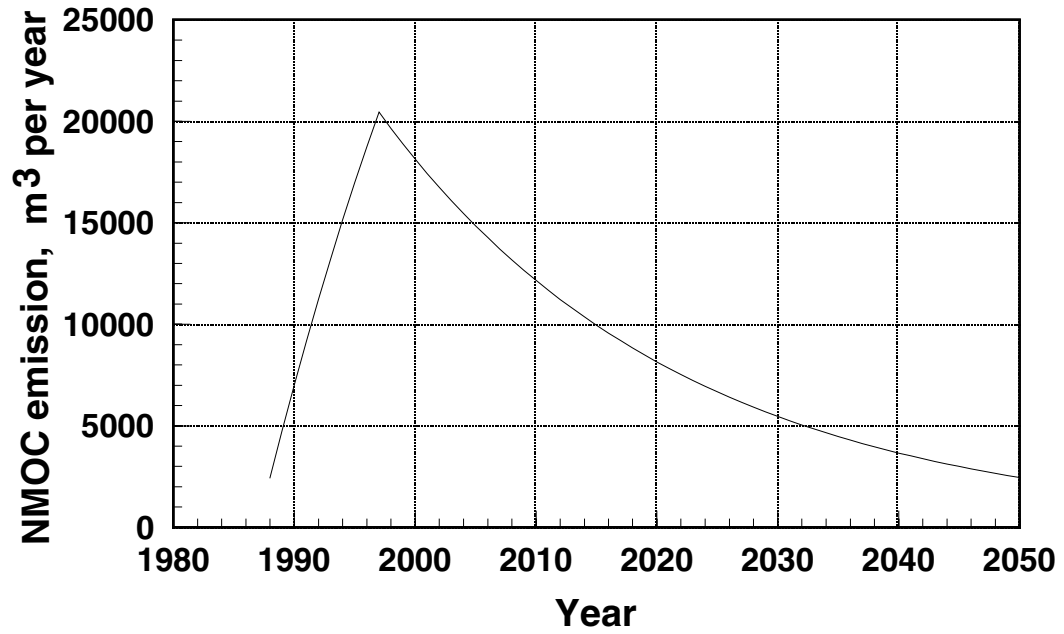


Figure C.2. NMOC emission plot for the landfill of Example 2

The emission of any other of the AP-42 listed compounds can similarly be calculated, as shown in Example 3.

Example 3: LAEEM methodology for calculating HAP emissions

Estimate the emission of acetone from the landfill of Examples 1 and 2. Use the AP-42 default acetone concentration of 7.01 ppmV.

- Calculate the rate of acetone using the AP-42 default partial pressure of 7.01 ppmV:

$$\text{Acetone generation} = 7.01 \times 10^{-6} \times 4,090,590 e^{-0.04t} = 28.68 e^{-0.04t} \frac{\text{m}^3}{\text{yr}}$$

- Results of spreadsheet implementation of above equations are shown in Figure C3:

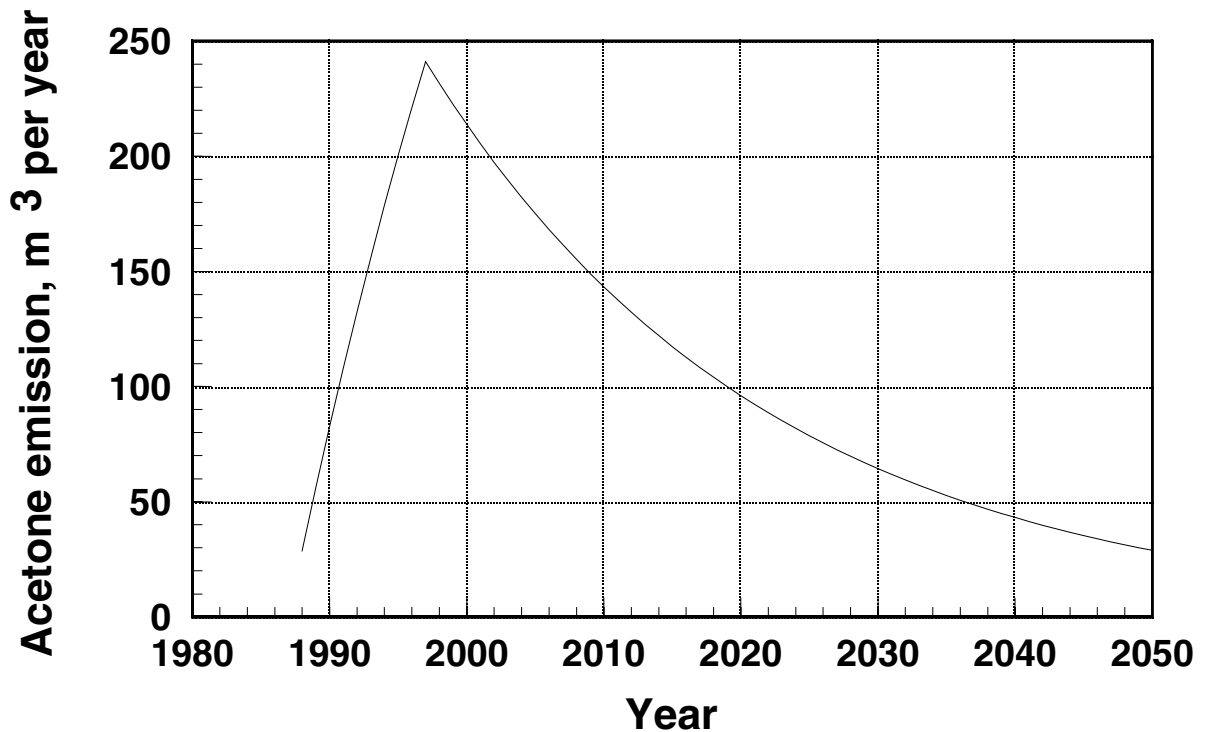


Figure C.3. Acetone emission plot for Example 3

The velocity can be calculated as shown in Example 4.

Example 4: Calculation of vertical gas velocity

The landfill of Example 1 has a predicted maximum methane emission of 12309 Mg /yr in 1997. The principal gas velocity is calculated as follows:

- Annual volumetric emission of CH₄:

$$12,309 \frac{\text{Mg CH}_4}{\text{yr}} \times \frac{\text{mol CH}_4}{16.0426 \text{ g CH}_4} \times \frac{10^6 \text{ g CH}_4}{\text{Mg CH}_4} \times \frac{22.414 \text{ L CH}_4}{\text{mol CH}_4} \times \frac{\text{m}^3 \text{ CH}_4}{1000 \text{ L CH}_4}$$

$$= 17,198,000 \text{ m}^3 \text{ CH}_4 / \text{yr}$$

- Annual volumetric emission of CO₂:

Assuming an equimolar methane – carbon dioxide mixture,

$$\text{CO}_2 \text{ emission} = \text{CH}_4 \text{ emission} = \frac{17,198,000 \text{ m}^3}{\text{yr}}$$

- Total principal gas emission:

Total emission = CH₄ emission + CO₂ emission

$$= 34,396,000 \frac{\text{m}^3}{\text{yr}}$$

- Surface area of the landfill in m²:

$$A = 100 \text{ acres} \times 4047 \frac{\text{m}^2}{\text{acre}} = 404,700 \text{ m}^2$$

- Velocity as $v = Q / A$:

$$v = \frac{(34,396,000 \frac{\text{m}^3}{\text{yr}})}{(404,700 \text{ m}^2)} = 84.99 \frac{\text{m}}{\text{yr}}$$

Example 5: Influence of k and L_0 values on gas emissions

Predict the principal gas velocity for the landfill of Example 1, for each of the following conditions: 1) default AP-42 values, $L_0 = 124.9056 \text{ m}^3/\text{Mg refuse}$, $k = 0.04 \text{ yr}^{-1}$, and 2) values consistent with the discussion in Section 3, $L_0 = 62.5 \text{ m}^3/\text{Mg refuse}$, $k = 0.02 \text{ yr}^{-1}$. To demonstrate the sensitivity of LAEEM to the assumptions of L_0 and k , a spreadsheet solution was performed, with the results shown in Figure C.4. The AP-42 default values suggest a maximum gas velocity almost twice that calculated with the selected values of k and L_0 .

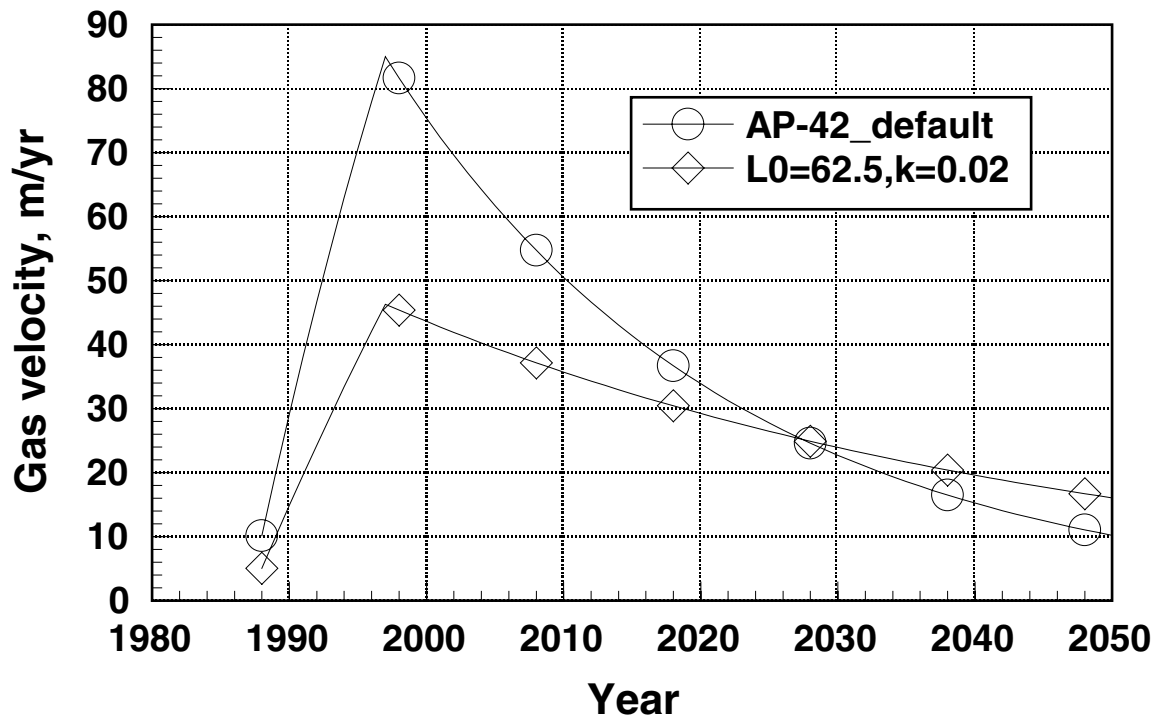


Figure C.4. Gas velocity prediction for landfill of Example 1 using LAEEM

Example 6: Time scales for each factor affecting HAP emissions

The landfill of Example 1 (30' deep) is saturated for a depth of 10' from the bottom of the landfill. The maximum principal gas velocity, calculated in Example 4, is predicted to be 85 m/yr.

Liquid and gas phase effective diffusivities are 150 and 0.015 m²/yr, respectively, and a first-order biodegradation rate for acetone is 150/yr (see Appendix Table B.1). The time scale for each of the fate and transport mechanisms associated with the release of acetone from the landfill may be calculated in the following manner:

- Assume a value for the porosity, $\phi = 0.40$.
- Ignore adsorptive effects, i.e. set $\beta = 0$.
- Calculate the time scales using Table C.1:

Convection: $\phi(1 + \beta) L / v$

Choose a characteristic length for convective transport:

$$L = 30 \text{ ft} * 1.0 \frac{\text{m}}{3.28 \text{ ft}} = 9.15 \text{ m}$$

$$\text{Solve for time scale} = 0.4 (1 + 0) 9.15 \text{ m} / 85 \text{ (m/yr)} * 365 \text{ days/yr}$$

Convection time scale = 16 days

Diffusion - liquid phase: $\phi(1 + \beta) L^2 / D$

Choose a characteristic length for diffusive transport in liquid:

$$L = 10 \text{ ft} * 1.0 \text{ m} / 3.28 \text{ ft} = 3.05 \text{ m}$$

$$\text{Solve for time scale} = 0.4 (1 + 0) 9.15^2 \text{ m}^2 / 0.015 \text{ (m}^2\text{/yr)}$$

Diffusive time scale in saturated zone = 2200 years

Diffusion - gas phase: $\phi(1 + \beta) L^2 / D$

Choose a characteristic length for diffusive transport in gas:

$$L = 20 \text{ ft} * 1.0 \text{ m} / 3.28 \text{ ft} = 6.10 \text{ m}$$

$$\text{Solve for time scale} = (0.4 (1 + 0) 6.10^2 \text{ m}^2 / 150 \text{ (m}^2\text{/yr)}) * 365 \text{ days/yr}$$

Diffusive time scale in saturated zone = 36 days

Biodegradation: $(1 + \beta) / k$

Solve for time scale = $((1 + 0) / (150/\text{yr})) * 365 \text{ days/yr} = 0.4 \text{ day}$

Biodegradation time scale = 1 day

- From a comparison of the various time scales involved, even without an exact or numerical solution to the transport equations the following conclusions seem apparent for this example situation:
 - 1) Biodegradation has such a short time constant that it appears likely to play a major role in the reduction of the acetone prior to its transport by either convection or diffusion;
 - 2) Both convection and gas phase diffusion play major roles in the movement of acetone;
 - 3) Liquid phase diffusion is a very slow process, and could result in the slow release of the acetone over a very long period, that is to say in the absence of biodegradation; and
 - 4) The presence of adsorption would have the effect of multiplying the time scales for each of the fate and transport mechanisms by a constant amount, and so their relative importance would remain unchanged.

Example 7: HAP flux from a closed, non-decomposing landfill

A pulp and paper industry landfill is experiencing no apparent decomposition. Estimate the emission of HAP. A sample of landfill gas taken from a depth of 20 ft below the ground surface revealed a HAP concentration of 200 ppmV as hexane. The following procedure may be used to estimate the emission of HAP that would occur as a result of diffusion only from the landfill surface area, which is 20 acres:

- Convert the HAP concentration from ppmV to g/m³; assume gas is at 25°C:

$$\frac{200 \times 10^{-6} \text{ atm}}{\left(\frac{0.08206 \text{ L} \cdot \text{atm}}{\text{mol} \cdot \text{K}}\right)(25 + 273)\text{K}} * \frac{86.1766 \text{ g hexane}}{\text{mol}} * \frac{1000 \text{ L}}{\text{m}^3} = 0.705 \frac{\text{g}}{\text{m}^3}$$

- Use Equation (B11) to estimate emission of HAP as hexane:

$$\frac{150 \frac{\text{m}^2}{\text{yr}} * \frac{0.705 \text{ g}}{\text{m}^3} * 20 \text{ acres} * \frac{4047 \text{ m}^2}{\text{acre}} * \frac{\text{Mg}}{10^6 \text{ g}}}{20 \text{ ft} * \frac{\text{m}}{3.28 \text{ ft}}} = 1.404 \frac{\text{Mg}}{\text{yr}}$$

- To convert this result to m³/yr:

$$\frac{1.404 \times 10^6 \text{ g hexane}}{\text{yr}} * \frac{\text{mol}}{86.1766 \text{ g hexane}} * \frac{22.414 \text{ L}}{\text{mol}} * \frac{\text{m}^3}{1000 \text{ L}} = 365 \frac{\text{m}^3}{\text{yr}}$$

Example 8: Influence of biodegradation on HAP emissions

The following procedure may be used to perform a sensitivity analysis for the results from Example 7, and assess the potential effects of biodegradation on the HAP emissions. First-order biodegradation rates of $0 - 250 \text{ yr}^{-1}$, are used to describe the range of values expected for HAPs.

- A spreadsheet was used to solve Equations (B.7) and (B.8). The dependence of the HAP emission rate on k_b on the HAP rate determined in Example 7, 1.4 Mg/yr , is shown in Figure (C.5).

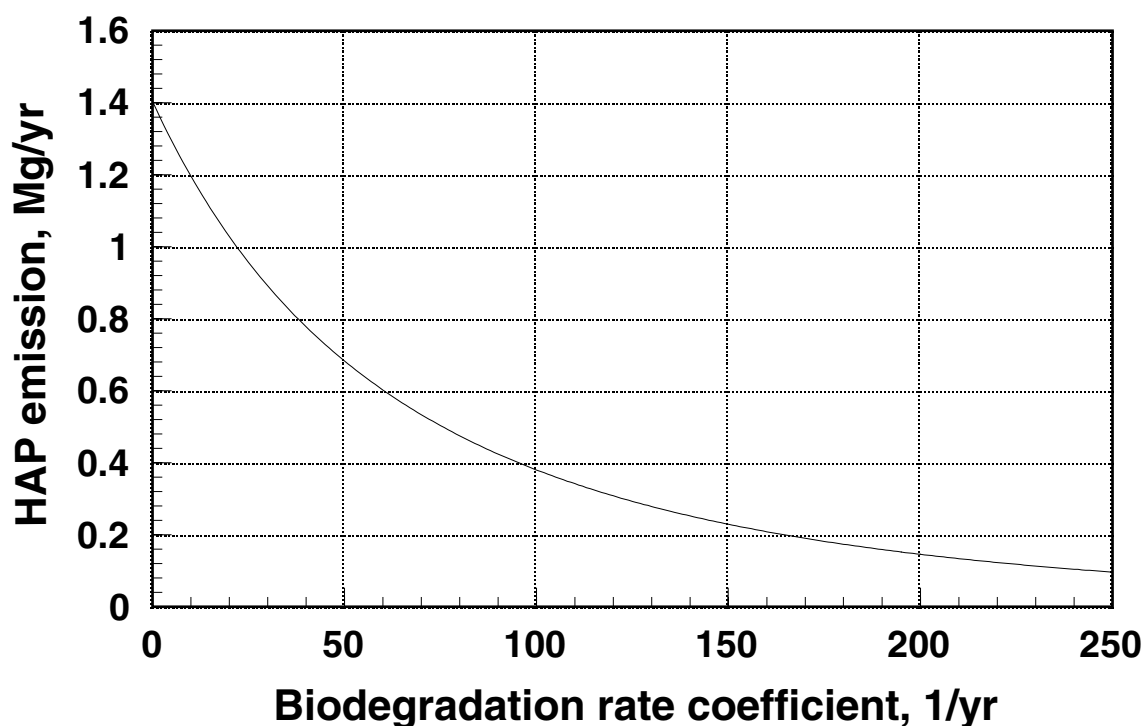


Figure C.5. The influence of biodegradation on HAP emissions for Example 7.

Example 9: Time varying HAP emissions

The following procedure demonstrates how the attenuation of HAP concentration by unsteady-state gas phase diffusion within the landfill can be estimated using Figure C.6.

$$\text{Tau} = t / H^2 \phi (1+\beta)/D$$

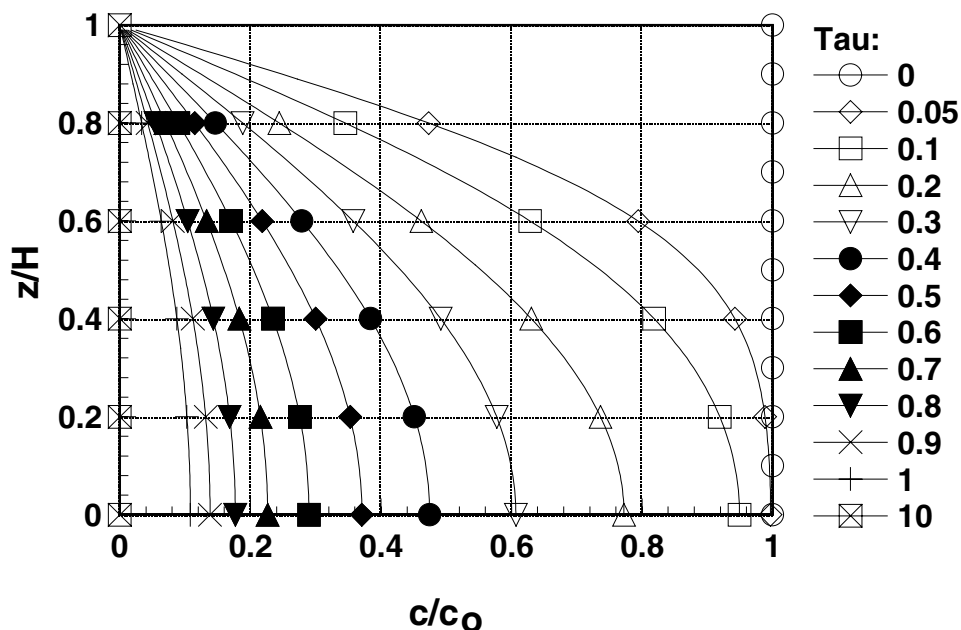


Figure C.6. Family of concentration profiles for unsteady diffusion-driven HAP emissions

The landfill of Examples 1 and 5 (20 ft deep unsaturated zone) is used for illustrative purposes.

- The time constant for gas phase diffusion was calculated in Example 5 as 36 days.
- After one year, the dimensionless time variable, τ , would be 365 days / 36 days = 10.
- From Figure C.6, at any depth within the unsaturated zone, the concentration profile c/c_0 is zero, i.e. all the HAPs have been attenuated through diffusion.
- After one week, $\tau = 7 \text{ days} / 36 \text{ days} = 0.2$. At a depth of 4 ft within the 20 ft deep unsaturated zone, $z/H = (20 - 4) / 20 = 0.8$, and c/c_0 is interpolated to be approximately 0.2. Hence we would expect that $(1 - 0.47) * 100 = 80\%$ attenuation would have occurred for HAPs at the 4 ft depth within a one week time period.

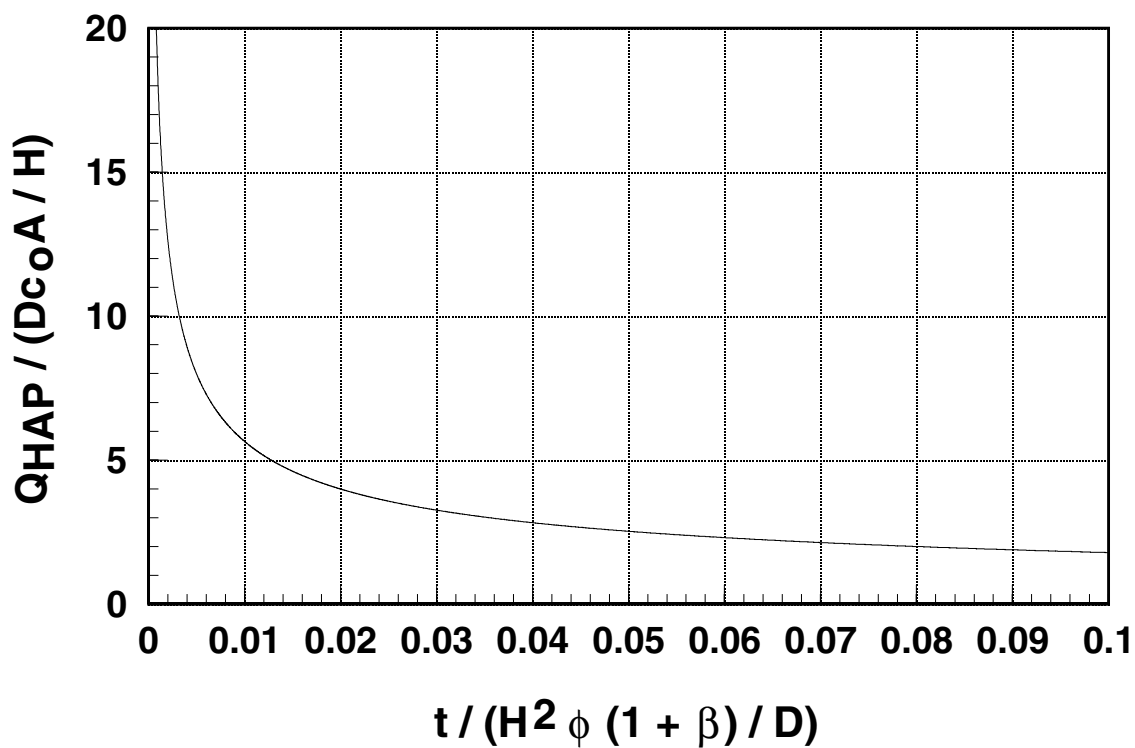


Figure C.7. Non-dimensionalized graph of HAP emissions vs. time for unsteady-state diffusion

It can be noted from Figure C.7 that gas phase emission from the unsaturated zone occurs very rapidly as the result of diffusion, which would tend to exhaust most of the HAPs within a short period of time, in the absence of HAP releases from the liquid phase.

