EPA-453/R-94-080A

AIR EMISSIONS MODELS
FOR WASTE AND WASTEWATER

U.S. EPA Contract No. 68D10118

November 1994

prepared for the
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park
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1.0 INTRODUCTION

1.1 BACKGROUND

This report was prepared for the U.S. Environmental Protection Agency's (EPA's) Office of Air Quality Planning and Standards (OAQPS) as part of the effort to develop air emission models for hazardous waste treatment, storage, and disposal facilities (TSDF). Basic to this effort is the determination of the means by which organic compounds escape to the environment from waste and wastewater.

Organic compounds in surface impoundments, land treatment facilities, landfills, wastepiles, or wastewater collection and treatment systems can depart through a variety of pathways, including volatilization, biological decomposition, adsorption, photochemical reaction, and hydrolysis. To allow reasonable estimates of organic compounds disappearance, one must know which pathways predominate for a given chemical, type of waste site, and set of meteorological conditions.

Analytical models have been developed to estimate emissions of organic compounds via various pathways from wastewater and waste management units. Some of these models have been assembled into a spreadsheet called CHEMDAT8 for use on an IBM PC, or compatible, microcomputer. A user's guide for CHEMDAT8 is included as a separate manual. Area emission sources for which models are included on the diskette are as follows:

- Nonaerated impoundments, which include quiescent surface impoundments and open top WWT tanks;
- Aerated impoundments, which include aerated surface impoundments and aerated WWT tanks;
- Disposal impoundments, which include nonaerated disposal impoundments;
- Land treatment; and
- Landfills.

These models can be used to estimate the magnitude of site emissions for regulatory purposes. Sample calculations using each model are also included in this report.

A computer program "WATER8" is available for estimating the fate of organic compounds in various wastewater treatment units, including collection systems (Chapter 4), aerated basins (Chapter 5), and other units (Chapter 6). WATER8 is written to run under Microsoft's disk operating system DOS without the need to purchase other programs (Windows or spreadsheets). WATER8 contains useful features such as the ability to link treatment units to form a treatment system, the ability for recycle among units, and the ability to generate and save site-specific compound properties.

The terms "volatile" and "semivolatile" are used to describe the tendency of an organic waste component to partition into the headspace of the waste container. Waste constituents similar to benzene and methylene chloride have relatively high vapor pressures (>10 mm Hg) and relatively high Henry's law constants (>10 mole fraction vapor/mole fraction liquid) and are considered volatile. Other waste constituents similar to phenol do not have high vapor pressures or Henry's law constants, but are considered semivolatile because some part of the semivolatiles can be lost to the atmosphere during waste handling and treating operations.

1.2 SCOPE

This report briefly describes the chemical and physical pathways for organic compounds and discusses their importance for different types of sites and sets of conditions. Models developed for estimating the relative magnitude of environmental release in the presence of competing pathways are presented, and physical characteristics of the parameters that serve as inputs to the models are identified.

The models provide an estimate of the relative magnitude of organic compounds pathways on a compound-specific basis. Models for aerated and nonaerated impoundments, lagoons, landfills, wastepiles, and land treatment facilities have been installed in an integrated spreadsheet program, CHEMDAT8, which allows a user to calculate the partitioning of organic compounds among various pathways depending on the particular parameters of the facility of interest. The program is structured to allow new data (e.g., compounds and model facility parameters) to be added (see CHEMDAT8 user's guide). The results of the calculated partitioning may be used to identify those characteristics that are important in determining relative organic compounds loss rates.

Source variability will significantly influence the relative importance of the pathways. For highly variable sources, it may be possible to exclude insignificantly small pathways from consideration. The relative magnitude of these pathways can then be compared by applying the methodology to a model facility to determine relative differences among various compounds.

1.3 REPORT ORGANIZATION

Chapter 2 describes each of the potential pathway mechanisms that determine the fate of various chemical species. Chapter 3 discusses the importance of the pathways for surface impoundments and aerated and non-aerated WWT facilities, land treatment sites, and landfills/wastepiles.

Chapter 4 presents air emission models that are applicable to collection systems. A number of different collection system elements are presented and a discussion of the use of the models is provided.

Chapter 5 presents air emission models that are applicable to conventional wastewater treatment units. A discussion of the estimates of the effects of biological reactions on the air emissions and water quality is presented. Recommendations for the use of models are also presented.

Chapter 6 presents air emission models for trickling filters, cooling towers, and API separators. In addition, this section provides recommendations for the use of the air emission models for a variety of waste management situations.

Chapters 7 and 8 describe the emission models applicable to landtreatment and landfill sites. Models for estimating emissions from transfer, storage, and handling operations are described in Chapter 9. Chapter 10 compares treatment emission model predictions with the field data that are available. Chapter 11 compares collection system model predictions with the field data that are available from collection systems.

This report compares relative rates of organic compounds destruction and volatilization to determine the most significant pathways. The rate of organic compounds volatilization destruction for any one pathway is calculated so that it can be expressed as a fraction of the loss/destruction from all pathways.

APPENDIX A presents an overview of the literature and APPENDIX B presents comprehensive source list that includes pertinent literature in addition to that cited in the sections and Appendixes of this report.

Properties of compounds of interest to TSDF pathways and emission estimation are presented in APPENDIX C. A subset of these compounds is a part of CHEMDAT8. The user's guide, available separately, describes the procedures that are used in estimating emissions using CHEMDAT8 or WATER8 and other procedures presented in the body of the report. The user's guide also contains instructions for modifying CHEMDAT8 to include additional compounds using the CHEM8 compound characteristics presented in APPENDIX C.

2.0 DESCRIPTION OF PATHWAYS

2.1 GENERAL

A pathway is considered here to be any process that removes volatile organics from a site. The removal may be physical (as in volatilization of a solvent from a surface impoundment) or chemical (as in oxidation of an alcohol in a wastewater treatment plant).

Pathways may be considered as rate processes, with rate often strongly dependent on concentration of the disappearing species and temperature of the system. Rates vary in order from zero to mixed, with first order predominating at low concentrations, that is:

$$rate = -\frac{dc}{dt} = k_v c \tag{2-1}$$

where,

c = concentration of disappearing substance, g/L;
t = time, s; and
k_v = volatilization constant, s^{-1}.

Half-life, the time required for one-half of the substance to disappear, is a useful concept. It provides an easily visualized measure of the time required for disappearance. For a first-order rate process:

$$t_{1/2} = (1n2)k_v^{-1} = 0.693\,k_v^{-1} \qquad (2\text{-}2)$$

where, $t_{1/2}$ = half-life, in seconds.

The half-life of a second-order equation is as follows:

$$t_{1/2} = k_s^{-1}\;C_o^{-1} \qquad (2\text{-}3)$$

where,

k_s = second-order volatilization constant, L/(g•s); and

C_o = initial concentration, g/L.

Note that first-order half-lives are independent of initial concentration while second order half-lives are not.

Much of the following material is taken from ICF.[1] The pathways described are physical (volatilization, adsorption, migration, and runoff) and chemical (biological decomposition, photochemical decomposition, hydrolysis, oxidation/reduction, and hydroxyl radical reaction).

2.2 VOLATILIZATION

Volatilization occurs when molecules of a dissolved substance escape to an adjacent gas phase. The driving force for this process in nonturbulent liquids is molecular diffusion. Equation (2-1) shows the rate of volatilization of an organic chemical from water. For this case, the rate constant can be estimated:[2]

$$k_v = \frac{1}{L}\left[\frac{1}{k_l^o\left(\dfrac{D_l^c}{D_l^o}\right)^m} + \frac{RT}{(10^6)Hk_g^w\left(\dfrac{D_g^c}{D_g^w}\right)^n}\right]^{-1} \qquad (2\text{-}4)$$

where,

L = mixing depth of water, cm;

k^0_l = mass transfer coefficient of oxygen in water, cm/s;

D_l = diffusion coefficient of the chemical (c) or oxygen (o) in water, cm^2/s;

m = liquid turbulence exponent, 0.5 to 1, dimensionless, from TABLE 2-1;

R = ideal gas constant, atm $cm^3/(mol \bullet K)$;

T = temperature, K;

H = Henry's law constant, atm m^3/mol;

k^w_g = mass transfer coefficient for water vapor in air,cm/s;

D_g = diffusion coefficient of the chemical (c) or water (w) in air, cm^2/s; and

n = gas turbulence exponent, 0.5 to 1.0, dimensionless, from Table 2-1.

Equation (2-4) requires values of diffusion coefficients and Henry's law constants. If tabulated values are not available, the following estimations can be used. For the diffusion of a chemical in air:[3]

$$D_g = 0.0067T^{1.5}(0.034 + M^{-1})^{0.5}\ M^{-0.17}[(M/2.5d)^{0.33} + 1.81]^{-2} \qquad (2\text{-}5)$$

where,

T = temperature, degrees Kelvin;
M = molecular weight of chemical, g/g mol;
d = density of liquid chemical, g/cm^3.

For diffusion coefficients in water:

$$D_1 = 1.518\,(10^{-4})\,V_{cm}^{-0.6} \qquad (2\text{-}6)$$

where V_{cm} = molar volume of chemical, cm^3/g mol.

This equation assumes the system temperature to be 300 deg. K. For other temperatures, a more rigorous form of the equation should be used, as in Perry.[4] Molar volume is estimated as the ratio of molecular weight to liquid density at room temperature.

TABLE 2-1. VALUES OF CONSTANTS FOR USE IN EQUATION 2-4[5]

Constant	Value	
	Rivers	Lakes
L (cm)	200	200
k^o_l (cm◦s^{-1})	0.0022	0.0005
m	0.7	1.0
T (K)	293	293
RT (m3◦atm◦mol^{-1})	2.40 x 10^{-2}	2.40 x 10^{-2}
K^w_g (cm◦s^{-1})	0.58	0.58
n	0.7	0.7

If ideal gases and solutions are assumed, Henry's law constant can be estimated from:

$$H = P/(14.7s) \tag{2-7}$$

where,

P = pure component vapor pressure, psia; and

s = solubility of chemical in water, g mol/m^3.

Values for other terms in Equation 2-4 have been tabulated by ICF and are given in TABLE 2-1.

In general, equations are available to estimate volatilization from wastewater treatment systems and surface impoundments.[6,7] In the case of land treatment and landfills, the models for volatilization are much less well developed and the supporting data are more limited than those of the aqueous systems. The rate of volatilization at a soil-air interface is a function of the concentration and properties of the escaping chemical, soil properties (moisture, temperature, clay, and organic content), and properties of the air at soil level (temperature, relative humidity, and wind speed).[8]

2.3 ADSORPTION

Adsorption takes place when molecules of a dissolved chemical (in a liquid-solid system) become physically attached to elements of the solid phase. Chemical bonding may also occur (chemisorption). An example of adsorption is molecules of solvent being sorbed by particles of silt in a surface impoundment. If the adsorptive capacity of the solid material is reached, no further net sorption will occur. With reductions in concentration in the bulk liquid of the chemical being sorbed (adsorbate), desorption may take place. The amount of material adsorbed depends on (1) the concentration of adsorbate, (2) the amount of solid phase (adsorbent), and (3) the temperature. For systems with constant adsorbent properties, primarily surface area per unit mass, the amount of material adsorbed at a particular concentration and temperature is proportional to the mass of adsorbent. For example, the Freundlich adsorption isotherm equation allows prediction of amount adsorbed as follows:

$$\frac{x}{m} = K_f C^{1/n} \qquad (2\text{-}8)$$

where,

x = mass of chemical adsorbed, g;

m = mass of adsorbent, g;

K_f = Freundlich adsorption coefficient, (g sorbate/ g sorbent)/(g sorbate/g solution);

C = concentration of chemical in solution at equilibrium, g sorbate/g solution; and

n = empirical constant, ranging from 0.7 to 1.1, typically 1.0 for soils, dimensionless.

A Langmuir adsorption isotherm can be derived from a kinetic rate theory describing the adsorption and desorption rates. The rate of adsorption is proportional to the rate of collisions between adsorbate molecules and free adsorbent surface. The rate decreases with lowering adsorbate concentration and with decreasing surface sites available for adsorbing molecules. The following rate equation applies:

$$\text{Rate of adsorption} = k_1 C\,(1-f) \qquad (2\text{-}9)$$

where,

k_1 = rate constant for adsorption, g/s;

f = fraction of adsorption sites occupied, dimensionless; and

C = concentration of chemical in solution at equilibrium, g sorbate/g solution.

For desorption:

$$\text{Rate of desorption} = k_2 f \qquad (2\text{-}10)$$

where,

f = fraction of adsorption sites occupied; and

k_2 = rate constant for desorption, g/s.

At equilibrium the two rates are equal, and

$$f = \frac{k_1C}{k_1C + k_2}. \qquad (2\text{-}11)$$

Adsorption rates are usually rapid compared to the other processes discussed here. However, mass transfer limitations may reduce effective rates, especially for poorly mixed systems. Lack of sorbent and its saturation may also reduce the effectiveness of adsorption.

For estimating adsorption partitioning, a linear relationship is assumed ($n = 1$ or $k_1C << k_2$). The equilibrium relationship for biomass is estimated from an equation of Matter-Muller,[9] based on the logarithm of the octanol-water partition coefficient, LOW. For land treatment and land-fills, the only partitioning of importance to fate predictions is gas-liquid partitioning.

2.4 MIGRATION

Migration occurs when chemicals applied to soils are transported through the soils to groundwater. Leaching and percolation are the mechanisms that physically remove chemical molecules from a point of deposit and carry them toward a water table. Capillary flow is a resisting mechanism that moves the molecules upward through the soil. The leachability of a chemical is a function of soil texture and cation exchange capacity, amount of soil organic content, amount and intensity of rainfall, and mechanical placement and adsorptive properties of the chemical.[10]

2.5 RUNOFF

Chemicals at or near the soil may be washed away by rain. The rate depends on soil and chemical characteristics and on rainfall rates and frequency. Clark, Viessman, and Hammer[11] state that runoff in any drainage area is a function of climate and the physical characteristics of the area. Significant factors include precipitation type; rainfall intensity, duration, and distribution; storm direction; antecedent precipitation; initial soil moisture conditions; soil type; evaporation; transpiration; and, for a given drainage area, its size, shape, slope, elevation, directional orientation, and land use characteristics. If rainfall is heavy shortly after application of a chemical, runoff and erosion can physically remove it. The chemical may be dissolved in runoff water, carried along by it, or adsorbed on eroding soil particles that move with runoff. For pesticide applications, about 3 to 10 percent of the applied material appears in runoff water. Below a certain intensity, rainfall will promote leaching of nonadsorbed chemical into the ground rather than result in runoff.

2.6 BIOLOGICAL DECOMPOSITION

Biological decomposition takes place when microbes break down organic compounds for metabolic processes. The rate of decomposition depends on the structure of the compound and on the needs of the microbes. If the compound is present in excess, the rate of population increase is as follows:

$$dx/dt = Rx \qquad (2\text{-}12)$$

where,

t = time, sec;

x = concentration of biomass, g/L; and

R = specific growth rate coefficient, s^{-1}.

If the compound is present in limited amount, the rate becomes a hyperbolic saturation function of the compound (substrate) concentration:[12]

$$\frac{dx/dt}{x} = R_{max} S/(K_s + S) \qquad (2\text{-}13)$$

where,

R_{max} = maximum specific growth rate coefficient (where substrate is in excess) s^{-1};

S = concentration of substrate, g/L; and

K_s = substrate concentration at which the rate of substrate utilization is one-half of the maximum rate, g/L.

Because the microbial population increases at the expense of the compound, the growth rate is proportional to the compound's rate of disappearance. The rate process may be of zero, first, or mixed order depending on concentration of the substrate. In the presence of multiple substrates, kinetics become complex.

For the case of S much greater than K_s, the equation approaches zero order, and Equation (2-13) becomes:

$$\frac{dx/dt}{x} = R_{max} \ . \qquad (2\text{-}14)$$

For cases where S is much less than K_s, the equation approaches first order:

$$\frac{dx/dt}{x} = SR_{max}/K_s \qquad (2\text{-}15)$$

with R_{max}/K_s being the first-order rate constant.

For intermediate values of S, the equation is mixed order, with the order dependent on values of the constants R_{max} and K_s.

2.7 PHOTOCHEMICAL DECOMPOSITION

Photochemical decomposition may occur in two ways. A chemical may absorb light and react (direct photolysis), or the chemical may react because of light absorption by surrounding elements (indirect photolysis).

For direct photolysis, the rate of reaction of a dilute solution of chemical in pure water is as follows:

$$K_p = b\ N\ E\ ,_8\ I_8\ [C] \qquad (2\text{-}16)$$

where,

k_p = rate of direct photolysis, g/(L s);

b = unit conversion constant, 3.8×10^{-21} g mol cm^4/(L photon);

N = reaction quantum yield, dimensionless;

$,_8$ = light absorption coefficient at wavelength interval 8, L/(g mol◦cm);

I_8 = light flux at wavelength interval 8, photons/(cm^3◦s); and

C = concentration of the chemical in water g/L.

Lyman[13] refers to Zeep and Cline;[14] Zepp;[15] and Mabey, Mill, and Hendry[16] for details of rate calculations in aquatic systems. In these systems, the rate constant K_p varies with the distribution of sunlight and its intensity. Time of day, season, cloud cover, and latitude all affect k_p so that a reference condition must be stated; e.g., a light flux of photons per second corresponding to a cloudless yearly average at a latitude of 40°N.

Reactions may be photocatalyzed. For example, a $Ti0_2$ catalyst can be photoexcited by light at wavelengths less than 360 mm. Ollis[17] examined the degradation of halogenated hydrocarbons with this catalyst and found a rate equation of the form:

$$\frac{1}{dC/dt} = \frac{1}{k_p} + \frac{1}{k_p K_b C} \qquad (2\text{-}17)$$

where,

k_p = photolysis rate constant, g chemical/(L◦s◦g catalyst); and

K_b = apparent binding constant of a reaction intermediate adsorbed on the illuminated catalyst surface, L/g chemical.

For 11 halocarbons, values of k ranged from 5.8 x 10^{-8} to 2.3 x 10^{-6} g/L◦s◦g of catalyst, with most about 2.8 x 10^{-7} to 1.7 x 10^{-6}. A twelfth halocarbon had a k value of 2.3 x 10^{-4}. Values of k_b for the 12 compounds ranged from 2 to 20 L/g.

2.8 HYDROLYSIS

Hydrolysis occurs when a chemical reacts with water. For organic compounds, the reaction usually replaces a functional group (X) with a hydroxyl:[18]

$$RX + H_2O = ROH + HX\,. \qquad (2\text{-}18)$$

Reaction rate constants may be pH-dependent; for a specific pH:

$$k_H = k_a\,[H^+] + k_n + k_b\,[OH^-] \qquad (2\text{-}19)$$

where,

k_H = first-order hydrolysis rate constant, s^{-1};

k_a = second-order rate constant for acid-promoted hydrolysis, L/(g mol◦s);

$[H^+]$ = hydrogen ion concentration, g mol/L;

k_n = first-order rate constant for pH-independent neutral hydrolysis, s^{-1};

k_b = second-order rate constant for base-promoted hydrolysis, L/(g mol◦s); and

$[OH^-]$ = hydroxyl ion concentration, g mol/L.

Equation (2-19) can be transformed to:

$$k_w = [H^+][OH^-] \tag{2-20}$$

where k_w = ionization constant for water ≈ 10^{-14} g mol^2/L^2.

The rate constant kH depends on system pH and on the relative values of k_a, k_b, and k_n.

$$k_H = k_a[H^+] + k_n + k_b k_w/[H^+]\ . \tag{2-21}$$

2.9 OXIDATION/REDUCTION

Organic compounds in aquatic systems may be oxidized by oxygen (particularly as singlet oxygen, $^1O_2$) or other oxidants such as hydroxyl radicals (OH) and peroxy radicals (RO_2). The OH radicals tend to be very reactive, but present only in low concentrations. The RO_2 radicals are less reactive than the OH radicals, but are present in greater concentrations. Singlet oxygen is highly reactive, but also selective. It has an affinity for electron-rich structures such as dienes and substituted olefins.

The oxidation rate can be calculated as:[19]

$$\frac{*C}{*t} = C\left(k_{RO_2}\ [RO_2] + k_{SO}\ [^1O_2] + k_x\ [X] \right) \tag{2-22}$$

where,

$k_{[RO2]}$ = rate constant for peroxy radicals, L/(g mol-s);

[RO2] = concentration of peroxy radicals, g mol/L;

k_{SO} = rate constant for singlet oxygen, L/(g mol-s);

$[^1O_2]$ = concentration of singlet oxygen, g mol/L;

k_x = rate constant for "other" oxidants, L/(g mol-s); and

[X] = concentrations of "other" oxidants, g mol/L.

In anaerobic environments, reduction reactions may take place. Organochlorines are particularly affected. The reduction rate can be calculated as:[20]

$$\frac{*C}{*t} = C \sum_i k_i [R_i] \qquad (2-23)$$

where,

k_i = rate constant for reductant i, L/g mol.s; and
$[R_i]$ = concentration of reductant i, g mol/L.

2.10 HYDROXYL RADICAL REACTIONS

Hydroxyl radical reactions may occur through addition of a hydroxyl radical, abstraction of a hydrogen atom, or both. In the addition, reaction molecules with high electron density portions attract electrophilic hydroxyl radicals. Hydrogen abstraction takes place when a carbon-hydrogen bond in an organic molecule is easily broken; it is controlled by electronic configuration and number of hydrogen reactions in the molecule. The rate constant for the reaction is often in the range of 6 to 60 x 108 L/(g mol-s).

A hydroxyl radical reaction rate can be calculated as:[21]

$$\frac{*C}{*t} = C\, k_{OH} [OH^-] \qquad (2-24)$$

where

k_{OH} = rate constant for hydrogen abstraction or hydroxyl addition, L/(g mol-s).

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3.0 IMPORTANCE OF PATHWAYS

3.1 INTRODUCTION

The importance of the nine pathways described in Chapter 2.0 for surface impoundments, open tanks, land treatment facilities, landfills, and wastepiles is described in this section. The discussion centers on the pathways used in the emission models described in subsequent sections. The pathways described in Chapter 2.0 are repeated below for convenience:

- Volatilization
- Adsorption
- Migration
- Runoff
- Biological decomposition
- Photochemical decomposition
- Hydrolysis
- Oxidation/reduction
- Hydroxyl radical reaction.

Section 3.2 presents the relative importance of these pathways based on the theoretical discussions appearing in Chapter 2.0, the data appearing in the literature, and engineering judgment. Section 3.3 summarizes in tabular form the results of the emission model analyses in Chapters 5.0 through 6.0 and the pathways forming the basis for the emission models.

3.2 THEORETICAL BASIS

The relative importance of the nine pathways for TSDF is discussed in the following text and summarized in Table 3-1.

TABLE 3-1. PATHWAYS FOR HAZARDOUS WASTE AREA EMISSION SOURCES[a]

Pathway	Surface impoundments	Wastewater treatment plants: Aerated	Wastewater treatment plants: Non-aerated	Land treatment	Landfill
Volatilization	I	I	I	I	I
Biodegradation	I	I	I	I	S
Photodecomposition	S	N	N	N	N
Hydrolysis	S	S	S	N	N
Oxidation/ reduction	N	N	N	N	N
Adsorption	N	S	S	N	N
Hydroxyl radical reaction	N	N	N	N	N
Migration[b]	N	N	N	N	N
Runoff[b]	N	N	N	N	N

I = Important.

S = Secondary.

N = Negligible or not applicable.

[a] Individual chemicals in a given site type may have dominant pathways different from the ones shown here.

[b] Water migration and runoff are considered to have negligible effects on ground and surface water in a properly sited, operated, and maintained RCRA permitted hazardous waste treatment, storage, and disposal facility.

These data were used as the basis for the emission models contained in CHEMDAT8.

Results of exercising these models to identify pathways of importance are discussed in Chapters 4.0 through 10.0 and are summarized in Section 3.3. A short discussion of the theoretical basis for pathways selection follows.

3.2.1 Surface Impoundments

Data reported by ICF show predominant removal mechanisms and halflives for 71 chemicals. Table 3-2 lists the mechanisms and statistics for six surface water pathways. Average half-lives range from about 1/2 to 8 days, with predominant mechanisms being volatilization and biodegradation. The rate of photodecomposition depends on the depth of the surface impoundment. The rate is negligibly low for depths as great as 3 meters and is indicated in Table 3-1 as S for a secondary effect.

3.2.2 Aerated and Nonaerated Wastewater Treatment

As in the case of the surface impoundments, volatilization and biodegradation are potentially significant mechanisms. The relative rates of these mechanisms depend on the particular component and treatment system. Photodecomposition is not expected to be a significant pathway due to the opacity of the system, the depth of the liquid, and the residence time of the processes. Adsorption is not expected to be significant except for large loadings of suspended solids and oils in the wastewater. The concentrations for many organic compounds are expected to be roughly the same in the biomass as in the aqueous phase.

3.2.3 Land Treatment

Based on available emission data and literature sources, volatilization and biodegradation are expected to be important in land treatment.[2-6] For highly volatile constituents, volatilization is expected to be the predominant pathway; for low volatile constituents, biodegradation is expected to be the predominant pathway. Adsorption of organic compounds onto organic carbon in the soil also occurs at land treatment sites. However, calculations of land treatment air emissions both with and without consideration of adsorption show a difference of only 10 percent. Therefore, adsorption is not considered a major pathway for organics removal.

The method of waste application and incorporation into the soil influence the importance of photochemical reactions in the degradation of organic wastes in land treatment facilities.[7] Photodecomposition can occur in land treatment between application and tilling (usually 24 hours), although exposure to sunlight is limited to daylight hours. While exact rates of photodegradation are not known, they are expected to be low. The oil in which the hazardous materials are suspended is semiopaque to sunlight, which would tend to keep photodecomposition low. After tilling, photodegradation is nonexistent because sunlight does not penetrate the soil surface.[8] Consequently, photodecomposition is not expected to be significant.

3.2.4 Landfills

Volatilization is expected to be a primary organic compounds pathway for landfills. Biodegradation is expected to be negligible for hazardous waste landfills. The toxic properties of the water are expected to inhibit biological processes and therefore biodegradation.[9]

Rates of diffusion in the gas phase may be important. Components can diffuse through unsaturated soils (air pockets present). Control of liquid infiltration into the landfill is expected to keep migration into the soil at a negligible level.

3.3 EMISSION MODELS

Based on the exercise of CHEMDAT8 in predicting and comparing pathways for TSDF processes, the pathways shown in Table 3-3 are used as the basis of the models. Insignificant emissions or inadequate data upon which to develop the model relationships are the principal reasons for limiting the models to the pathways shown in Table 3-3.

It should be noted that CHEMDAT8 includes provisions to activate the unused pathways should further investigations and field tests indicate the desirability of incorporating additional pathways in the emission models.

TABLE 3-2. STATISTICS FOR SURFACE WATER PATHWAYS

	Pathway					
	Volatilization	Biodegradation	Photodecomposition[a]	Hydrolysis	Oxidation/reduction	Adsorption
Range of half-lives, days	0.9-15	0.04-96	0.04-900	0.0003-35	0.1-5	0.04-1.5
Average half-life	2.24	8.05	76.3 1.37	5.39	2.05	0.55
Standard deviation	2.85	19.4	259.0 1.82	10.8	2.40	0.83
Number of chemicals	38	26	12	11	4	3

[a] Statistics are given for chemicals with and without an outlier.

TABLE 3-3. PATHWAYS FOR TSDF SITES

Type of facility	Pathways included in model
Quiescent storage and treatment impoundments	Volatilization
Mechanically aerated impoundments	Volatilization Biodegradation
Quiescent disposal impoundments	Volatilization
Land treatment facilities	Volatilization Biodegradation
Closed landfills	Volatilization (diffusion through cap) Barometric pumping
Active landfills	Volatilization (diffusion through waste)
Wastepiles	Volatilization

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4.0 COLLECTION SYSTEM AIR EMISSIONS

4.1 INTRODUCTION

This chapter presents the methods used to estimate air emissions from wastewater collection systems. Air emission factors are developed that can be used to predict the release of volatiles to the atmosphere from liquid wastes discharged in the waste collection system. As a waste stream containing a volatile waste constituent is discharged into a collection system, the volatile constituent can be emitted into the atmosphere through the mechanism of mass transfer to the air flowing through the collection system. Air can enter and leave a collection system by openings in drains, open channels, channels with grates, openings in manhole covers, junction boxes, sumps, and other openings. Estimation of the flow of air in a collection system unit (drain, manhole) relative to the flow of wastewater flowing under the collection system unit permits an estimation of the fraction of the volatile constituent lost to the atmosphere as it passes under the unit.

The assumptions that were made to characterize chemical collection conduit designs include the following:

- The design depth in the drain channel is assumed to be half full.
- The flow in the channel for estimating fractional emissions is assumed to be 80 percent of design depth. (Lower depths result in higher emissions.)
- The air exiting the system is assumed to be at equilibrium with the volatiles in the channels.

- A typical wind velocity is assumed to be 1.6 m/s (3.5 MPH).

The assumption of equilibrium in wastewater collection units is considered an appropriate approximation for national emission estimates. For certain site specific emission estimates mass transfer may be a more suitable method. Additional information concerning the unit to be modeled will be needed if the mass transfer approach is taken.

The emission factors for the collection units are sensitive to the magnitude of the flow rates in the channels. The loss of volatiles in the channels could be less than the equilibrium amount if the rate of mass transfer from the bulk of the wastewater to the air was slow enough. This mass transfer rate is expected to be sensitive to the depth in the channel, with equilibrium not achieved for high flows of air across deep channels. For the case of channel depths at a fraction of the design depths and relatively low air rates (manhole covers and enclosed collection systems), the assumption of equilibrium is expected to be appropriate.

The assumption of equilibrium in wastewater collection units is expected to be more accurate for systems with restricted headspace ventilation. Mass transfer is not expected to be the rate controlling mechanism in the situation of restricted ventilation, and the assumption of equilibrium will limit air emissions to the equilibrium value.

Since the air emission factors are sensitive to environmental factors such as temperature, humidity, and wind pressure, the measured air emissions from wastewater collection systems are expected to be variable. Monte Carlo methods are used to simulate the effect of variable environmental factors on a waste collection system. Because of the degree of difficulty in performing the Monte Carlo calculations with site specific calculations, a short-cut technique using unit emission factors is presented here. The fraction lost from waste passing under specific units is estimated for common unit types and waste constituents of varying volatility.

For the model systems a temperature difference of 5 degrees Celsius was chosen as a temperature difference between the ambient air and the collection system temperature. This temperature difference was used to estimate gas flows due to air density differences. The actual temperature differences would be site specific.

4.2 COLLECTION SYSTEM EMISSION FACTORS

4.2.1 The Use of Emission Factors

The emission factors developed in this document are expressed in terms of the fraction of material in the collection conduit main emitted per unit. The collection conduit is the subsurface pipe or covered trench that the wastewater flows in by gravity from unit to unit on the path of the waste to the wastewater collection system. When the path of the waste placed in the collection system is specified, the amount of material remaining in the original waste stream is recalculated each time the waste flows under a unit with a potential emission source (drain connection, manhole, lift station, sump, etc.):

Emissions from unit = amount present x unit emission factor
New amount present = amount present - emissions from unit.

Table 4-1 illustrates how the toluene emissions from a waste discharge into a collection system can be estimated. The waste flows into an open trench drain. Forty feet downstream, additional waste flows into the trench for an additional 20 ft. The flow in the trench discharges into a drain. The subsurface channel in the collection conduit has an additional drain connection and a manhole before discharge into a covered sump with a vent.

This application of the unit emission factors to a wastewater collection system for toluene wastes indicates that a substantial fraction of the original toluene in the waste can be lost due to mass transfer to the air that flows in the collection system. Another way of interpreting these data is that for every 70 g of toluene that enter the wastewater treatment plant, 30 g are emitted in the collection system before the waste reaches the wastewater treatment plant (43 percent).

TABLE 4.1 EXAMPLE OF THE USE OF EMISSION FACTORS

Unit	Emission factor	Amount present, (g)	Emissions, (g)
Open trench drain (40 ft)	0.045	100	4.5
Open trench drain (20 ft)	0.022	95.5	2.1
Drain	0.08	93.4	7.5
Drain connection	0.08	85.9	6.7
Manhole at junction	0.0083	79.2	0.66
Covered sump with vent	0.11	78.5	8.6
Overall collection units	0.30	70	30

These emission factors for wastewater collection systems are not expected to be applicable for all systems. They are for a wastewater collection system designed to aerate the wastewater, either for safety, for corrosion reduction, or for odor control. There are a number of equipment changes that can reduce the air emissions to levels much lower than can the system presented here. Emissions can be reduced by using covers for sumps, manhole covers with fewer and smaller openings, seals on drain openings, or solid metal covers for trenches; by purging the system with excess water; and by other methods. Increasing the external wind speed will increase emissions from the collection systems, according to the models. The collection system air emissions can be increased by any discharge of steam into the collection conduit, the presence of open sumps or open junctions, and the presence of a complex collection systems with many units (potential emission sources) before discharge.

Computational techniques that have been used to improve the accuracy of the estimates of emission factors include considering mass transfer at the liquid-gas interface and using Monte Carlo simulation of collection system characteristics.

4.2.2 Collection System Units

Ten cases for induced airflow in collection conduits are illustrated with cases A1-D1. Cases A1, A2, and A3 illustrate potential airflows from process drains. Cases B1, B2, and B3 illustrate air emissions from manholes. Cases C1, C2, and C3 illustrate airflow out of collection conduit lines. Case D1 represents emissions from a covered sump with an open vent, and Case D2 illustrates airflow out of drain grates. The following brief explanations describe some of the assumptions used in estimating the induced flow of air for each of these units:

- Case A1 estimates airflow into a drain annulus induced by water flow. The air drawn in will escape somewhere and be in equilibrium with the water at that point.

- Case A2 estimates airflow into a collection conduit through a drain annulus. No water is flowing into the drain. The air comes to equilibrium with the water flowing in the collection conduit and escapes at some point upstream or downstream of the drain.

- Case A3 estimates airflow from saturated air rising from a drain annulus due to a density difference between the air in the collection conduit and the ambient air. No water is flowing through the drain. The air is drawn in at a point upstream or downstream of the drain and reaches thermal and chemical equilibrium with the wastewater flowing in the collection conduit by the time it reaches the drain.

- Case B1 estimates airflow from manhole cover vents caused by a density difference between air in the collection conduit and the ambient air. The air flowing out of the vents is in thermal and chemical equilibrium with the water flowing in the collection conduit at that point.

- Case B2 estimates airflow through manhole cover vents induced by wind blowing in the upstream end of a collection conduit that is blocked off after the manhole. The air is in equilibrium with the water in the manhole.

- Case B3 estimates the airflow from manhole cover vents induced by wind blowing in one end of a collection conduit and flowing past the manhole to some point downwind. The air is in equilibrium with the water in the collection conduit at the manhole. No drains or vents are in the line between the upwind collection conduit end and the manhole.

- Case C1 estimates the airflow induced by wind blowing in one end of a collection conduit and out another. The air is in equilibrium with water at the downwind end of the collection conduit.

- Case C2 estimates the airflow into the collection conduit from a junction box induced by water flow through the junction box. This air escapes somewhere (e.g., the next junction box downstream) in equilibrium with the water flowing through at that point.

- Case C3 estimates airflow from the discharge end of a partially filled collection conduit resulting from density differences between the ambient air and the warm humid air in equilibrium with the wastewater.

- Case D1 estimates the airflow induced through a stack on an enclosed sump. Air is in equilibrium with the wastewater and is drawn into the system at some point upstream or downstream of the sump.

- Case D2 estimates airflow from an open trench based upon mass transfer in the rapid flowing water.

Enviromega of Burlington, Ontario, Canada recently measured air emissions from a laboratory simulation of industrial wastewater collection system elements[1]. The new measurement data has been used to test and refine existing analytical procedures used to estimate emissions from air and water sources. Models for four separate cases are developed on the basis of data collected by Enviromega. The models are as follows:

- Case E1 estimates air emissions from wastewater in a J trap without wastewater flow into the trap,
- Case E2 estimates air emissions from the wastewater flowing into a J trap,
- Case E3 estimates air emissions from a lift station where the pump is periodically lifting wastewater from a splash filled covered sump, and
- Case E4 estimates air emissions from wastewater flow into open sumps or junction boxes.

4.2.3 A Listing of Emission Factors

Air emissions factors are presented for induced airflow in collection conduit systems accepting hazardous aqueous waste. The major sources of induced airflow into and out of a collection conduit system are process drains, manholes, and junction boxes. Tables 4-2 through 4-8 describe the estimated fraction of the organic emitted from the three units of the collection conduit. The emission factors are listed for five different organic compounds that differ in volatility: 1,3-butadiene, toluene, naphthalene, 1-butanol, and phenol.

The airflow induced by the wind is sensitive to the geometry of the source, the direction of flow of the wind, and the velocity of the wind. Because of the large numbers of significant factors that could conceivably influence the rate of emissions due to wind, the emission estimates are presented as a range, with zero as the lower bound of the range and a combination of values from the three cases as the upper range. The upper range is not the greatest possible value of the estimated emissions, because higher collection system temperatures or higher wind speed could increase the emission rate. The choice of a specific value to be used for estimating emission factors from induced airflow in the collection conduit component is also presented in Tables 4-2 to 4-8. In some cases, the effects of the various mechanisms for airflow can be additive, but in some cases the effects would tend to cancel each other.

The summary of the result of the model weir calculations are presented in Table 4-8.

TABLE 4-2. AIR EMISSION ESTIMATES FOR DILUTE AQUEOUS 1,3-BUTADIENE SOLUTIONS FLOWING THROUGH WASTE COLLECTION SYSTEM NETWORKS[a]
(FRACTION EMITTED)

CASE	DRAINS (A)	MANHOLES (B)	COLLECTION CONDUITS (C)
Case 1	0.63	0.087	0.95
Case 2	0.73	0.21	0.79
Case 3	0.54	0.147	0.56
Typical value	0.63	0.15	0.77

[a] Case A1 is Unit A with Case 1 conditions. For a discussion of units and cases, see the discussion on pages 4-6 and 4-7.

TABLE 4-3. AIR EMISSION ESTIMATES FOR DILUTE AQUEOUS TOLUENE SOLUTIONS FLOWING THROUGH WASTE COLLECTION SYSTEM NETWORKS[a] (FRACTION EMITTED)

CASE	DRAINS (A)	MANHOLES (B)	COLLECTION CONDUITS (C)
Case 1	0.073	0.0045	0.48
Case 2	0.113	0.0123	0.148
Case 3	0.053	0.008	0.057
Typical value	0.08	0.0083	0.23

[a] Case A1 is Unit A with Case 1 conditions. For a discussion of units and cases, see the discussion on pages 4-6 and 4-7.

TABLE 4-4. AIR EMISSION ESTIMATES FOR DILUTE AQUEOUS NAPHTHALENE SOLUTIONS FLOWING THROUGH WASTE COLLECTION SYSTEM NETWORKS[a] (FRACTION EMITTED)

CASE	DRAINS (A)	MANHOLES (B)	COLLECTION CONDUITS (C)
Case 1	0.014	0.0008	0.14
Case 2	0.022	0.0022	0.03
Case 3	0.0098	0.0014	0.02
Typical value	0.015	0.0015	0.06

[a] Case A1 is Unit A with Case 1 conditions. For a discussion of units and cases, see the discussion on pages 4-6 and 4-7.

TABLE 4-5. AIR EMISSION ESTIMATES FOR
DILUTE AQUEOUS 1-BUTANOL SOLUTIONS
FLOWING THROUGH WASTE COLLECTION SYSTEM NETWORKS[a]
(FRACTION EMITTED)

CASE	DRAINS (A)	MANHOLES (B)	COLLECTION CONDUITS (C)
Case 1	0.0001	0.000006	0.00123
Case 2	0.00017	0.000017	0.00023
Case 3	0.00007	0.000011	0.00008
Typical value	0.00012	0.00001	0.0005

[a] Case A1 is Unit A with Case 1 conditions. For a discussion of units and cases, see the discussion on pages 4-6 and 4-7.

TABLE 4-6. AIR EMISSION ESTIMATES FOR
DILUTE AQUEOUS PHENOL SOLUTIONS
FLOWING THROUGH WASTE COLLECTION SYSTEM NETWORKS[a]
(FRACTION EMITTED)

CASE	DRAINS (A)	MANHOLES (B)	COLLECTION CONDUITS (C)
Case 1	0.0000053	$3\ 10^{-7}$	0.000063
Case 2	0.0000086	$8.5\ 10^{-7}$	0.000012
Case 3	0.0000038	$5.5\ 10^{-7}$	0.0000041
Typical value	0.000006	$6\ 10^{-7}$	0.000026

[a] Case A1 is Unit A with Case 1 conditions. For a discussion of units and cases, see the discussion on pages 4-6 and 4-7.

TABLE 4-7. AIR EMISSION ESTIMATES FOR WASTEWATER IN AN OPEN TRENCH SECTION FLOWING THROUGH WASTE COLLECTION SYSTEM NETWORKS[a] (FRACTION EMITTED)

COMPOUND	PARTITION COEFFICIENT (Y/X)	FRACTION EMITTED TO AIR
1,3-Butadiene	7900	0.059
Toluene	371	0.045
Naphthalene	65.6	0.025
Butanol	0.494	0.0004
Phenol	0.0252	0.0002

[a] These compounds represents different compound types, according to the value of the partition coefficient or Henry's law constant.

TABLE 4-8. FRACTION OF A VOLATILE COMPONENT EMITTED FROM A MODEL WEIR.

Component	Fraction Emitted
1,4 Butadiene	0.35
Toluene	0.20
Naphthalene	0.056
1-Butanol	0.00062
Phenol	0.000033

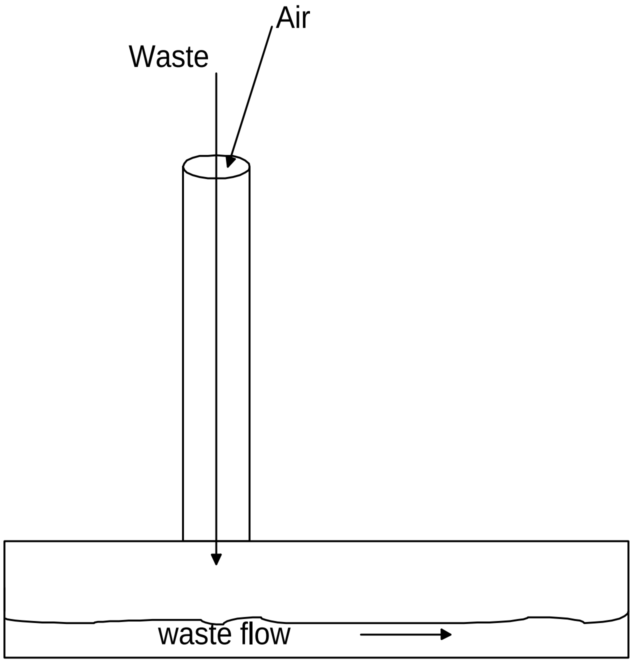
4.3 AIR EMISSION MODELS

4.3.1 Case A1 Air Flow Induced by Waste Flow into Drain

Case A1 considers airflow into a drain induced by wastewater discharged to the collection conduit through a pipe inserted in the drain. The air is assumed to be drawn into the annulus with a velocity equal to that of the flowing water at the air/water interface. The velocity of the induced air is assumed to decrease to zero at the wall of the drain. The assumed air velocity profile has not been experimentally confirmed. The air drawn into the drain is assumed to escape at some other point in the system after coming to equilibrium with the wastewater. In relatively tight systems or systems with long runs of collection conduit between openings, the resistance to airflow will inhibit this mechanism of air induction. An illustration of this case is presented in Figure 4-1.

The calculation requires the following inputs: flow rate of wastewater, ratio of wastewater pipe area to drain pipe area, partition coefficient applicable to the pollutant of interest at the wastewater temperature, concentration of wastewater stream, and temperature of the ambient air. The molar air density is calculated at the ambient temperature based on the ideal gas law assuming an ambient pressure of one atmosphere. The influent flow rate of organics is calculated from the mass flow rate of wastewater and the mass fraction of organics in the wastewater. The influent air linear flow rate is calculated as one-fourth the linear wastewater flow rate based on the assumed airflow profile. This is converted to a molar airflow rate by multiplying by the area ratio (drain pipe area to wastewater pipe area) and the molar density of air.

The fraction emitted is calculated by multiplying the dimensionless partition coefficient by the ratio of molar flows of air to the total molar flow of air and water.



Parameter	Symbol	Units	Value
Ratio of the area of waste to area of air flow in drain	Arr	dimensionless	4
Fraction of entering organic lost to atmosphere	F		0.21
Partition coefficient	K	mol fraction gas per mol fraction liquid	371
Temperature	Ta	degrees K	298
Temperature	T(C)	degrees C	25

Figure 4-1. Case A1. Air flow induced by waste flow into drain.

$$F = \frac{Arr\ 0.25\ \frac{0.0121}{Ta}\ K}{Arr\ 0.25\ \frac{0.0121}{Ta}\ K + 0.0555} \qquad (4\text{-}1)$$

The above symbols are defined in Figure 4.1. Note that, within the limits of the assumption, a smaller wastewater pipe flowing at an equivalent volumetric flow rate will induce a greater airflow (and cause greater emissions) due to its higher linear velocity.

Note also that slightly greater emissions will occur on cooler days because more moles of denser ambient air will be drawn in (it is assumed that this air will come to thermal equilibrium with the wastewater before it escapes from the system).

The calculation results are presented in Table 4-9.

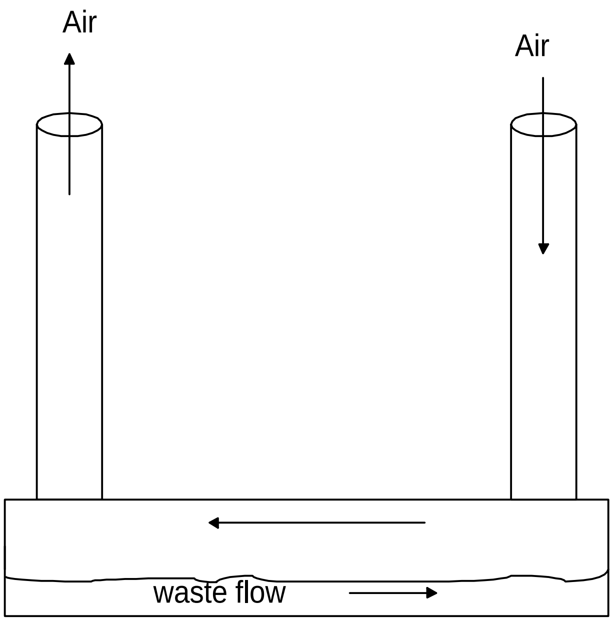
4.3.2 Case A2 Air Flow in Drain Due to Wind Pressure

Case A2 considers airflow into a drain and through the collection conduit. No water is flowing down the drain. The pressure creating the airflow is due to changes in wind velocity. The air pressure is estimated from the maximum pressure obtained from wind flowing at 160 cm/s (3.5 mph) with the pitot tube pointed into the wind. The drain would not normally be oriented into the wind, but wind flow patterns and pressures are expected to be influenced by the location of the drain relative to wind, buildings, sumps, etc. An illustration of this case is presented in Figure 4-2.

The air flowing into the drain is assumed to escape at some other point in the system after coming to equilibrium with the wastewater. The frictional drag on the drain and in the headspace of the collection conduit will determine the flow of air in response to the pressure exerted by the wind. The general assumptions about case A2 are presented in Table 4-10.

TABLE 4-9. RESULTS OF CALCULATIONS FOR AIR EMISSIONS FROM A DRAIN.

arr	K	Ta	T(C)	F
4	371	298	25	0.21
4	371	273	0	0.23
4	0.5	298	25	0.00037
4	0.5	273	0	0.0040
13.7	371	298	25	0.48
13.7	371	273	0	0.50
13.7	0.5	298	25	0.00125
13.7	0.5	273	0	0.00137



Parameter	Units	Value
Length of collection conduit	m	12.2
Length of drain	m	0.61
Underflow rate	m^3/s	0.042
Diameter of drain	m	0.203
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Wind velocity	m/s	1.56
Relative humidity	percent	50
Collection system temperature	deg.C	25

Figure 4-2. Case A2. Air flow induced by wind

TABLE 4-10. GENERAL ASSUMPTIONS AND CALCULATIONS FOR CASE A2

Air temperature	25 °C
Relative humidity	50 percent
Collection conduit temperature	30 °C
Friction factor for air	0.006
Wind velocity	156 cm/s (3.5 MPH)
Radius of collection conduit	30.48 cm (12 in)
Depth of liquid in collection conduit	24.4 cm (9.6 in)
Headspace hydraulic radius	10.9 cm
Flow of water in collection conduit	42,000 cm^3/s
Headspace area in collection conduit	1,830 cm^2
Density of air at 25 °C	0.0012 g/cm^3
K partition coefficient (Y/X)	371
Weight fraction organics in water	0.0005
Flow of organics in collection conduit water	21.1 g/s
Molar density of air in collection conduit	0.00004 mol/cm^3.

The maximum pressure exerted by the wind is calculated based on a solution of the Bernoulli equation:

$$)P = <^2 \frac{D}{2\ g_c} \qquad (4\text{-}2)$$

where,

)P = calculated pressure, g force/cm^2;

< = wind velocity, 156 cm/s (3.5 mph);

D = density of air at 25 °C, 0.0012 g/cm^3; and

g$_c$ = 980.665 g-cm/gF-s^2.

$$)P = \frac{156^2\ \ 0.0012}{2\ \ 980.665} = 0.015\ \frac{g\ force}{cm^2}$$

This value of the maximum pressure is equated to the energy of the air velocity in the collection conduit and the frictional losses in the collection conduit:

$$\frac{)P}{D} = (\ 1 + Ke + \frac{4\ F\ L}{D}\ Arr^2 + \frac{4\ F\ L2}{D2} + K1\ )\ \frac{<^2}{2\ g_c} \qquad (4\text{–}3)$$

where,

△P = pressure, 0.015 g force/cm^2;

D = density of air, 0.0012 g/cm^3;

Ke = diameter change coefficient, 0.31;

F = friction factor of air, 0.006;

L = length of collection conduit, (1,220 cm for example case A2); and

D = equivalent diameter of the headspace in the collection conduit, 40.4 cm (four times the hydraulic radius).

Arr = area ratio of collection conduit segment, 0.219

L2 = length of drain, (61 cm x 2 drains = 122 cm for Case A_2

D2 = diameter of drain, 20.3 cm

K1 = loss coefficient, 5

g_c = 980.665 g-cm/gF-s2

Solving for <, the velocity of air in the drain is 62 cm/s (122 ft/min). The sectional area of the drain is 324 cm^2 permitting a calculated airflow of 20,000 cm^3/s.

$$M = D\ Q\ =\ 0.81$$

where,

M = molar flow rate of air, mol/s;

D = density of air, 4 10^{-5} mol/cm^3; and

Q = volumetric flow rate, 2 10^4 cm^3/s.

The molar flow rate of the air is then calculated as 0.81 mol/s.

The flow rate of organics in the air at equilibrium with the initial concentration of organics in the water is as follows:

$$O = M\ K\ C\ Mw \qquad (4\text{-}4)$$

$$2.7 = (.81)(371)(0.0005)(18)$$

where,

O = molar flow rate of organic in air, mol/s;

M = molar flow rate of air, 0.81 mol/s;

K = organic partition coefficient 371 mol/mol;

C = concentration of organic, 0.0005 g/g water; and

Mw = molecular weight of water, 18 g/mol.

The flow of organic in the exit air is then 2.7 g/s.

The fraction of organics present in the air at equilibrium, f, is independent of concentration (as long as K is a constant).

The fraction of organics in the air is the ratio of the mass flow in the air divided by the sum of the mass flow in the air and water:

$$f = O / (O + M) \qquad (4\text{-}5)$$

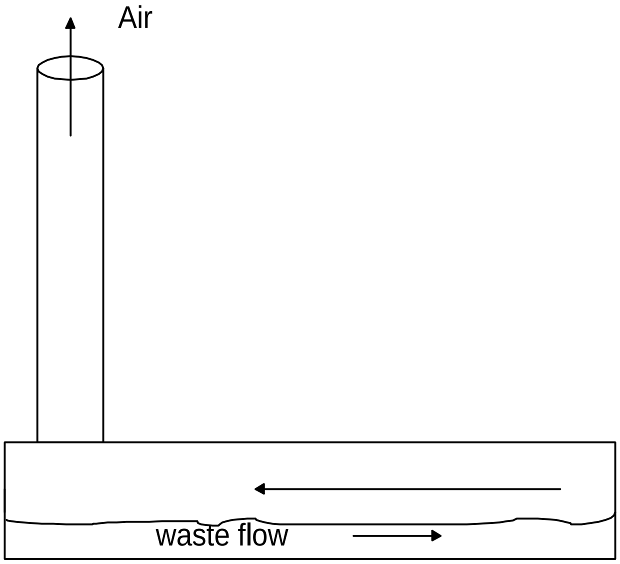
$$f = 2.7/(21.1 + 2.7)$$

$$f = 0.11.$$

The fraction of organics present in the air is also the fraction lost as air emissions.

4.3.3 Case A3 Airflow Induced by Density Differences

Case A3 considers airflow up from a drain induced by density differences between the ambient air outside the manhole and the warm humid air in the collection conduit. No water is flowing in the drain. The wastewater in the collection conduit is assumed to be flowing in a direction perpendicular to the airflow through the vents; the air is assumed to be saturated with water and at chemical and thermal equilibrium with the wastewater. In the case considered, the drain is assumed to be 10 cm (4 in.) in diameter and 61 cm (2 ft) long. Frictional losses through both the drain and the collection conduit are considered, based on a friction factor of 0.06. The height of the "stack" is assumed to be 61 cm (2 ft). This is the vertical distance between the level of the water in the collection conduit and the drain. Ambient conditions are assumed to be 25 °C and 50 percent relative humidity. The wastewater temperature is assumed to be 30 °C, and a greater difference in the ambient temperature and the sewer temperature would tend to increase the effect of density differences. An illustration of this case is presented in Figure 4-3. The assumptions about Case A3 are presented in Table 4-11. These assumptions are used for the calculations in this section.



Parameter	Units	Value
Length of collection conduit	m	12.2
Drain length	m	0.61
Underflow rate	m^3/s	0.042
Length of drain	m	0.203
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Ambient temperature	deg.C	25
Relative humidity	percent	50
Collection system temperature	deg.C	30

Figure 4-3. Case A3. Air flow induced by density differences

TABLE 4-11. GENERAL ASSUMPTIONS AND CALCULATIONS FOR CASE A3

Air temperature	25 °C
Relative humidity	50 percent
Collection conduit temperature	30 °C
Friction factor for air	0.006
Radius of collection conduit	30.48 cm
Depth of liquid in collection conduit	24.4 cm
Headspace hydraulic radius	10.9 cm
Flow of water in collection conduit	42,000 is
Headspace area in collection conduit	1,828 cm2
Density of saturated air at 40 °C	0.00117 g/cc
Density of air at 25 °C	0.0012 g/cc
K partition coefficient (Y/X)	371
Weight fraction organics in water	0.0005
Flow of organics in collection conduit water	21.3 g/s
Molar density of air in collection conduit	0.00004 mol/cm^3.

The densities of ambient air and warm humid collection conduit air are calculated, and the density difference across the drain system is calculated as 0.0000839 g/cm^3. The maximum pressure from density differences is the product of the density difference and height. This value of the maximum pressure from density differences is equated to the energy of the air velocity in the collection conduit and the frictional losses in the collection conduit:

$$< \;=\; \sqrt{\frac{\dfrac{2\,g_c\;)P}{\mathrm{D}}}{\left(1 + Ke + \dfrac{4\,F\,L}{D}\,Arr^2 + \dfrac{4\,F\,L2}{D2} + K1\right)}} \qquad (4\text{-}6)$$

where,

$<$ = the velocity of air exiting the drain hub (cm/s);

ΔP = pressure, 0.0019 g force/cm^2;

D = density of air, 0.0012 g/cm^3;

Ke = diameter change coefficient, 0.31;

F = friction factor of air, 0.006;

L = length of collection conduit, 610 cm;

D = equivalent diameter of the headspace in the collection conduit, 43.6 cm (four times the hydraulic radius);

Arr = area ratio of collection conduit segment, 0.219;

L2 = length of drain, 61 cm;

D2 = diameter of drain, 20.3 cm;

K1 = loss coefficient, 3; and

g_c = 980.665 g-cm/gF-s^2.

Solving for <, the velocity of air in the drain hub is 26.9 cm/s (53 ft/min). The sectional area of the drain hub is 324 cm2 permitting a calculated airflow of 8,716 cm^3/s. The molar density of the air is $4.0\ 10^{-5}$ mol/cm^3. a molar airflow rate is then calculated as (8,716 cm^3/s)($4.0\ 10^{-5}$ mol/cm^3), or 0.35 mol/s. The flow rate of organics in the air at equilibrium with the initial concentration of organics in the water is calculated using Equation 4-4:

$$O = (0.35\ mol/s)(371)(0.0005\ g/g)(18\ g/mol).$$

$$O = 1.17\ g/s.$$

The fraction of organics present in the air at equilibrium is independent of concentration (as long as K is a constant). The fraction of organics in the air is the ratio of the mass flow in the air divided by the sum of the mass flow in the air and water:

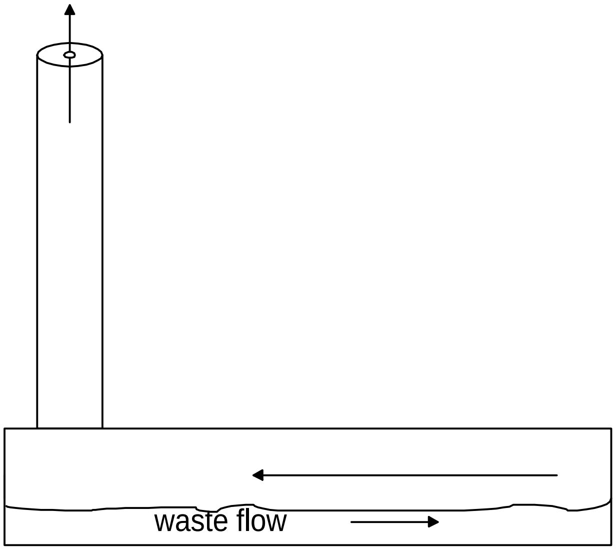
$f = O / (O + M)$, where the variables are as previously defined in case A2,

$$f = 1.17 / (1.17 + 21.3)$$

$$f = 0.053.$$

4.3.4 Case B1 Manhole venting due to density effects

Case B1 considers airflow from the vents in a manhole cover induced by density differences between the ambient air outside the manhole and the warm humid air in the collection conduit. An illustration of this case is presented in Figure 4-4. The wastewater in the collection conduit is assumed to be flowing in a direction perpendicular to the airflow through the vents; the air is assumed to be saturated with water and at chemical and thermal equilibrium with the wastewater. In the case considered, the manhole cover is assumed to have four vent holes of 2.5 cm (1 in.) diameter. Frictional losses through the manhole are assumed negligible relative to losses through the manhole cover vents. The height of the "stack" is assumed to be 67 cm (2 ft). This is the vertical distance between the level of the water in the collection conduit and the manhole cover.



Parameter	Units	Value
Length of collection conduit	m	12.2
cross-sectional area of vent holes	cm^2	20
Underflow rate	m^3/s	0.0425
Height of manhole cover above surface	m	0.61
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Ambient temperature	deg.C	25
Relative humidity	percent	50
Collection system temperature	deg.C	30

Figure 4-4. Case B1. Manhole venting induced by density differences

Ambient conditions are assumed to be 25 °C and 50 percent relative humidity. The wastewater temperature is assumed to be 30 °C.

The densities of ambient air and warm humid collection conduit air are calculated, and the density difference across the manhole cover is determined. The gas velocity through the manhole cover vents was then calculated from the density difference using the equation for a sharp edged orifice:

$$< \, = 0.61 \, (\, 2 \, g_c \, h \, \frac{)D}{D} \,)^{0.5} \qquad (4\text{-}7)$$

where,

< = linear velocity through the vent hole, cm/s;

g_c = Gravitational constant, 981 cm/s^2;

h = height of manhole above conduit, 61 cm (2 ft);

△D = density difference of air above and below manhole, 3.2 10^{-5} g/cm^3; and

D = density of warm humid air, 0.00117 g/cm^3.

(Frictional losses through the thickness of the cover are negligible.)

$$< \, = 0.61 \left(\, 2 \, (\, 981 \,) \, 61 \, \frac{3.2 \; 10^{-5}}{0.00117} \right)^{0.5}$$

The air velocity is converted to a volumetric flow rate by multiplying by the cross-sectional area of the vent holes, 20 cm^2

$$< \, = 34.9 \, \frac{cm}{s}$$

(0.022 ft^2) by the vent velocity 34.9 cm/s. Based on this airflow, 710 cm^3/s, the wastewater flow in the collection conduit, and a partition coefficient appropriate for the compound of interest at the wastewater temperature, the fractional emission is calculated. (The wastewater flow is 2,360 mol/s and was calculated from an assumed collection conduit size, slope, roughness, and an assumed wastewater depth in the collection conduit.) The fraction emitted is calculated as

$$F = G\ K/(G\ K + L) \tag{4-8}$$

$$F = \frac{0.0285 \times 371}{0.0285 \times 371 + 2360}$$

$$F = 0.0045$$

where,

F = fraction emitted through cover vents, dimensionless;

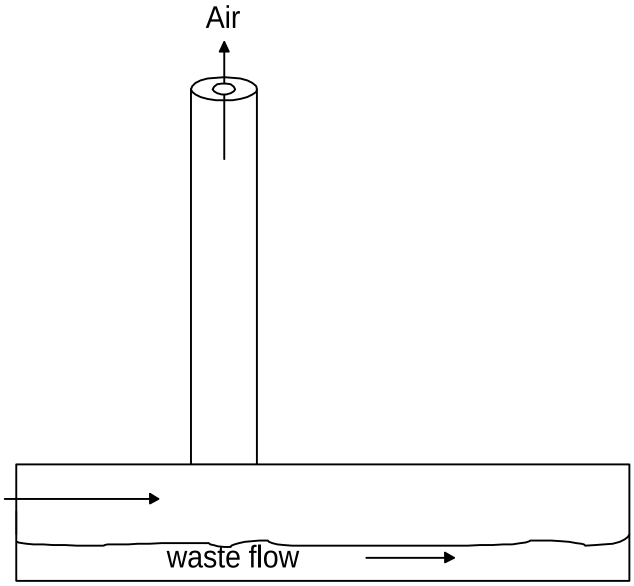
G = airflow rate from the cover vents, 0.0285 mol/s;

K = 371, air/water partition coefficient for compound of interest at wastewater temperature, dimensionless; and

L = wastewater flow rate through collection conduit, 2,360 mol/s.

4.3.5 Case B2 Manhole Venting Due to Wind

Case B2 estimates airflow through manhole cover vents resulting from wind blowing into the upstream end of a collection conduit. An illustration of this case is presented in Figure 4-5. The air flows down the collection conduit to the manhole where further airflow is obstructed. This might occur where a collection conduit ends at a pump sump or where a change in pipe size or slope results in a completely filled pipe with no air space. The airflow rate is estimated by calculating the air velocity through the manhole cover vents that would result in a frictional head loss equal to that available from the wind blowing into the



Parameter	Units	Value
Length of collection conduit	m	12.2
cross-sectional area of vent holes	cm^2	20
Underflow rate	m^3/s	0.042
Height of manhole cover above surface	m	0.61
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Wind velocity	m/s	1.56
Collection system temperature	deg.C	30

Figure 4-5. Case B2. Manhole venting due to wind

upstream end of the collection conduit. Frictional losses through the collection conduit, the manhole, and the cover thickness are assumed to be negligible in comparison to losses through the cover vents.

Frictional losses through the cover vents are calculated using an equation for flow through a sharp-edged orifice:

$$< = 0.61 \left(<_w^2 \frac{D_a}{D_s} \right)^{0.5} \qquad (4\text{-}9)$$

where,

$<$ = linear velocity through vent cover, cm/s;

$<_w$ = wind velocity, 156 cm/s (3.5 mph);

Da = ambient air density, 0.0012 g/cm^3; and

Ds = density of warm humid air in collection conduit, 0.00117 g/cm^3.

Substituting into Equation 4-9 to estimate the velocity out of the manhole vent cover openings,

$$< = 0.61 \left(156^2 \frac{.0012}{.00117} \right)^{0.5}$$

$$< \ = 96.3 \text{ cm/s (2.1 mph)}$$

The manhole cover is assumed to have four vents of 2.5 cm (1 in.) diameter. The wind velocity in the direction of the collection conduit is assumed to be 156 cm/s (3.5 mph). The factor of 0.61 is an orifice coefficient that will be approximately constant for the range of flows considered.

The molar airflow rate can be calculated from the linear velocity through the cover vents (96.3 cm/s) by multiplying by the total area of the four vents, 20 cm^2 (0.022 ft^2), and by the molar density at the warm humid collection conduit conditions, 0.00004 mol/cm^3.

$$0.078 \text{ mol/s} = (96.3 \text{ cm/s})(20\text{cm}^2)(0.00004)$$

The wastewater flow rate in the collection conduit is implicitly specified on the basis of assumed collection conduit depth, diameter, slope, and roughness (2,360 mol/s).

The fractional emission of organics is calculated from Equation 4-8, using the molar flow rates of air and water, and a dimensionless partition coefficient appropriate for the compounds of interest at the wastewater temperature:

$$F = \frac{GK}{GK + L}$$

where,

G = airflow rate, 0.078 mol/s;

K = 371, dimensionless partition coefficient; and

L = water flow rate, 2,360 mol/s.

F = (0.078)(371)/ [(0.078)(371)+ 2360]

F = 0.121

4.3.6 Case B3 Manhole venting due to wind underflow

Case B3 considers emissions from manhole cover vents over a flowing, partially filled collection conduit. Air resulting from wind blowing in one end of the collection conduit is flowing in the upper portion of the collection conduit. The direction of the airflow relative to the water flow is not considered; it is assumed that the air in the collection conduit is at thermal and chemical equilibrium with the wastewater at the location of the manhole. An illustration of this case is presented in Figure 4-6.

The air velocity resulting from the wind pressure is calculated from a Bernoulli equation based on frictional losses through the unfilled section of the pipe;

$$< = \left(\frac{<_w^{2} \frac{\mathrm{D}_a}{\mathrm{D}_s}}{1 + \frac{4 f L}{D}} \right)^{0.5} \qquad (4\text{-}10)$$

where,

$<$ = linear velocity of air through unfilled section of collection conduit, 80 cm/s (1.79 mph);

$<_w$ = velocity of wind, 156 cm/s (3.5 mph);

Da = density of ambient air, 0.0012 g/cm^3;

Ds = density of humid air in collection conduit, 0.00117 g/cm^3;

f = friction factor for air, assumed constant at 0.006, dimensionless;

L = length of collection conduit, 4,570 cm; and

D = equivalent diameter (four times the hydraulic radius) of unfilled section of collection conduit, 40.4 cm.

$$< = \left(\frac{156^2 \; \frac{.0012}{.00117}}{1 + \frac{4\,(.006)\,(4570)}{40.4}} \right)^{0.5}$$

$<$ = 80 cm/s (1.79 mph).

The velocity is then used to calculate the pressure drop through the shorter length of collection conduit between the manhole and the discharge end of the collection conduit:

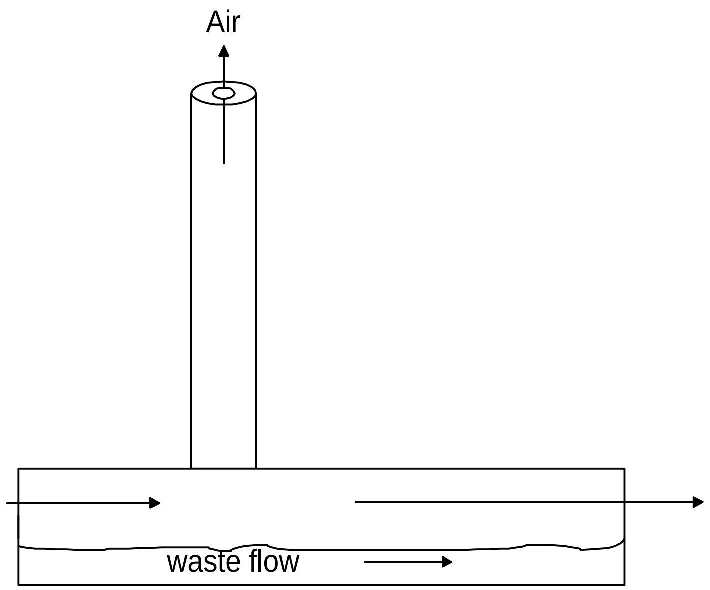
$$)P = \frac{4\, f\, L_s <^2 D_s}{2\, g_c\, D}$$

where:

)P = pressure drop through collection conduit between manhole and discharge end, g force/cm2

Ls = length of collection conduit between manhole and gas exit, 3,050 cm

g_c = gravitational constant, 981 g cm/g force-52



Parameter	Units	Value
Length of collection conduit	m	45.7
Length after manhole	m	30.5
cross-sectional area of vent holes	cm^2	20
Underflow rate	m^3/s	0.042
Height of manhole cover above surface	m	0.61
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Wind velocity	m/s	1.56
Collection system temperature	deg.C	30

Figure 4-6. Case B3. Manhole venting due to wind underflow

$$)P = \frac{4\ (.006)\ (3050)\ (80)^2\ (.00117)}{2\ (981)\ (40.4)}$$

$$)P = 0.0069$$

This pressure (0.0064 g force/cm2) is then used as the driving force in the equation for flow through a square-edged orifice to calculate the linear velocity of air emitted from the manhole cover vents:

$$<_c = 0.61\ (2\ g_c\ \frac{)P}{D_s})^{0.5}$$

where:

$<_c$ = linear velocity through the cover vents, cm/s

0.61 = orifice coefficient (dimensionless) appropriate for the velocity range expected.

$$<_c = 0.61\ (\ 4\ f\ L_s\ \frac{<^2}{D})^{0.5}$$

$$<_c = 65.7\ \frac{cm}{s}$$

Note that the above equations can be combined:

$$<_c = 0.61 \left(2\ (981)\ \frac{(.0069)}{(.00117)} \right)^{0.5}$$

The linear velocity can be converted to a molar flow rate by multiplying by the cross-sectional area of the vents, 20 cm2 (four vents each 2.5 cm [1 in.] in diameter assumed in the example), and the molar density of warm humid air at the wastewater temperature, $4 \bullet 10^{-5}$ mol/cm^3. The wastewater flow rate, 2,360 mol/s, has been implicitly specified in the example from the depth, diameter, slope, and roughness of the collection conduit. The fraction of organics emitted is calculated from Equation 4-8, using the molar flow rates and a dimensionless partition coefficient appropriate for the compound of interest at the wastewaters' temperature:

$$F = \frac{GK}{GK + L}$$

where,

F = fraction of organics emitted through manhole cover vents;

G = airflow rate through manhole cover vents, 0.053 mol/s;

K = partition coefficient, 371, dimensionless; and

L = wastewater flow rate, 2,360 mol/s.

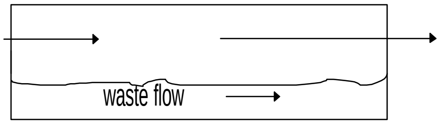
$$F = \frac{(.053)(371)}{(.053)(371) + 2360}$$

$$F = 0.008$$

4.3.7 Case C1 Conduit air flow due to wind

Case C1 considers air blowing directly into one end of a collection conduit, reaching thermal and compositional equilibrium within the collection conduit and exiting a junction box. An illustration of this case is presented in Figure 4-7. The general assumptions of Case C1 are presented in Table 4-12.

The maximum pressure exerted by the wind is calculated based on a solution of the Bernoulli equation (see Equation 4-2):



Parameter	Units	Value
Length of collection conduit	m	45.7
cross-sectional area of vent holes	cm^2	20
Underflow rate	m^3/s	0.042
Height of manhole cover above surface	m	0.61
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Wind velocity	m/s	1.56
Relative humidity	percent	50
Collection system temperature	deg.C	30

Figure 4-7. Case C1. Conduit air flow induced by wind

TABLE 4-12. GENERAL ASSUMPTIONS AND CALCULATIONS FOR CASE C1:

Air temperature	25 °C
Relative humidity	50 percent
Collection conduit temperature	30 °C
Friction factor for air	0.006
Wind velocity	156 cm/s (3.5 MPH)
Radius of collection conduit	30.48 cm (12 in.)
Depth of liquid in collection conduit	24.4 cm (9.6 in.)
Headspace hydraulic radius	10.9 cm
Flow of water in collection conduit	42,196 cm^3/s
Headspace area in collection conduit	1,828 cm^2
Density of air at 25 °C	0.0012 g/cm^3
K partition coefficient (Y/X)	371
Weight fraction organics in water	0.0005
Flow of organics in collection conduit water	21.1 g/s

Molar density of air in collection conduit 0.00004 mol/cm^3.

$$)P = <^2\ \frac{D}{2\ g_c}$$

where,

)P = calculated pressure, g force/cm^2;

< = wind velocity, 156 cm/s (3.5 mph);

D = density of air at 25 °C, 0.0012 g/cm^3; and

g_c = 980.665 g-cm/gF-s^2.

$$)P = \frac{156^2\ \ 0.0012}{2\ \ 980.665} = 0.015\ \frac{g\ force}{cm^2}$$

This value of the maximum pressure is equated to the energy of the air velocity in the collection conduit and the frictional losses in the collection conduit:

$$\frac{)P}{D} = (\ 1 + \frac{4\ F\ L}{D}\ )\ \frac{<^2}{2\ g_c} \qquad (4\text{-}11)$$

where,

△P = pressure, 0.015 g force/cm^2;

D = density of air, 0.0012 g/cm^3;

F = friction factor of air, 0.006;

L = length of collection conduit, 4570 cm;

D = equivalent diameter of the headspace in the collection conduit, 40.4 cm (four times the hydraulic radius), and

g_c = 980.665 g-cm/gF-s^2.

Solving for <, the velocity of air in the collection conduit is 80 cm/s (1.8 mph). The sectional area of the headspace is 1,828 cm^2 permitting a calculated airflow of 146,000 cm^3/s. The molar density of the air is $4\ 10^{-5}$ mol/cm^3; a molar airflow rate is then calculated as ($1.46\ 10^{5}$ cm^3/s) ($4\ 10^{-5}$ mol/cm^3), or 5.8 mol/s. The concentration of organics in the air at equilibrium with the initial concentration of organics in the water is as follows:

(5.8 mol/s)(371)(0.0005 g/g)(18 g/mol) or 19.4 g/s .

The fraction of organics present in the air at equilibrium is independent of concentration (as long as K is a constant). The fraction of organics in the air is estimated with Equation 4-8, using the ratio of the mass flow in the air divided by the sum of the mass flow in the air and water:

$f = O / (O + M)$, where the variables are as previously defined in case A2,

$f = 19.4 / (21.1 + 19.4)$

$f = 0.48.$

4.3.8 Case C2 Conduit Air Flow Induced by Water Flow

Case C2 estimates airflow into a collection conduit from a junction box, induced by water flow in the collection conduit. This air reaches thermal and compositional equilibrium within the collection conduit and is discharged from the collection conduit at the next junction box. An illustration of this case is presented in Figure 4-8. The assumptions are presented in Table 4-13.

The velocity profile for the surface of the water in the collection conduit is assumed to be given by the following empirical relationship:

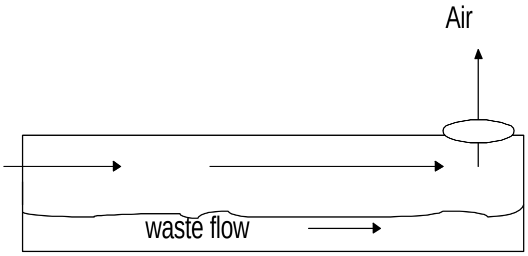
$$<^{+} = 8.5 + 2.5 \ln\left(\frac{Y}{e}\right) \qquad [\, Y > e \,] \qquad (4\text{-}12)$$

where:

$<^{+}$ = velocity quotient, the ratio of the velocity to the friction velocity,

e = surface roughness, cm

Y = distance from a point on the surface to the nearest wall surface interface, cm.



Parameter	Units	Value
Underflow rate	m^3/s	0.042
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244

Figure 4-8. Case C2. Conduit air flow induced by water flow

TABLE 4-13. GENERAL ASSUMPTIONS AND CALCULATIONS, CASE C2.

Air temperature	25 °C
Relative humidity	50 percent
Collection conduit temperature	30 °C
Friction factor for air	0.006
Radius of collection conduit	30.48 cm
Depth of liquid in collection conduit	24.4 cm
Headspace hydraulic radius	10.9 cm
Flow of water in collection conduit	42,196 cm^3/s
Headspace area in collection conduit	1,828 cm^2
Density of air at 25 °C	0.0012 g/cm^3
g partition coefficient (Y/X)	371
Weight fraction organics in water	0.0005
Flow of organics in collection conduit water	21.1 g/s
Molar density of air in collection conduit	0.00004 mol/cm^3
Reynolds number for airflow	2,100
Average velocity of water	39 cm/s
Surface velocity of water	42 cm/s
Roughness of collection conduit wall	0.21 cm
Slope of collection conduit	0.000431.

The average velocity in the collection conduit is estimated as 38.7 cm/s integrating the above equation for average flow. The average surface velocity was 42.2 cm/s. The perimeter of the surface was 60 cm, and the perimeter of the collection conduit headspace was 108 cm. The average velocity of the airflow was established as follows:

$$< (\frac{cm}{s}) = 42.2\ \frac{cm}{s} \left(\frac{60\ cm}{60\ cm + 108\ cm} \right) \quad .$$

This average air velocity of 15.07 cm/s is 36 percent of the water velocity in the collection conduit. This estimated ratio of air velocity to water velocity compares favorably to a reported percentage of 35 for laminar airflow due to liquid drag[2]. The estimated Reynolds number for the above flow conditions suggests that the flow of air may be in the transitional zone. The assumption of laminar flow of air may have overestimated the flow of air by 20 percent.

The estimated velocity of air in the collection conduit is 15 cm/s (0.33 MPH). The sectional area of the headspace is 1,828 cm2 permitting a calculated airflow of 27,000 cm^3/s. The molar density of the air is 4 10^{-5} mol/cm^3; a molar airflow rate is then calculated as (2.7 10^4 $cm^3/5$)(4 10^{-5} mol/cm^3), or 1.08 mol/s. The flow rate of organics in the air at equilibrium with the initial concentration of organics in the water is as follows:

(1.08 mol/s)(371)(0.0005 g/g)(18 g/mol) or 3.61 g/s .

The fraction of organics present in the air at equilibrium is independent of concentration (as long as K is a constant). The fraction of organics in the air is estimated with Equation 4-8, using the ratio of the mass flow in the air divided by the sum of the mass flow in the air and water:

f = O / (O + M), where the variables are as
previously defined in case A2,

f = 3.61 / (21.1 + 3.61), and

f = 0.146.

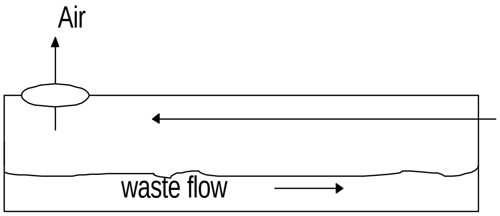
4.3.9 Case C3 Conduit air flow due to density differences

This calculation considers airflow from the discharge end of a partially filled collection conduit to the influent end of the collection conduit resulting from a density difference between the cooler ambient air and the warm humid air in equilibrium with the wastewaters. The air flowing from the collection conduit is assumed to be in thermal and chemical equilibrium with the wastewater. Air and water flow countercurrently. An illustration of this case is presented in Figure 4-9.

The ambient temperature and relative humidity and the wastewater temperature are used to calculate the density difference; the slope and length of the collection conduit are used to calculate the elevation difference producing the "stack effect." Based on the length, diameter, and depth in the collection conduit, the frictional resistance to airflow is determined as a function of air velocity. The air velocity is calculated from a balance of the "stack effect" and the frictional losses using a form of the Bernoulli equation (see Equation 4-6):

$$< = \left[\frac{2\, g_c \;)D\, h}{D \left(1 + \frac{4FL}{D} \right)} \right]^{0.5} \qquad (4\text{-}13)$$

where,



Parameter	Units	Value
Length of collection conduit	m	45.7
Underflow rate	m^3/s	0.042
Elevation of exit relative to entrance	m	0.006
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Ambient temperature	deg.C	25
Relative humidity	percent	50
Collection system temperature	deg.C	30

Figure 4-9. Case C3. Conduit air flow induced by air density differences

< = velocity of air through the collection conduit headspace, 5.3 cm/s;

g_c = acceleration of gravity, 981 cm/s^2

)D = density difference between ambient air and warm humid air in collection conduit, 3.2 10^{-5} g force/cm2;

h = elevation difference determined from collection conduit length and slope, 2 cm;

D = density of warm humid air in collection conduit, 0.00117 g/cm^3;

F = friction factor for airflow through collection conduit, assumed constant at 0.006, dimensionless;

L = collection conduit length, 4,570 cm; and

D = diameter of circle having equivalent area to the cross section of the collection conduit headspace, 40.4 cm.

This velocity is converted to a molar flow rate by multiplying by the equation cross-sectional area of the headspace in the collection conduit, 1,828 cm^2 and the molar density of air at the wastewater temperature, 4.0 10^{-5} mol/cm^2.

$$M = D\ A\ V = 0.387$$

where,

M = molar flow rate of air, 0.382 mol/s;

D = density of air, 0.00004 mol/cm^3;

A = cross-sectional area, 1828 cm^2; and

V = velocity, 5.3 cm/s.

The water flow rate (2,360 mol/s) is specified implicitly by the slope, diameter, depth, and roughness of the collection conduit. The fraction of influent organics that is emitted is calculated from the molar flow rates of water and air and the dimensionless partition coefficient for the compound of interest at the wastewater temperature. Air emitted from the collection conduit is assumed to be in equilibrium with influent wastewater. The fractional emissions are calculated as:

$$F = G\,K / (G\,K + L) = 0.057,$$

where,

G = airflow rate, 0.387 mol/s;

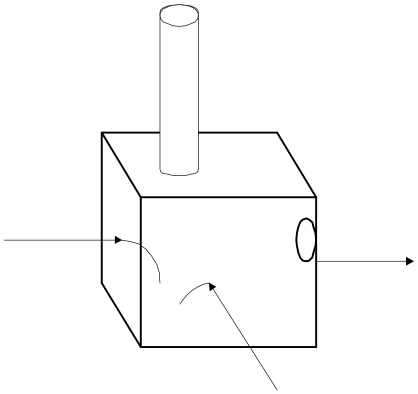
K = 371, dimensionless partition coefficient for compound of interest; and

L = wastewater flow rate, 2,360 mol/s.

4.3.10 Case D1 Stack Vent Air Flow

Case Dl considers emissions from a stack on a sump. The stack was designed to promote the discharge of fumes above workers' heads so that their exposures to environmental releases would be reduced. Case Dl uses a method identical to Case A3 to estimate the airflow due to the stack effect. An illustration of this case is presented in Figure 4-10. The assumptions are presented in Table 4-14.

Case Dl considers airflow up from a sump; through a vent induced by density differences between the ambient air outside the sump and the warm humid air in the collection conduit. The wastewater in the collection conduit is assumed to be flowing in a direction perpendicular to the airflow through the vents; the air is assumed to be saturated with water and at chemical and thermal equilibrium with the wastewater. In the case considered, the vent is assumed to be 10 cm (4 in.) in diameter and 366 cm (12 ft) long. Frictional losses through both the drain and the collection conduit are considered, based on a friction factor of 0.06. The height of the "stack" is assumed to be 366 cm (12 ft). This is the vertical distance between the top of the sump and the vent top. Ambient conditions are assumed to be 25 °C and 50



Parameter	Units	Value
Length of collection conduit	m	30.48
Underflow rate	m^3/s	0.042
Stack length	m	3.66
Stack diameter	cm	20
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Ambient temperature	deg.C	25
Relative humidity	percent	50
Collection system temperature	deg.C	30

Figure 4-10. Case D1. Closed junction box vent induced by air density differences from open exit conduit.

TABLE 4-14. GENERAL ASSUMPTIONS AND CALCULATIONS, CASE D-1.

Air temperature	25 °C
Relative humidity	50 percent
Collection conduit temperature	30 °C
Friction factor for air	0.006
Radius of collection conduit	30.48 cm
Depth of liquid in collection conduit	24.4 cm
Headspace hydraulic radius	10.9 cm
Flow of water in collection conduit	42,000 cm^3/s
Headspace area in collection conduit	1,830 cm^2
Density of saturated air at 30 °C	0.00117 g/cm^3
Density of air at 25 °C	0.0012 g/cm^3
K partition coefficient (Y/X)	371
Weight fraction organics in water	0.0005
Flow of organics in collection conduit water	21.3 g/s
Molar density of air in collection conduit	0.00004 mol/cm^3.

percent relative humidity. The wastewater temperature is assumed to be 30°C.

The maximum pressure from a warm humid collection conduit air is calculated from the product of the density difference and height. This value of the maximum pressure from density differences is equated to the energy of the air velocity in the collection conduit and the frictional losses in the collection conduit (see Equation 4-3):

$$\frac{)P}{D} = \left(1 + Ke + \frac{4\ F\ L}{D}\, Arr^{2} + \frac{4\ F\ L2}{D2} + K1 \right) \frac{<^{2}}{2\ g_{c}}$$

where,

)P = pressure, 0.0117 g force/cm^2;

D = density of air, 0.0012 g/cm^3;

Ke = diameter change coefficient, 0.378;

F = friction factor of air, 0.006;

L = length of collection conduit, 3,048 cm;

D = equivalent diameter of the headspace in the collection conduit, 43.6 cm (four times the hydraulic radius);

Arr = area ratio of collection conduit segment, 0.055;

L2 = length of drain, 366 cm;

D2 = diameter of vent stack, 10 cm;

K1 = loss coefficient, 3; and

g_c = 980.665 g-cm/gF-s2.

Solving for <, the velocity of air in the vent stack is 62 cm/s (118 ft/min). The sectional area of the vent is 324 cm^2 permitting a calculated airflow of 20,000 cm^3/s. The molar density of the air is 4.0 10^{-5} mol/cm^3. a molar airflow rate is then calculated as (20,000 cm^3/s)(4.0 10^{-5} mol/cm^3), or 0.8 mol/s. The flow rate of organics in the air at equilibrium with the initial concentration of organics in the water is as follows:

(0.8 mol/s)(371)(0.0005 g/g)(18 g/mol) or 2.7 g/s .

The fraction of organics present in the air at equilibrium is independent of concentration (as long as K is a constant). The fraction of organics in the air is the ratio of the mass flow in the air divided by the sum of the mass flow in the air and water:

$f = O / (O + M)$, where the variables are as previously defined in case A2,

$f = 2.7 / (21.3 + 2.7)$

$f = 0.11$.

4.3.11 Case D2 Stack Vent Working Loss

Case D2 considers emissions from a stack on a sump due to working losses in the enclosed headspace of the sump. An illustration of this case is presented in Figure 4-11. The stack is designed to promote the discharge of working loss fumes above workers' heads so that their exposures to environmental releases would be reduced. Case D2 assumes that the working losses are assumed to be saturated with water and at chemical and thermal equilibrium with the wastewater. In the case considered, the sump has a working loss due to flow variability in the system.

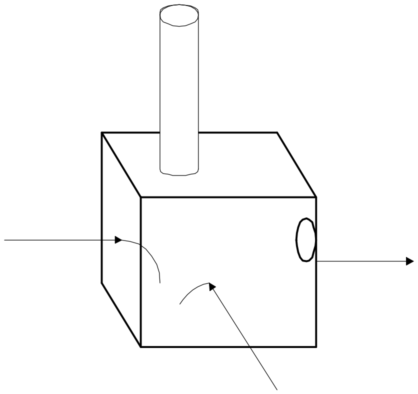
$$Q = 1.157\ 10^{-5}\ V\ T$$

where,

Q = flow rate of air from vent, L/s;
V = volume of headspace in the sump, 10,000 L; and
T = turnovers of headspace, 3 per day.

$$Q = 1.157\ 10^{-5}\ (10{,}000L)\ (3\ per\ day)$$

$$Q = 0.35\ L/s\ (350\ cm^3/s).$$



Parameter	Units	Value
Length of collection conduit	m	30.48
Underflow rate	m^3/s	0.252
Stack length	m	3.66
Stack diameter	cm	20
Radius of underflow conduit	m	0.3048
Depth of liquid in underflow	m	0.244
Turnovers	per day	3
Volume of system	m^3	10
Collection system temperature	deg.C	30

Figure 4-11. Case D2. Closed junction box vent induced by working losses from water seal on entrance and exit conduit.

The molar density of the air is 4.0 10^{-5} mol/cm3; a molar airflow rate is then calculated as (350 cm^3/s)(4.0 10^{-5} mol/cm^3), or 0.014 mol/s. The flow rate of organics in the air at equilibrium with the initial concentration of organics in the water is as follows:

(0.014 mol/s)(371)(0.0005 g/g)(18 g/mol) or 0.047 g/s .

The fraction of organics present in the air at equilibrium is independent of concentration (as long as K is a constant). The fraction of organics in the air is estimated from Equation 4-8, using the ratio of the mass flow in the air divided by the sum of the mass flow in the air and water:

$f = O / (O + M)$, where the variables are as previously defined in case A2,

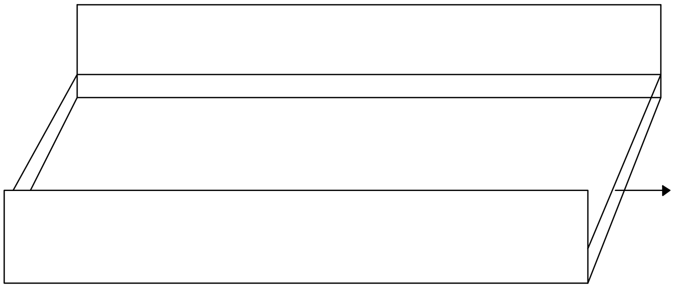
$f = 0.047 / (21.3 + 0.047)$

$f = 0.0022$.

4.3.12 Case D3 Trench volatilization loss

Case D3 considers emissions from open trenches around process equipment. These trenches are used to collect process wastes, tank cleaning wastes, unplanned leaks, and water. Air blows across the top of a grate covering the open top channel of the trench. An illustration of this case is presented in Figure 4-12.

The mass transfer coefficient of the gas phase is estimated from a modified "j factor" equation. The average velocity is required for that equation. The average wind speed is estimated as one half the specified wind speed. The modified equation converts a specified wind speed to an estimated average wind speed.



Parameter	Units	Value
Length of trench	m	12.2
Flow velocity	m/s	0.4572
Depth of liquid in trench	m	0.0762

Figure 4-12. Case D3. Open trench.

The modified equation is as follows:

$$k_g = 2.3\ 10^{-6} \quad V^{0.804} \quad l^{-0.194} \quad D_v{}^{0.667}$$

with,

kg = mass transfer coefficient,
$1.6\ 10^{-5}$ gmol/cm^2 s (0.0038 m/s);
V = wind velocity, 447 m/s;
l = characteristic length, 1000 cm; and
Dv = diffusion coefficient, 0.088 cm^2/s.

The liquid mass transfer coefficient is calculated by Owens, Edwards, and Gibbs[3].

$$Kal = 21.6\ \frac{V^{0.67}}{H^{1.85}}\ \frac{K}{K_o} \qquad (4\text{-}14)$$

where,

Kal = liquid mass transfer coefficient, 176 /day;

v = velocity, 1.5 ft/s;

H = depth, 0.25 ft; and

K/Ko = ratio of mass transfer coefficients of toluene and air, 0.477.

Equation 4-14 was developed for highly volatile components and therefore provides the liquid mass transfer coefficient. Because the overall mass transfer coefficient is needed for more general use, the overall mass transfer coefficient is obtained by modifying Equation 4-14. The desired overall equation is obtained by summing the resistance of the two regions of mass transfer in series:

$$Ka = \left(\frac{1}{Kal} + \frac{H}{(C\ Kg\ K\ 0.000736)} \right)^{-1} \qquad (4\text{-}15)$$

where:

Ka = the overall mass transfer coefficient, 150/day, calculated from the above equation;

Kal = 176, calculated from Equation 4-14;

H = 0.25 ft;

C = a conversion factor, 24 x 3,600 / 12 / 2.54 x 100 (ft/day) (s/m);

Kg = 0.00325 m/s;

0.00736 = a conversion factor; and

K = 371 (Y/X).

The residence time in a 40-ft length of channel is 40 ft / 1.5 ft/s) or 27 s or 3.1 10^{-4} days. The fraction lost during flow through the 40-ft channel is estimated with the following equation:

$$f = 1 - \mathrm{EXP}\ (-Ka\ t)$$

$$f = 1 - \mathrm{EXP}\ \{-(150/\mathrm{day})(0.00031\ \mathrm{days})\}$$

$$f = 0.045,$$

where f and Ka are defined above, and t is the time in days. Therefore, 4.5 percent of toluene is estimated to be emitted over the 40-ft section of channel.

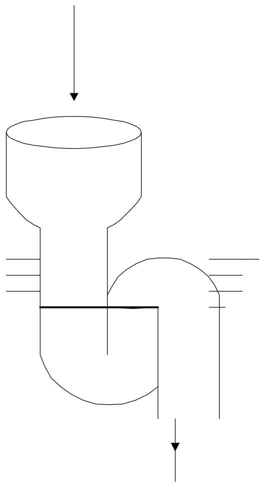
4.3.13 Case E1 J Trap Sealed with Wastewater with No Wastewater Flow

Case E1 applies to the case where a waste flows periodically into a drain hub with a J trap. Waste is retained in the J trap and emissions occur by diffusion and air flow out of the drain hub. Air flow out of the hub is generated when changes in the level of the liquid in the J trap displaces air in the column above the waste. Fluctuations in the liquid level are caused by pressure changes in the collection system induced by either wind fluctuations or wastewater flow rate fluctuations. The air displaced from over the surface in the J trap mixes with the air in the drain hub in the proposed theoretical model. An illustration of this case is presented in Figure 4-13.

Air emissions from a J trap during the time when no wastewater flow is occurring into the hub can be described by the following equations.

The equation for air loss is:

$$D_{eff} = \frac{h^2}{t} \qquad (4\text{-}16)$$



Parameter	Units	Value
Depth of liquid under top of drain hub	m	.457
Cross-section area of drain	cm^2	81
Period of level fluctuation	minutes	0.5
distance of level fluctuation	cm	7.62

Figure 4-13. Case E1. Open J drain trap with waste: no waste flow.

where,

D_{eff} = the effective diffusivity, cm^2/s;

h = the waste displacement, cm; and

t = the period of the displacement, s.

This equation can be used to estimate the emission rate with the following equation:

$$e = \frac{D_{eff}}{d} A \tag{4-17}$$

where,

D_{eff} = the effective diffusivity, cm^2/s;

d = the distance from the waste to the top of the hub, cm;

A = the hub cross-section open area, cm^2; and

e = the emission rate, cm^3/s.

The emission rate in units more conventient for emissions estimation is estimated from Equation 4-18.

$$E = K \frac{18}{24400} e \tag{4-18}$$

where,

K = the partition coefficient, y/x;

18 = the weight of a mol of water, g/mol;

24400 = the volume of a mol of gas, cm^3/mol;

e = the emission rate, cm^3/s; and

E = the emission rate, g/s per weight fraction in the wastewater.

The following example calculation illustrates the use of these equations to estimate emissions of toluene from a 4 inch diameter hub.

The following conditions are assumed for Case E1.

h = 7.62 cm (3 in)
t = 30 s (0.5 min)
d = 45.7 cm (1.5 ft)
A = 81 cm^2
K = 357 (y/x)

The effective diffusivity, D_{eff}, is calculated as follows:

$$D_{eff} = \frac{(7.62)^2}{30} = 1.935\ \frac{cm^2}{s}$$

The value of the emission rate, e, is estimated.

$$e = \frac{(1.935)\ (81)}{45.7} = 3.43\ \frac{cm^3}{s}$$

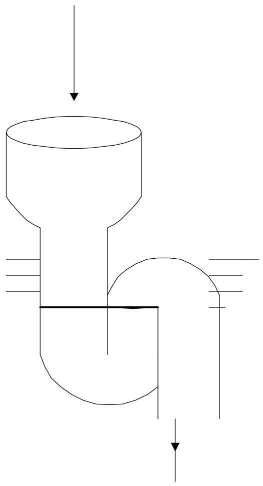
The emission rate E is calculated as follows.

$$E = \frac{(357)\ (18)\ (3.43)}{24{,}400} = 0.9034\ \frac{g}{s}\ per\ weight\ fract.\ toluene\ water$$

The ratio of the emission rate of toluene to the underflow rate is (0.9034 g/s)/(2833 g/s), or .00032.

4.3.14 Case E2 J Trap Water Sealed with Wastewater Flow

Case E2 applies to a case where a waste flows continuously into a drain hub with a J trap. An illustration of this case is presented in Figure 4-14. The flow of waste is exposed to the wind for a short distance over the top of the drain hub. The model approach is to identify correlations of the mass transfer coefficients with the drain characteristics. These correlations were developed empirically using Enviromega data[1] rather than



Parameter	Units	Value
Depth of liquid under top of drain hub	m	.457
Cross-section area of drain hub opening	cm^2	81
waste flow rate	cm^2/s	250
diameter of waste pipe	cm	5
drop distance	cm	3.81

Figure 4-14. Case E2. Open J drain trap with waste flow.

from first principles. Extrapolation beyond the range of waste flow and physical dimensions upon which the correlation is based should be used with caution.

This case can be described by the following equations. The equation for the gas phase mass transfer coefficient is composed of an empirical constant with a correction for the gas diffusion coefficient.

$$k_g = .178 \left(\frac{D_g}{0.088} \right)^{.66} \tag{4-19}$$

where, K_g = the gas phase mass transfer coefficient, m/s,

0.088 = the reference gas diffusion coefficient, cm^2/s, and

D_g = the gas phase diffusion coefficient, cm^2/s.

The equation for the liquid phase mass transfer coefficient is composed of an empirical constant with a correction for the liquid diffusion coefficient and a correction for the waste velocity. The mass transfer coefficient is assumed to be proportional to the velocity of waste entering the hub.

$$k_l = .0041\, V \left(\frac{D_l}{0.0000088} \right)^{.66} \tag{4-20}$$

where,

K_l = the liquid phase mass transfer coefficient, m/s;

V = the waste velocity, cm;

0.0000088 = the reference liquid diffusion coefficient, cm^2/s; and

D_l = the liquid phase diffusion coefficient, cm^2/s.

The overall mass transfer from a two-resistance model, K_o , is a combination of the gas and the liquid mass transfer coefficients:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\ K_g\ K} \right)^{-1} \qquad (4\text{-}21)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s); and

K = the partition coefficient (atm-m^3/mol).

The air losses, f_{air}, from the two-resistance model are as follows:

$$f_{air} = 1 - EXP\left(- \frac{K_o\ A}{q}\right) \qquad (4\text{-}22)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (cm/s);

q = the liquid flow rate (cm^3/s);

A = the area of the exposed surface (cm^2);

f_{air} = the fraction of the component emitted to the air.

The area of the mass transfer surface is assumed to equal the product of the circumference of the inlet pipe and the depth of fall of the wastewater stream before it enters the hub.

The following example calculation illustrates the use of these equations to estimate air emissions of toluene.

The assumed conditions are:

K = 357 (y/x)
q = 250 cm^3/s
pipe diameter = 2 in
pipe cross section area = 20.27 cm^2
pipe circumference = 15.96 cm
distance from pipe exit to hub inlet = 3.81 cm(1.5 in)

The waste velocity can be calculated as follows:

$$V = \frac{250\ \frac{cm^3}{s}}{(20.27\ cm^2)} = 12.33\ \frac{cm}{s}\ .$$

The values of the gas and liquid diffusivities are almost identical to the reference values in the correlations, and the ratio can be assumed to equal unity. The liquid phase mass transfer coefficient can be estimated as follows.

$$k_l = (0.0041)(12.33)(1)^{.66} = 0.05\ \frac{m}{s}\ .$$

This value of the liquid phase mass transfer coefficient is approximately 6 times greater than an estimate for the turbulent zone of an agitated aeration basin.

The gas phase mass transfer coefficient can be estimated:

$$k_g = (0.178)(1)^{.66} = 0.178\ \frac{m}{s}\ .$$

This value of the gas phase mass transfer coefficient is approximately 25 times as much as the mass transfer surface of a quiescent impoundment. The higher value for the gas phase mass transfer coefficient may be related to the form induced eddies around the stream of water and the much smaller eddy size near the flowing water when compared to the quiescent impoundment.

The overall mass transfer coefficient can be calculated as follows (based on liquid concentrations).

$$K_o = \left(\frac{1}{(0.178)(357/55555)(40.9)} + \frac{1}{0.05} \right)^{-1} = 0.024 \ \frac{m}{s} \ .$$

The distance from the pipe exit to the entrance of the hub is 3.81 cm (1.5 in). The circumference of the pipe opening is 15.96 cm (2 in dia.). The value of the area of mass transfer is the product of these two values, 61 cm^2.

The fraction emitted is estimated as follows:

$$f_e = 1 - Exp\left(- \frac{(2.4)(61)}{250} \right) = 0.44$$

4.3.15 Case E3 Lift Station with Periodic Pumping of Wastewater

Case E3 applies to a case where a waste flows continuously into an enclosed sump. The wastewater is lifted by pump from the sump to a collection main at higher elevation. The pump rate is substantially greater than the typical wastewater flow rate (providing excess capacity). The wastewater flows into the sump by splashing at least part of the time. The gas flows out of the headspace as the sump fills. The model approach is to assume a fractional approach to equilibrium in the sump and in the exiting gas. This fractional approach is assumed to be 50%, based in part upon data provided by Enviromega[1]. An illustration of this case is presented in Figure 4-15.

This case can be described by the following equations. The equation for the concentration in the gas phase is obtained from the partition coefficient:

$$C_g = \frac{f\ H\ C_l}{0.0244} \tag{4-23}$$

where,

C_g = the gas phase concentration of the constituent, moles/m^3 gas;

C_l = the liquid phase concentration of the constituent, moles/m^3 wastewater;

H = the partition coefficient, atm m^3 /mol; and

f = the fractional approach to equilibrium in the gas phase.

The fraction emitted from lift stations is estimated from the ratio of the concentration in the gas to the concentration in the liquid, since it is assumed that the volumetric flow rate of gas out of the sump equals the volumetric flow rate of the wastewater into the sump.

$$f_e = \frac{C_g}{C_l} = \frac{f\,H}{0.0244} \qquad (4\text{-}24)$$

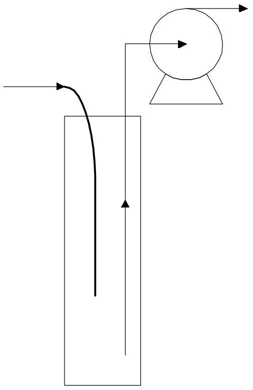
The following example calculation illustrates the use of these equations to estimate air emissions of toluene. The assumed conditions are:

H = 0.00643 atm-m^3/mol

f = 0.5

The fraction of toluene that is emitted as air emissions is estimated as follows:

$$f_e = \frac{(0.5)(.00643)}{0.0244} = 0.13$$



Parameter	Units	Value
Fraction equilibrium for headspace		0.5

Figure 4-15. Case E3. Lift station with periodic pumping.

4.3.16 Case E4 Open Surfaces in Sumps

Case E4 applies to a case where a waste flows continuously into a sump or junction box and the surface of the waste in the sump or junction box is open to the atmosphere. Enviromega collected data for two situations[1], (1) flow of waste below the surface and (2) the flow of waste into the surface from a partially filled inlet wastewater conduit. The model approach is to identify a method for applying the turbulent flow mass transfer model (trench model) to flow in sumps and junction boxes. The Enviromega data[1] was used as the basis of the development of this extension of the trench model. The equation developed here may be applicable to other open surfaces in sumps and junction boxes. An illustration of this case is presented in Figure 4-16.

This case can be described by the following equations. The equation for the liquid phase mass transfer coefficient is composed of an empirical constant with a correction for the liquid diffusion coefficient, the depth of flow, and the waste velocity in the sump. The trench model for liquid phase mass transfer is modified, equating the depth of flow to the depth of entrance flow. The width of flow is assumed to equal the square root of the surface area:

$$k_l = 1.41\ 10^{-4}\ \frac{V^{.67}}{d^{.85}} \left(\frac{D_l}{0.000021} \right)^{.83} \qquad (4\text{-}25)$$

where,

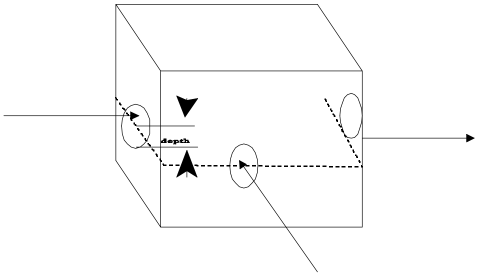
K_l = the liquid phase mass transfer coefficient, m/s;

V = the waste velocity, cm/s, equals the flow rate cm^3/s divided by both the depth and the width;

d = the depth of liquid flow into the sump, cm;

0.000021 = the reference liquid diffusion coefficient, cm^2/s; and

D_l = the liquid phase diffusion coefficient, cm^2/s.



Parameter	Units	Value
Depth of inlet flow base	m	.19
Flow rate of inlet waste	m^3/s	0.00188
Area of surface	m^2	1.77
Depth of sump liquid	m	1.37

Figure 4-16. Case E4. Open junction box with submerged flow.

The equation for the gas phase mass transfer coefficient is composed of the empirical model developed by McKay[4].

The overall mass transfer from a two-resistance model, K_o , is a combination of the gas and the liquid mass transfer coefficients:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\, K_g\, H} \right)^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s); and

H = the partition coefficient (atm-m^3/mol).

The air losses, f_{air}, from the two-resistance model are as follows:

$$f_{air} = \frac{K_o\, A}{K_o\, A + q} \tag{4-27}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate (m^3/s);

A = the area of the exposed surface (m^2); and

f_{air} = the fraction of the component emitted to the air.

The area of the mass transfer surface is the area of the surface of the wastewater in the sump or junction box.

The following example calculation illustrates the use of these equations to estimate air emissions of toluene.

The assumed conditions are:

H = 0.00643 atm-m3/mol, 357 (y/x);
q = 0.001888 m^3/s;
d = 19 cm (15 cm inside pipe diameter + 4 cm submerged) pipe fraction full on surface inlet = 0.5;
h = 1.37 m; and
A = 1.77 m2.

In the case where the waste discharges below the surface of the sump, the water is assumed to flow across the entire cross section of the sump. As an approximation, the cross sectional area of that flow is assumed equal to the product of the square root of the sump area (the sump width) and the depth of wastewater in the sump. The waste velocity in the subsurface flow case can be calculated as follows:

$$V = \frac{q}{A^{1/2}\, d} = \frac{.001888}{(1.77^{1/2})\ (.19)} = 0.0074\ \frac{m}{s}\ .$$

where V = the waste velocity across the surface of the sump, m/s.

If the waste discharges from a pipe that is located at the surface of the sump, the water will flow across the surface of the sump. The depth of flow, d, is one half of the pipe diameter, or 0.075 meters. As a rough approximation, the cross sectional area of that flow is assumed equal to the product of the width of the sump and the depth of flow in the entrance conduit. The waste velocity in the surface flow case can be estimated as follows:

$$V = \frac{q}{A^{1/2}\, d} = \frac{.001888}{(1.77)^{1/2}\ (0.075)} = 0.01892\ \frac{m}{s}\ .$$

The values of the gas and liquid diffusivities are almost identical to the reference values in the correlations, and the ratio can be assumed to equal unity. The liquid phase mass transfer coefficient can be estimated as follows using Equation 4-25.

$$k_l = 1.41\ 10^{-4}\ \frac{0.746^{.67}}{19^{.85}} \left(\frac{0.0000086}{0.000021} \right)^{.83} = 4.52\ 10^{-6}\ \frac{m}{s}$$

The overall mass transfer from a two-resistance model, K_o , is obtained from a combination of the gas and the liquid mass transfer coefficients:

$$k_g = 0.00521\ \frac{m}{s}$$

The air losses, f_{air}, from the two-resistance model are estimated using the following equation with the previously defined terms:

$$K_o = \left(\frac{1}{4.52\ 10^{-6}} + \frac{1}{(40.9)\ (0.00521)\ (0.00643)} \right)^{-1} = 4.5\ 10^{-6}$$

$$f_{air} = \frac{K_o\ A}{K_o\ A + q}$$

$$f_{air} = \frac{(4.5\ 10^{-6})\ 1.77}{(4.5\ 10^{-6})\ 1.77 + 0.001888} = 0.00422$$

4.3.17 Case F1 Primary Clarifier Weir

An illustration of this case is presented in Figure 4-17. Albert Pincinci[5] (11/7/89) presented equations for the air emissions from a primary clarifier weir:

$$\ln(r) = 0.042\, Z^{0.872}\, q^{0.509} \qquad \textit{primary} \tag{4-28}$$

$$\ln(r) = 0.077\, Z^{0.623}\, q^{0.66} \qquad \textit{secondary} \tag{4-29}$$

where,

r = Ci/Co deficit ratio;

Ci = inlet concentration;

Co = outlet concentration;

Z = distance of fall (m); and

q = flow rate per length of weir (m3/h-m).

The fraction lost to the air over the weir is calculated from the ratio r:

$$f_{air} = 1 - \frac{1}{r} \tag{4-30}$$

The equivalent liquid mass transfer coefficient is as follows:

$Kl = (m/s) = f_{air} \quad q/(3600\ Z)$ (4-31).

The overall mass transfer from a two-resistance model, K , is a combination of the gas and the liquid mass transfer coefficients:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\, K_g\, K} \right)^{-1}$$

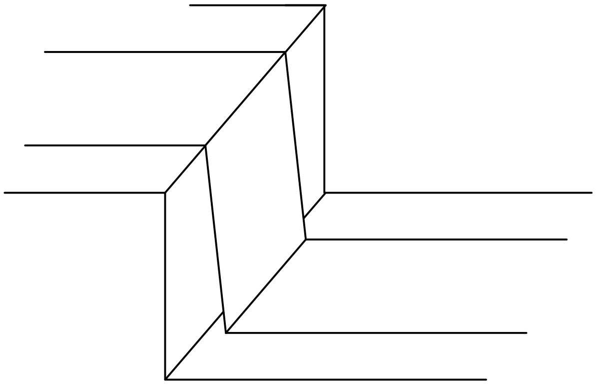
where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s); and

K = the partition coefficient (atm-m^3/mol).



Parameter	Units	Value
Drop distance of waterfall	m	1.22
Flow rate of water over the weir	m^3/s	0.065
Length of weir	m	2
Tail water depth	m	1

Figure 4-17. Case F1. Flow over a weir.

The air losses, f_{air}, from the two-resistance model are as follows:

$$f_{air} = 1 - EXP\left(-\frac{K_o Z}{q}\right)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate per length of the weir (m^3/h-m);

Z = the distance of fall (m); and

f_{air} = the fraction of the component emitted to the r.

The input parameters are as follows:

Diameter of clarifier, d	19.5 m
Depth	2.4 m
Flow of liquid, q	0.07 m3/s
Height of waterfall, Z	0.3 m
Clarifier weir/circumference	1
Partition coefficient (Y/X)	305
The circumference of the clarifier is	B d = 61.30 m
Kl from secondary clarifier model	1.05 x 10-3 g-mol/cm2-s
The gas mass transfer coefficient	1.13 x 10-5 g-mol/cm2-s
The area of the waterfall (61 m) (0.3 m)	18.4 m2

$$K_o = \frac{1}{\frac{1}{0.00105} + \frac{1}{(1.13x10^{-5})\,(305)}}$$

K_o = 8.0 x 10^{-4} g-mol/cm2-s (1.44 x 10^{-4} m/s)

The fraction of VO lost to air is

f_{air} = 1 - EXP [-Ko (area)/q]

= 1 - EXP (-1.44 x 10^{-4} x 18.4/0.07)

= 0.0371 .

4.3.18 Case F2 Secondary Clarifier Weir

Albert Pincinci[1] presented the following equation for the air emissions from a secondary clarifier weir:

$$\ln(r) = 0.077\, Z^{0.623}\, q^{0.66} \qquad (\mathit{secondary})$$

where,

r = Ci/Co deficit ratio;
Ci = inlet concentration;
Co = outlet concentration;
Z = distance of fall (m); and
q = flow rate per length of weir (m3/h-m).

4.3.18 Case F3 General Weir Model

The preceding two models were obtained by Princinci for volatiles flowing over clarifier weirs. For the general weir model, the model presented by Nakasone[6] is adapted for use for weirs. The model is modified to account for gas phase resistance.

$$\ln(r) = 0.0785\, Z^{1.31}\, q^{0.428}\, h^{0.310} \qquad (4\text{-}33)$$

where,

r = Cs/(Cs-Co) deficit ratio, assumes that there is no oxygen before the weir;
Cs = saturated oxygen concentration;
Co = outlet oxygen concentration;
Z = distance of fall (m), includes 1.5 times the distance from the weir top to the critical depth above the weir;
q = flow rate per length of weir (m3/h-m); and
h = the tailwater depth (m).

The constants in the above equation are a function of the flow rate and the distance of fall. Table 4-15 presents constants that can be used in the above equation.

It is assumed that the rate limiting step for the diffusion of oxygen is the mass transfer in the liquid phase (oxygen is only slightly soluble in the water). From this equation, a value of the liquid phase mass transfer coefficient can be estimated for organics, after correcting for the relative diffusion coefficient of the organic and oxygen in water.

$$K_l = \frac{q}{Z} \left(\frac{D_{lv}}{D_{lo}} \right)^{0.66} \ln(r) \left(\frac{hr}{3600\ s} \right) \qquad (4\text{-}34)$$

where,

K_l = the mass transfer coefficient of the organic in water (m/s);

ln(r) = the natural log of the deficit ratio for oxygen in the water flowing over the weir;

D_{lv} = the diffusion coefficient of the organic in water (cm2/s);

Z = distance of fall (m), includes 1.5 times the distance from the weir top to the critical depth above the weir; and

q = flow rate per length of weir (m3/h-m).

The gas phase mass transfer coefficient of the flow at the weir is assumed to equal 0.05 for benzene. This is approximately the magnitude for mechanically aerated systems. The assumption of a gas phase mass transfer coefficient of this magnitude will lower the estimate of the oxygen transfer from the correlation by only a few percent. Significantly lower gas phase mass transfer coefficients will lower the predicted oxygen transfer to an extent not predicted by the correlation.

$$k_g = 0.05 \left(\frac{D_{gv}}{D_{go}} \right)^{0.66} \qquad (4\text{-}35)$$

where,

Kg = the mass transfer coefficient of the organic in air (m/s);

Dgv = the diffusion coefficient of the organic in air (cm2/s);

Dgo = the diffusion coefficient of the reference material in air (0.088 cm2/s); and

0.05 = the assumed mass transfer coefficient of a turbulent surface.

TABLE 4-15 . PARAMETERS FOR USE IN THE EQUATION OF H. NAKASONE.

applicable range		constant	Z exponent	q exponent
Z <= 1.2 m	q<=235	0.0785	1.31	0.428
Z > 1.2 m	q<=235	0.0861	0.816	0.428
Z <=1.2 m	q >235	5.39	1.31	-0.363
Z >1.2 m	q >235	5.92	0.816	-0.363

The value of the overall mass transfer coefficient is estimated by combining the liquid and gas mass transfer coefficients.

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\ K_g\ K} \right)^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s); and

K = the partition coefficient (atm-m^3/mol).

The fraction of the components that are emitted to the air is estimated by the following relationship:

$$f_{air} = 1 - EXP\left(- \frac{K_o\, Z}{q}\ \frac{3600\ \mathrm{sec}}{hr}\right) \qquad (4\text{-}36)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate per length of the weir (m^3/h-m);

Z = the distance of fall (m); and

f_{air} = the fraction of the component emitted to the air.

In the example case of toluene, the deficit ratio is calculated using the following equations:

$$\ln\,(r) = 0.0861\, Z^{0.816}\, q^{0.428}\, h^{0.310}$$

where the above constants are for the situation where Z > 1.2 m and q < 235 (See TABLE 4-15).

r = Cs/(Cs-Co) deficit ratio, assumes that there is no oxygen before the weir;

Cs = saturated oxygen concentration;

Co = outlet oxygen concentration;

Z = distance of fall (1.219 m), includes 1.5 times the distance from the weir top to the critical depth above the weir;

q = flow rate per length of weir (117 m3/h-m); and

h = the tailwater depth (1 m).

The natural log of the deficit ratio, ln(r), is calculated as 0.7769. Next, the liquid phase mass transfer coefficient is estimated.

$$K_l = \frac{q}{Z}\left(\frac{D_{lv}}{D_{lo}}\right)^{0.66} \ln(\,r\,)\left(\frac{hr}{3600\ s}\right) \qquad (4\text{-}37)$$

$$K_l = \frac{117}{1.219} \left(\frac{0.86}{2.5} \right)^{0.66} 0.7769 \left(\frac{hr}{3600\ s} \right)$$

$$K_l = 0.0102 \frac{m}{s}$$

TABLE 4-16 . PLANT PARAMETERS FOR A MODEL WEIR.

Parameter	Units	Symbol	Value
distance of fall	m	Z	1.22
flow rate	m3/s	Q	0.065
length of weir	m		2
flow rate per length	m3/h-m	q	117
tail water depth	m	h	1

Using (0.86/2.5) as the ratio of the diffusion coefficients of toluene and air, the estimated value of kl is 0.0102 m/s.

Next, the gas phase mass transfer coefficient of toluene is estimated, based upon the reference mass transfer coefficient of benzene.

$$k_g = 0.05 \left(\frac{D_{gv}}{D_{go}} \right)^{0.66}$$

where,

Kg = the mass transfer coefficient of the organic in air (m/s);

Dgv = the diffusion coefficient of the organic in air (0.087 cm2/s);

Dgo = the diffusion coefficient of the reference material in air (0.088 cm2/s); and

0.05 = the assumed mass transfer coefficient of a turbulent surface.

$$k_g = 0.05 \left(\frac{0.087}{0.088} \right)^{0.66}$$

$$k_g = 0.0496 \frac{m}{s}$$

The estimated gas phase mass transfer coefficient is 0.0496.

Next, the overall mass transfer coefficient is calculated:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9 \, K_g \, K} \right)^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (0.0102 m/s);

K_g = the gas phase mass transfer coefficient (0.49624 m/s); and

K = the partition coefficient (0.00668 atm-m^3/mol).

$$K_o = \left(\frac{1}{0.01024} + \frac{1}{(40.9)\,(0.0496)\,(0.00668)} \right)^{-1}$$

$$K_o = 0.00583 \frac{m}{s}$$

The overall mass transfer coefficient is 0.00583 m/s. Next, the fraction of air emissions are estimated.

$$f_{air} = 1 - EXP\left(- \frac{K_o \, Z}{q} \, \frac{3600 \text{ sec}}{hr}\right)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (0.00583 m/s);

q = the liquid flow rate per length of the weir(117 m^3/h-m);

Z = the distance of fall (1.2192 m); and

f_{air} = the fraction of the component emitted to the air.

$$f_{air} = 1 - EXP\left(- \frac{0.00583\ 1.219}{117} \frac{3600\ sec}{hr}\right)$$

The fraction of toluene that is emitted to the air is 0.20.

$$f_{air} = 0.2$$

4.4 REFERENCES

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5.0 SURFACE IMPOUNDMENTS AND OPEN TANKS

This section discusses the approach used to estimate air emissions from surface impoundments and open top tanks. The emission models are described, model facilities are defined, and example calculations are presented.

5.1 NARRATIVE DESCRIPTION OF EMISSIONS AND MODEL UNITS

Emissions from surface impoundments and open tanks originate from the uncovered liquid surface that is exposed to the air. The model used to estimate emissions from the liquid surface is based on an overall mass transfer coefficient that incorporates two resistances to mass transfer in series--the liquid-phase resistance and the gas-phase resistance. Numerous correlations are available to estimate the individual mass transfer coefficients (or resistances), and they depend upon the compound's properties and the system's parameters. The recommended correlations and their applicability are described in subsequent sections. The emission estimating procedure also incorporates a flow model that describes the method of operation. For flowthrough systems, the impoundment's or tank's contents may be completely mixed, plug flow, or somewhere in between with varying degrees of backmixing or axial dispersion. Biologically active impoundments and aeration tanks can be designed for either completely mixed or plug flow, and both types of flow models are discussed for these types of systems. For disposal impoundments, the contents are assumed to be well mixed, and the bulk concentration is expressed as a function of time. An expression for biodegradation is incorporated for those units specifically designed for biodegradation, such as treatment impoundments or wastewater treatment tanks. For these units, the relative rates of air emissions and biodegradation are determined to assess the predicted extent of each mechanism.

The general approach that is used to estimate emissions compares the relative rates of air emissions, biodegradation, and removal with the effluent. Several different types of model units are presented and include mass transfer to the air from quiescent, mechanically aerated, diffused-air, and oil-film liquid surfaces. The other major difference among the types of model units is the type of flow model that is used. For flow-through systems, the degree of mixing can range from complete mixing to plug flow (no mixing), and both cases are presented. For disposal units with no flow out, emissions are a function of time, and average emissions are estimated for some specified time since disposal. The major difference in the emission equations is the liquid-phase concentration that is used for the driving force for mass transfer to the air. The simplest case is represented by well-mixed systems in which the driving force is represented by C_L, the liquid-phase concentration in the bulk liquid, which is also equal to the effluent concentration. Relative removal rates can be compared for this well-mixed case from a simple material balance.

For plug flow, integration is required because the driving force for mass transfer changes as the liquid flows through the system. This concentration is a function of location or time (which are equivalent in plug flow) and is expressed as C_t (denoting a dependence on time). The effluent from a plug flow system is denoted as C_e. For disposal impoundments, the driving-force concentration changes with time and is also denoted as C_t; however, there is no effluent from a disposal impoundment. The integration required for plug flow is from t = 0, when the material first enters the unit, to t = residence time, when the material leaves the unit. For disposal units, the integration is from t = 0, when the material is first placed in the unit, to t = time since disposal, which must be specified to estimate average emissions. The integrated forms of these emission equations are very similar.

The well-mixed flow model is recommended and is the model used in the computer program accompanying this report. This flow model is more generally applicable than plug flow, the calculations are more straightforward, and the two types give similar results. The only exception is a flowthrough impoundment with an oil film surface, which uses the plug flow model because the oil film inhibits mixing. Both models yield an estimate of air emissions, biodegradation, and the quantity leaving with the effluent. It is important to recognize that the quantity leaving with the effluent may also eventually contribute to air emissions, especially for treatment units in series or for discharges to streams or publicly owned treatment works.

Equations are presented for estimating the various removal rates, and example calculations for different types of impoundments are also provided. Example calculations are not presented separately for open tanks because the procedure is analogous to that used for impoundments. In general, open tanks will have different input parameters that will account for differences in emission rates compared to impoundments. For example, the liquid surface area for open tanks will be less, and the fetch-to-depth (F/D) ratio will be much lower for tanks. If the open tank has a wind barrier to reduce the wind velocity, the reduced wind velocity can be used in the mass transfer correlations. In addition, the modeling approach accounts for the shorter retention times in tanks (on the order of hours) compared to impoundments (on the order of days). For open tanks, the mass transfer correlation of Springer is recommended for windspeeds less than 3.25 m/s, and the correlation of MacKay and Yeun is recommended for windspeeds greater than 3.25 m/s. Both are discussed in the following section.

5.2 QUIESCENT SURFACES WITH FLOW

5.2.1 Emission Model Equations

The primary focus on emissions from impoundments and wastewater treatment tanks is on aqueous solutions contaminated with organics because aqueous waste is the most common waste type handled in these facilities. For aqueous systems, the basic relationship describing mass transfer of a volatile constituent from the open liquid surface to the air is:

$$E = KAC_L \tag{5-1}$$

where,

E = air emissions from the liquid surface, g/s;
K = overall mass transfer coefficient, m/s;
A = liquid surface area, m^2; and
C_L = concentration of constituent in the liquid phase, g/m^3.

The overall mass transfer coefficient (K) is estimated from a two-phase resistance model that is based on the liquid-phase mass transfer coefficient (k_L in m/s), the gas-phase mass transfer coefficient (k_G in m/s), and Henry's law constant in the form of a partition coefficient (Keq). The two resistances act in series and the overall resistance is expressed as:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{k_G\ Keq} \tag{5-2}$$

where,

K = overall mass transfer coefficient, m/s;
k_L = liquid-phase mass transfer coefficient, m/s;
k_G = gas-phase mass transfer coefficient, m/s; and
Keq = equilibrium constant or partition coefficient, concentration in gas phase/concentration in liquid phase where both concentrations are in the same units.

Henry's law constant (H in atm•m^3/g mol) is estimated for the constituents of interest by dividing the constituent's vapor pressure (in atmospheres) by its solubility in water (in g mol/m^3). The equilibrium constant is estimated by:

$$Keq = H/RT \tag{5-3}$$

where,

H = Henry's law constant, atm•m^3/g mol;

R = universal gas constant, 8.21×10^{-5} atm•m^3/g mol•K; and

T = temperature, K.

For a standard temperature of 25 °C, the expression for Keq reduces to:

$$K_{eq} = 40.9 \times H \tag{5-4}$$

The units associated with K_{eq} in Equation (5-4) are the ratio of gas-phase to liquid-phase concentrations and require that both be expressed in the same units of mass/volume.

Several mathematical models have been developed to estimate the individual liquid- and gas-phase mass transfer coefficients. The models are based on different systems, constituents, and sometimes different theoretical considerations. Many of these models yield similar results. The procedures used in this section to estimate the individual mass transfer coefficients rely primarily on existing mass transfer correlations that are believed to be generally applicable.

The liquid-phase mass transfer coefficient (k_L) has been shown to be a function of the constituent's diffusivity in water, windspeed, and liquid depth.[1,2] Work performed at the University of Arkansas by Springer et al.[3] confirmed these effects and resulted in the correlations given in Table 5-1. Springer used simulation studies in a wind tunnel water tank of a constant fetch (2.4 m) and variable depth (4.7 cm to 1.2 m). Fetch is defined as the linear distance across the liquid surface in the direction of the wind flow, and the F/D ratio is defined as the fetch divided by the depth of the impoundment. Ethyl ether was used as the volatile component in the desorption experiments, in which the wind velocity and F/D ratio were varied. Springer's results shown in Table 5-1 yield three different correlations for k_L that depend upon the combination of windspeed and F/D ratio of interest. Springer's model implies that k_L is constant for windspeeds of 0 to 3.25 m/s. Although Springer examined only the mass transfer of ethyl ether, his results are extrapolated to other compounds by the ratio of the compound's and ether's diffusivities in water to the 2/3 power. The windspeed in Springer's correlation is defined as the windspeed 10 m above the liquid surface. For practical application of his correlation, typically reported values of windspeed are used. Springer's model does not include the case in which the F/D ratio is less than 14 and the windspeed is greater than 3.25 m/s. For this specific case, k_L was estimated from MacKay and Yeun's correlation shown in Table 5-1.[7,8] MacKay and Yeun[9] did not address the effect of depth; however, their correlation is based on data from 11 organic compounds in a well-mixed system, the compounds represent a broad range of Henry's law constants, and their general correlation is applicable for the case described above that is not covered by Springer's correlation.

The gas-phase coefficient (k_G) was estimated from the correlation of MacKay and Matasugu as shown in Table 5-1.[10] This correlation was developed from experiments on the evaporation of isopropyl benzene, gasoline, and water into air. These researchers verified that previous work, which assumed that the wind velocity profile follows a power law, could be used to quantify the rate of evaporation from a smooth liquid surface. The result was a correlation that expressed k_G as a function of windspeed and the fetch or effective diameter of the liquid surface.

The individual mass transfer coefficients estimated from the correlations in Table 5-1 are used in Equation (5-2) to estimate

TABLE 5-1. EQUATIONS FOR CALCULATING INDIVIDUAL MASS TRANSFER COEFFICIENTS FOR VOLATILIZATION OF ORGANIC SOLUTES FROM QUIESCENT SURFACE IMPOUNDMENTS

Liquid phase

Springer et al.[4] (for all cases except F/D3.25 m/s):

$$k_L = 2.78 \times 10^{-6} \left[\frac{D_w}{D_{ether}}\right]^{2/3} \qquad (0 < U_{10} < 3.25 \quad \text{(All F/D ratios)}$$

$$k_L = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}]\, U_{10}^2 \left[\frac{D_w}{D_{ether}}\right]^{2/3}$$

$(U_{10} > 3.25)$ (m/s) $(14 < F/D < 51.2)$

$$k_L = 2.611 \times 10^{-7}\, U_{10}^2 \left[\frac{D_w}{D_{ether}}\right]^{2/3} \qquad (U_{10} > 3.25) \text{ (m/s)} \quad (F/D > 51.2)$$

where,

U_{10} = windspeed at 10 m above the liquid surface, m/s;

D_w = diffusivity of constituent in water, cm^2/s;

D_{ether} = diffusivity of ether in water, cm^2/s; and

F/D = fetch-to-depth ratio (fetch is the linear distance across the impoundment).

Gas phase

MacKay and Matasugu (in Hwang[5]):

$$k_G = 4.82 \times 10^{-3}\, U^{0.78}\, Sc_G^{-0.67}\, d_e^{-0.11} \qquad \text{(m/s)}$$

where,

U = windspeed, m/s;

Sc_G = Schmidt number on gas side = $\frac{\mu_G}{D\, D_G\, a}$;

μ_G = viscosity of air, g/cm•s;

(continued)

TABLE 5-1 (continued)

D_G = density of air, g/cm^3;

D_a = diffusivity of constituent in air, cm^2/s;

d_e = effective diameter of impoundment = $*\frac{4A}{B}*^{0.5}$, m; and

A = area of impoundment, m^2.

Liquid phase

MacKay and Yeun[6] (for F/D 3.25 m/s):

$k_L = 1.0 \times 10^{-6} + 34.1 \times 10^{-4}\ U^* \ Sc_L^{-0.5}$ (U^*>0.3) (m/s)

$k_L = 1.0 \times 10^{-6} + 144 \times 10^{-4}\ U^{*2.2}\ Sc_L^{-0.5}$ (U^*< 0.3) (m/s)

where,

U^* = friction velocity (m/s) = $0.01\ U_{10}\ (6.1 + 0.63\ U_{10})^{0.5}$;

U_{10} = windspeed at 10 m above the liquid surface, m/s;

Sc_L = Schmidt number on liquid side = $\frac{\mu_L}{D_L Dw}$;

μ_L = viscosity of water, g/cm•s;

D_L = density of water, g/cm^3; and

D_w = diffusivity of constituent in water, cm^2/s.

the overall mass transfer coefficient. The equilibrium constant for a constituent dissolved in water at 25 °C is estimated from Equation (5-4). However, an estimate of the concentration in the liquid phase (C_L) is needed in Equation (5-1) to estimate emissions.

The concentration C_L in Equation (5-1) is the driving force for mass transfer. For an impoundment that is instantly filled with waste, the driving force (C_L) is the initial concentration in the waste. However, this concentration will decrease with time as the constituent is lost to the air, which suggests that emissions may also decrease with time (assuming constant K and A). For flowthrough systems, the concentration may be cyclical if the loading of the process is cyclical. Continuous flowthrough systems may attain some equilibrium concentration.

The flow model assumed for quiescent impoundments and tanks with no biodegradation is that the contents of the system are well mixed and that the bulk concentration (driving force) in the system is equal to the effluent concentration, C_L. A material balance around this system yields:

$$QC_i = KAC_L + QC_L \tag{5-5}$$

or

$$C_L = QC_i/(KA+Q) \tag{5-6}$$

where,

Q = volumetric flow rate, m^3/s;

C_i = initial concentration in the waste, g/m^3;

C_L = equilibrium or bulk concentration in the impoundment, g/m^3;

K = overall mass transfer coefficient, m/s; and

A = liquid surface area, m^2.

The well-mixed assumption is made for the sake of simplicity and assumes that bulk convection and wind-induced eddies combine to mix the basin contents. Axial dispersion in the flow direction is also possible, and some systems may be designed specifically for plug flow (e.g., some biological treatment tanks). An assumption of plug flow instead of well-mixed flow would yield slightly higher estimates of emissions; however, the difference is small. Calculations presented by Thibodeaux for an aerated basin that was well-mixed or had plug flow showed that the plug-flow assumption yielded estimates that were higher by 11 percent for acetaldehyde, 5 percent for acetone, and 0 percent for phenol.[11]

The approach described to estimate emissions from quiescent impoundments with no biodegradation includes the following steps:

1. Estimate the individual mass transfer coefficients from Table 5-1.
2. Estimate the equilibrium constant from Equation (5-3).
3. Estimate the overall mass transfer coefficient from Equation (5-2).
4. Estimate the liquid-phase concentration from Equation (5-6).
5. Estimate emissions from Equation (5-1).

The major assumptions associated with this procedure are:

- The two-resistance model and the correlations for the individual mass transfer coefficients are applicable to the system of interest.
- The impoundment's contents are well mixed.
- There is no significant removal by biodegradation, seepage, adsorption, or other forms of degradation.
- The waste material of interest is aqueous waste with no separate organic phase.
- The estimate of Henry's law constant (equilibrium partitioning between the vapor and liquid) is reasonably accurate.

The recommended procedure for quiescent impoundments is to assume that the liquid is well mixed. This assumption is used in the computer model accompanying this report and is illustrated in the example calculations. However, impoundments and tanks with quiescent surfaces can also be designed for plug flow with the use of baffles or other design techniques to reduce the extent of backmixing. In a plug-flow system, the rate of air emissions at any point in the system changes as the material flows through the system. There is no uniform liquid concentration within the plug-flow unit as there was in the well-mixed system, and the lowest concentration occurs in the effluent (i.e., there is no backmixing of the effluent with the influent). For plug flow, the rate of disappearance of a compound by air emissions is given by:

$$- \frac{\delta(C_t\ V)}{\delta t} = K\ A\ C_t \qquad (5\text{-}7)$$

where,

C_t = concentration after the plug has traveled t seconds;
t = time, s;
V = volume, m^3;
and with the other symbols as previously defined.

Rearranging Equation (5-7) yields:

$$\frac{\delta(C_t)}{C_t} = - \frac{K\ A}{V}\ \delta t \qquad (5\text{-}8)$$

Integrating Equation (5-8) from $C_t = C_i$ at t = 0 to $C_t = C_L$ at t = V/Q (one residence time) gives:

$$\left(\frac{C_L}{C_i} \right) = EXP \left(- \frac{K\ A}{Q} \right) \qquad (5\text{-}9)$$

where C_L = effluent concentration, g/m^3, and with the other symbols as previously defined.

The residence time, J in seconds, equals V/Q and V = AD (area times depth); consequently, A/Q = J/D. Substituting into Equation (5-9) yields an equivalent expression:

$$\left(\frac{C_L}{C_i} \right) = 1 - \left(- \frac{K \tau}{D} \right) \qquad (5\text{-}10)$$

The ratio C_L/C_i represents the fraction removed with the effluent; therefore, 1 - C_L/C_i represents the fraction that is emitted (f_{air}) from the plug-flow system:

$$f_{air} = \left(1 - \frac{C_L}{C_i} \right) = 1 - EXP \left(- \frac{K \tau}{D} \right) \qquad (5\text{-}11)$$

The average emission rate is calculated from:

$$E = f_{air} \; Q \; C_i \qquad (5\text{-}12)$$

where,

E = emissions, g/s;

f_{air} = fraction emitted from Equation (5-11);

Q = flow rate, m^3/s; and

C_i = influent concentration, g/m^3.

5.2.2 Model Plant Parameters for Quiescent Impoundments

A model facility was developed for quiescent impoundments to illustrate the emission estimating procedure. A 1981 survey compiled by Westat[12] showed that the median surface area for storage impoundments was approximately 1,500 m^2 and that the median depth was 1.8 m. Detention times ranged from 1 to 550 days, with over half of the values at 46 days or less. For this example, a detention time of 20 days was chosen. The area and depth yield a total volume of 2,700 m^3, and the detention time of 20 days yields a flow rate of 1.6 L/s (0.0016 m^3/s).

Meteorological conditions are also needed as input parameters for the emission models. For this emission estimate, a standard temperature of 25 °C and a windspeed of 4.47 m/s (10 mi/h) were used. Benzene was chosen as an example constituent at a concentration of 10 g/m^3 (10 ppm) to estimate emissions from the model facility. The properties of benzene that are used include Henry's law constant (5.5×10^{-3} $atm \bullet m^3/g$ mol), diffusivity in air (0.088 cm^2/s), and diffusivity in water (9.8×10^{-6} cm^2/s). Table 5-2 lists the input parameters for the estimate of emissions given in Section 5.2.3.

5.2.3 Example Calculation for Storage Impoundments

This section presents a step-by-step example calculation for emissions from storage impoundments. The equations described in Section 5.2.1 are used with the model unit parameters given in Section 5.2.2 to estimate emissions from an aqueous waste containing 10 g/m^3 of benzene.

a. Calculate liquid-phase mass transfer coefficient, k_L. Use Springer's model (see Table 5-1):

$$\text{Effective diameter} = *\frac{Area}{B}*^{0.5} \times 2 = *\frac{1,500}{B}*^{0.5} \times 2 = 43.7 \text{ m}$$

$$F/D = \text{Effective diameter/depth} = \frac{43.7}{1.8} = 24.3 \text{ .}$$

Windspeed = 4.47 m/s ($U_{10} \geq 3.25$ m/s)

F/D = 24.3

$$k_L = [2.605 \times 10^{-9} (F/D) + 1.277 \times 10^{-7}] U_{10}^2 \; * \frac{D_w}{D_{ether}} *^{0.67} \quad m/s$$

where,

U_{10} = windspeed = 4.47 m/s

D_w = 9.8×10^{-6} cm^2/s (benzene)

D_{ether} = 8.5×10^{-6} = cm^2/s (ether)

F/D = 24.3.

TABLE 5-2. INPUT PARAMETERS--STORAGE IMPOUNDMENT

Area	1,500 m^2
Depth	1.8 m
Volume	2,700 m^3
Retention time	20 days
Flow	0.00156 m^3/s
Temperature	25 °C
Windspeed	4.47 m/s
Constituent	Benzene in water
Influent concentration	10 g/m^3
Henry's law constant	5.5×10^{-3} atm•m^3/g mol
Diffusivity in air (benzene)	0.088 cm^2/s
Diffusivity in water (benzene)	9.8×10^{-6} cm^2/s
Diffusivity in water (ether)	8.5×10^{-6} cm^2/s
Viscosity of air	1.81×10^{-4} g/cm•s
Density of air	1.2×10^{-3} g/cm^3

Then,

$$k_L = [2.605 \times 10^{-9}(24.3) + 1.277 \times 10^{-7}](4.47)^2 \left[\frac{9.8 \times 10^{-6}}{8.5 \times 10^{-6}}\right]^{0.67}$$

$$k_L = [2.605 \times 10^{-9}\ (24.3) + 1.277 \times 10^{-7}]\ (4.47)^2\ (1.1)$$

$$k_L = 4.2 \times 10^{-6} \text{ m/s.}$$

b. Calculate gas-phase mass transfer coefficient, k_G. Use MacKay and Matasugu (see Table 5-1):

$$k_G = 4.82 \times 10^{-3}\ U^{0.78}\ Sc_G^{-0.67}\ \ d_e^{-0.11} \qquad \text{(m/s)}$$

where,

U = windspeed, 4.47 m/s

$$Sc_G = \begin{matrix}\text{Schmidt No.}\\ \text{for gas}\end{matrix} = \frac{\text{viscosity of gas}}{\text{(gas density)(diffusivity of i in gas)}}$$

Gas = air

Viscosity (air) = 1.81×10^{-4} g/cm•s

Density (air) = 1.2×10^{-3} g/cm^3

Diffusivity (benzene in air) = 0.088 cm^2/s

$$Sc_G = \frac{1.81 \times 10^{-4} \text{ g/cm•s}}{(1.2 \times 10^{-3} \text{ g/cm}^3)\ (0.088 \text{ cm}^2\text{/s})} = 1.71$$

d_e = effective diameter = 43.7 m .

Then,

$$k_G = (4.82 \times 10^{-3})\ (4.47)^{0.78}\ (1.71)^{-0.67}\ (43.7)^{-0.11}$$
$$= 7.1 \times 10^{-3} \text{ m/s} \ .$$

c. Calculate overall mass transfer coefficient (K) from Equation (5-2):

$$\frac{1}{K} = \frac{1}{K_L} + \frac{1}{K_{eq}\ k_G}$$

where

$$Keq = \frac{H}{RT} = \frac{5.5 \times 10^{-3} \text{ m}^3\text{•atm/mol}}{(8.21 \times 10^{-5})(\frac{\text{atm•m}^3}{\text{mol•K}})\ (298 \text{ K})} = 0.225 \ .$$

Then,

$$\frac{1}{K} = \frac{1}{4.2 \times 10^{-6}} + \frac{1}{(0.225)(7.1 \times 10^{-3})} = 2.39 \times 10^{5}$$

$$K = 4.2 \times 10^{-6}\ \text{m/s} \quad .$$

d. Estimate emissions for a well-mixed system:

$QC_i = KC_oA + QC_o$ (from material balance of Equation (5-5))

$$C_o = \frac{QC_i}{KA + Q}$$

Retention time = 480 h

Volume = 2,700 m^3

Where,

$$Q = \text{flow rate} = *\frac{2,700\ \text{m}^3}{480\ \text{h}}*\ *\frac{1\ \text{h}}{3,600\ \text{s}}* = 0.00156\ \text{m}^3/\text{s};$$

C_i = 10 g/m^3; and

$K = 4.2 \times 10^{-6}$ m/s.

$$C_o = \frac{(0.00156\ \text{m}^3/\text{s})(10\ \text{g/m}^3)}{(4.2 \times 10^{-6}\ \text{m/s})(1,500\ \text{m}^2) + (0.00156\ \text{m}^3/\text{s})} = 1.98\ \text{g/m}^3$$

$A = 1,500\ \text{m}^2$.

Air emissions = KC_oA (Equation 5-2)

$= (4.2 \times 10^{-6}\ \text{m/s})(1.98\ \text{g/m}^3)(1,500\ \text{m}^2) = 0.012$ g/s

= 3.8 Mg/yr .

e. Estimate emissions for a plug-flow system:

$f_{air} = 1 - \exp(-KJ/D)$ (Equation 5-11)

$K = 4.2 \times 10^{-6}$ m/s (Step c)

$J = 480\ \text{h} = 1.73 \times 10^{6}$ s

$D = 1.8$ m

$$f_{air} = 1 - \exp(-4.2 \times 10^{-6}\ \text{m/s} \bullet 1.73 \times 10^{6}\ \text{s}/1.8\ \text{m}) = 0.98$$

$$E = f_{air}\ Q\ C_o \quad \text{(Equation 5-12)}$$

$f_{air} = 0.98$;
$Q = 0.00156\ m^3/s$; and
$C_o = 10\ g/m^3$.

$$E = (0.98)(0.00156\ m^3/s)(10\ g/m^3)$$
$$E = 0.015\ g/s = 0.47\ Mg/yr.$$

5.3 BIODEGRADATION

This section identifies some of the major design features of biological treatment processes, such as activated sludge units and impoundments designed for biodegradation. Mathematical models for biodegradation are also presented and incorporated into predictive fate models.

5.3.1 Description of Biological Active Systems

The activated sludge process is an aerobic biological treatment in which the pollutants are degraded by microorganisms suspended uniformly in the reaction tank. Oxygen is introduced by mechanical means, and the microorganisms are maintained by recycling the activated sludge that is formed. In most units, the sludge is removed by settling in a separate unit, a portion of the sludge is recycled, and a small portion is wasted (removed from the system) on a continuous basis. Oxidation or stabilization impoundments and aerated impoundments are used to treat entire plant wastes as well as to polish the effluent from other treatment processes. Solids usually settle out in the impoundment or are removed in a separate vessel. Generally, the solids are not recycled; however, if the solids are returned, the process is the same as a modified activated sludge process.[13]

Typical design parameters for an activated sludge process are given in Table 5-3. Two of the most commonly used parameters are the food-to-microorganism (F/M) ratio and residence time. The F/M ratio describes the organic loading on the biological system and is calculated as the weight of BOD_5 (biochemical

TABLE 5-3. DESIGN PARAMETERS FOR ACTIVATED SLUDGE PROCESSES[14]

Process	F/M,[a] kg BOD/kg biomass•day	Loading, kg BOD/m^3•day	MLSS,[b] g/L	Retention time, h
Conventional[c]	0.2-0.4	0.3-0.6	1.5-3.0	4-8
CSTR[d]	0.2-0.6	0.8-2.0	3.0-6.0	3-5
Contact	0.2-0.6	1.0-1.2	1.0-3.0[e]	0.5-1[e]
Stabilization			4.0-10[f]	3-6[f]
Extended aeration	0.05-0.15	0.1-0.4	3.0-6.0	18-36
O_2 systems	0.25-1.0	1.6-3.3	6.0-8.0	1-3

[a] F/M = Food to microorganism ratio.
[b] MLSS = Mixed liquor suspended solids.
[c] Plug flow design.
[d] CSTR = Continuous stirred-tank reactor.
[e] Contact unit.
[f] Solids stabilization unit.

oxygen demand from a 5-day test) that enters the system in a 24-hour period divided by the total weight of biological solids in the system. The biological solids may be roughly estimated from the mixed liquor suspended solids (MLSS) if substantial quantities of inorganics (such as silt) are not present. If inorganic solids are present, the biological solids may be better approximated by the mixed liquor volatile suspended solids (MLVSS).[15] For municipal wastewater systems, the volatile solids comprise about 60 to 80 percent of the total suspended solids in the sludge; consequently, in the absence of a direct measurement of MLVSS, the biological solids in municipal wastewater can be estimated as 60 to 80 percent of the total suspended solids.[16] Conventional plants, which use an activated sludge process that has long and narrow basins designed to approach plug flow, operate with an F/M ratio of 0.2 to 0.4, but values as low as 0.05 are not unusual. High F/M values indicate a high loading, as from a sudden influx of organics or the loss of biological solids, and will lead to a deterioration in effluent quality.[17]

Aeration tanks are usually constructed of reinforced concrete, are open to the atmosphere, and are usually rectangular in shape. Treatment plants may consist of several tanks, operated in series or parallel. Some of the largest treatment plants may contain 30 to 40 tanks arranged in several groups or batteries.[18]

Typical parameters associated with biologically active impoundments are given in Table 5-4. The loading parameter is expressed in terms of area or volume, and typical retention times in aerated impoundments range from 7 to 20 days. The level of suspended solids in these impoundments is over an order of magnitude less than the level in activated sludge processes. Although the parameters in Table 5-4 are listed as "typical," large variations exist among real facilities, and at a single

TABLE 5-4. IMPOUNDMENTS DESIGNED FOR BIODEGRADATION[19,20]

Type	Application	Typical daily loading, kg $BOD_5/m^3 \cdot day$	Retention time, day	Typical depth,m	Suspended solids, g/L
Facultative	Raw municipal wastewater Effluent from primary treatment, trickling filters, aerated ponds, or anaerobic ponds	0.0011 - 0.0034[a]	25-180	1.2-2.5	0.11-0.40
Aerated	Industrial wastes Overloaded facultative ponds Situations where limited land area is available	0.008 - 0.32	7-20	2-6	0.26-0.30
Aerobic	Generally used to treat effluent from other processes, produces effluent low in soluble BOD_5 and high in algae solids	0.021 - 0.043[b]	10-40	0.3-0.45	0.14-0.34
Anaerobic	Industrial wastes	0.16 - 0.80	20-50	2.5-5	0.08-0.16

[a] Based on a typical depth of 2 m.

[b] Based on a typical depth of 0.4 m.

facility the values may change with time. For example, a study conducted over 12 months at an aerobic impoundment used to treat municipal wastewater reported suspended solids levels of 0.02 to 0.1 g/L and volatile suspended solids of 0.01 to 0.06 g/L.[21]

Another study of eight quiescent impoundments at four different sites with confirmed biological activity estimated active biomass concentrations from the rate of oxygen consumption that ranged from 0.0014 to 0.22 g/L with an average of 0.057 g/L.[22]

The biomass concentration is an important parameter in estimating biodegradation rates. The best value to use for a specific site is a direct measurement such as volatile suspended solids for the system of interest. In the absence of site-specific data, a number may be chosen from the ranges for suspended solids given in Tables 5-3 and 5-4. Alternatively, typical or default values for biomass concentration given in Table 5-5 may be used.

TABLE 5-5. TYPICAL OR DEFAULT VALUES FOR BIOMASS CONCENTRATION[a]

Unit	Biomass concentration, g/L
Quiescent impoundments	0.05[b]
Aerated impoundments	0.25[c]
Activated sludge units	4.0[d]

[a] These values are recommended for use in the emission equations when site-specific data are not available.

[b] Based on the range (0.0014 to 0.22) and average (0.057) from actual impoundments as discussed in the text.

[c] From the data in Table 4-4 for aerated impoundments. Assumes biomass is approximated by the suspended solids level. Range is typically 0.05 to 0.30.

[d] Midrange value from Table 4-3 for CSTR based on mixed liquor suspended solids.

The major mechanisms of organic removal in biologically active systems include biodegradation, volatilization, removal with the effluent, and removal by adsorption on the waste sludge. A study by Petrasek et al. of purgeable volatile organics in a pilot-scale wastewater treatment system showed that less than 0.4 percent (generally less than 0.1 percent) of the volatiles were found in the waste-activated sludge.[23] Bishop, in a study of municipal wastewater treatment, concluded that only a modest amount of purgeable toxics were transferred to the sludge.[24] Hannah et al.[25] found that the concentrations of volatile organics in sludges from pilot-scale systems were generally comparable to or less than the corresponding concentrations in the process effluent. This indicated that volatile organics do not have a high affinity for wastewater solids and do not concentrate in the sludges. Kincannon and Stover found that 0 to 1 percent of three compounds (1,2-dichloroethane, phenol, and 1,2-dichlorobenzene) was adsorbed on the sludge.[26] Melcer, in a review of biological removal studies, concluded that polycyclic aromatic hydrocarbons, pyrene, anthracene, fluoranthene, and chrysene were the most commonly occurring priority pollutants found in sludges.[27] These studies suggest that the compounds most likely to be emitted to the air (volatiles) do not concentrate on sludges; however, some of the relatively nonvolatile organics may be adsorbed. Consequently, the modeling approach presented in this section assumes that the removal of volatile organics with the waste sludge is not significant. The major removal mechanisms that are considered include volatilization, biodegradation, and removal with the effluent.

5.3.2 Rate of Biodegradation

Numerous models have been proposed for the removal of organic compounds by biodegradation and include design equations for activated sludge systems and stabilization or oxidation impoundments.[28,29] There is general agreement in the literature that, for high organic loadings relative to biomass, the biodegradation rate is zero-order with respect to concentration (i.e., the rate is independent of organic concentration). For lower residual levels, the rate becomes first order with respect to concentration or follows Monod-type kinetics.[30,31,32] The Monod-type biodegradation rate equation can be written as follows:

$$r_B = V\ K_{max}\ b_i C/(K_s+C_L) \tag{5-13}$$

where,

r_B = biodegradation rate, g/s;

V = volume, m^3;
b_i = biomass concentration, g/m^3;
K_{max} = maximum rate constant, g/s-g biomass;
C_L = component concentration, g/m^3; and
K_s = half saturation constant, g/m^3.

The Monod model was originally developed to describe microbial growth rates for a single microbial population based upon a single, rate-limiting substrate. A yield coefficient was subsequently employed to determine the utilization rate of that substrate. For convenience of use, the biodegradation rate model given in Equation (5-13) has been written directly for component disappearance in terms of overall biomass concentration. It is assumed that Equation (5-13) applies to each organic constituent in the waste (although the rate constants will be different for each constituent), and that the biodegradation of any one constituent is independent of the concentrations of other constituents. Subsequent references to the Monod or the Monod-type model in this report refer specifically to Equation (5-13). The significant features of this model are:

1. At high concentrations (specifically, $C >> K_s$), C dominates the denominator and can, therefore, be eliminated from Equation (5-13). The biodegradation rate is then independent of (i.e., zero order with respect to) the component concentration.

2. At low concentrations ($C < K_s$, and the biodegradation rate becomes directly proportional (i.e., first order with respect) to the component concentration. The apparent first-order rate constant is: $K_1 = K_{max}/K_s$.

Theoretical Monod curves for several different compounds are presented in Figure 5-1 to illustrate these features.

A literature review was conducted to determine appropriate rate constants for the Monod model. References that served as primary sources of biodegradation rate data included: Pitter,[33] Kincannon et al.,[34] Petrasek et al.,[35] and Hannah et al.[36] Data obtained from each reference included rate constants as reported, influent concentrations, effluent concentrations, biomass concentration, retention time (RT), and fraction of the amount of component removed by biodegradation (F_B). Using this information and field data collected during specially designed biodegradation rate studies, Coburn et al. developed a base of component-specific biological removal rates that contains nearly 500 entries and removal data for 90 different organic constituents.[37]

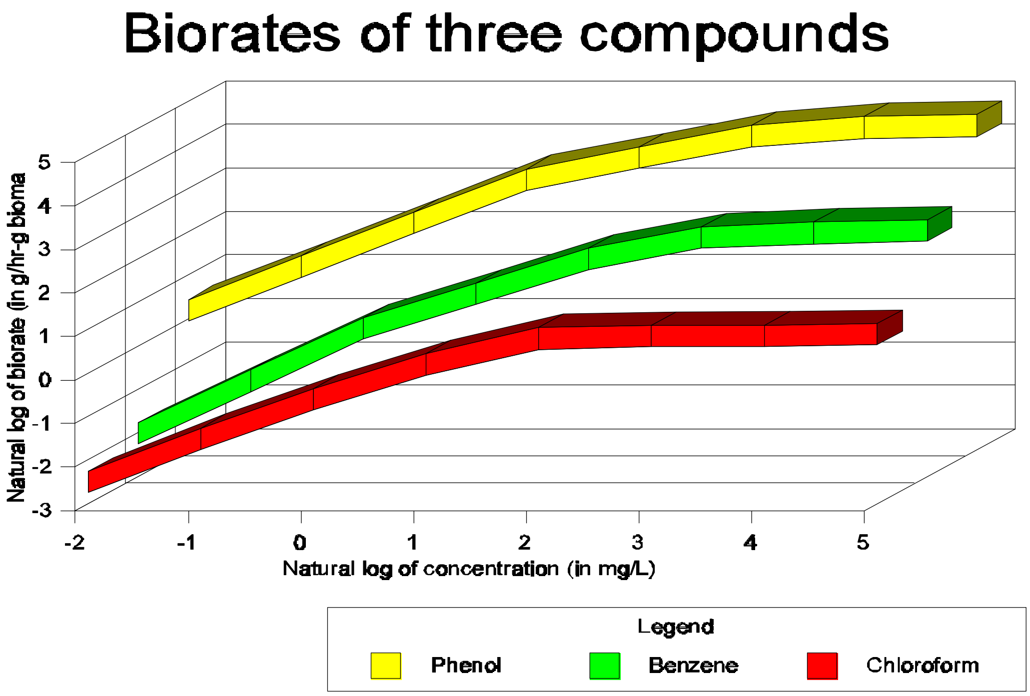

Figure 5-1. Theoretical relationship between concentration and biodegradation rates normalized by the amount of biomass as predicted using the Monod model for phenol, benzene, and chloroform.

Appendix C contains a listing of the Monod parameters for 88 compounds. Some of these 88 compounds do not have a listing for both Monod parameters. The values of the Monod parameters presented in Appendix C were selected primarily from the Coburn data base. The following paragraphs describe how these biorates were derived.

For most compounds, there were inadequate biodegradation rate data to determine the Monod rate constants using traditional methods (e.g., Lineweaver-Burke plot). However, when reported, values for K_s were generally between 1 and 10 mg/L for a variety of different compounds. Thus, the Monod constant, K_{max}, was calculated from organic removal data when high concentrations ($C_L > 10$ mg/L) were employed by assuming strict zero-order kinetics as follows:

$$K_{max} = F_B(C_i - C_L)/[(RT)\ b_i] \qquad (5\text{-}14)$$

where,

F_B = the fraction of component removal attributed to biodegradation;

C_o = inlet concentration, g/m^3;

C_L = bulk liquid and effluent concentration, g/m^3; and

(RT) = residence time, s.

Note that, with zero-order kinetics, Equation (5-14) applies to both continuous, well-mixed systems and to plug-flow and batch systems.

The half-saturation constant K_s was estimated (knowing K_{max}) from the apparent first-order rate constants when low concentrations were present (specifically, $K_s = K_{max}/K_1$). The equation used to calculate the apparent first-order rate, K_1, depends on the type of experimental system that was employed. For continuous, well-mixed systems, K_1 was calculated as follows:

$$K_1 = F_B(C_i - C_L)/[(RT)b_iC_L] \ . \tag{5-15}$$

For batch systems and for continuous, plug-flow systems, the equation used to calculate K_1 was:

$$K_1 = F_B \ln(C_o/C_L)/[(RT)b_i] \ . \tag{5-16}$$

Using this approach, rate constants for specific compounds in the biodegradation rate data base were determined. These rate constants are provided in Appendix C, Table C-2. Upon evaluating the biodegradation rate data from several different laboratory and field studies, it is recognized that biodegradation rates can vary widely from site to site. Therefore, the following priority schedule is provided as guidance in determining the appropriate biodegradation rate constants to be employed in the emission models:

- Use site-specific biodegradation rate data in experiments controlled for air emissions where available.
- Use the rate constants suggested in Appendix C, Table C-2, as available.
- Estimate the biodegradation rate constants using the following methodology:

-- Approximate K_{max} from available data for K_{max} for compounds of similar structure and/or functional groups; and

-- Approximate K_1 either by using the correlation:

$$K_1 = 3.75 \times 10^{-8} K_{ow}^{0.38} \qquad (5\text{-}17)$$

where

K_{ow} = octanol-water partitioning coefficient,or by using the default (average) value for K_1, which is: K_1 = 1 L/h/g (2.78 x 10^{-7} $m^3/s/g$), and then calculate K_s as: $K_s = K_{max}/K_1$.

The correlation provided in Equation (5-17) was developed based upon the assumption that biodegradation was primarily an intracellular phenomenon. As such, the first-order biodegradation rate can be limited either by the rate of the internal reaction or by the rate of diffusion of the chemical through the cell membrane and into the cell. If the internal component concentrations are assumed to be proportional to the concentration of components absorbed onto the cell membranes, then, regardless of what limits the first-order biodegradation rate, the limiting first-order biodegradation rate will be directly proportional to the concentration of constituent absorbed onto the membrane. Because the octanol-water partitioning coefficient has been used to correlate the absorption partitioning of organic chemicals onto biomass,[38,39] it follows that the octanol-water partitioning coefficient may also be used to correlate the limiting first-order biorate constant since the observed biorate is based on bulk liquid concentrations. To that end, the limiting first-order rate constants for a variety of compounds were plotted versus their corresponding octanol-water partitioning coefficient. The results, presented in Figure 5.2, indicate a fair correlation between the octanol-water partitioning coefficients and the limiting first-order rate constants for most compounds. The primary discrepancies are for ionizable or polar compounds.

The simple correlation with K_{ow} should be used with caution. Figure 5-2 indicates a range of 25, with most of the data scattered between a line five times the correlation and another line one-fifth of the correlation. Some compounds may biologically react slowly. For those compounds, the K_{ow} correlation would significantly overpredict the biorate.

Activated sludge biorates are published in the literature and can be a useful data source. Published biorates can be useful if the biorate accounts for volatilization, if the waste treatment system is the same as the system used for the published biorates, and if the waste and operational parameters are similar to the system as used for the published biorates. The biorate is expected to be a strong function of several system variables. The recommended priority schedule for the selection of biorates reflects procedures that are based on an average biorate for many different systems. It is possible that the literature biorate may not accurately reflect the performance of specific systems, and the error could possibly be greater than some of the simple correlations presented in the priority schedule.

Assuming continuous, steady-state operation for a system that is well-mixed, a mass balance on the system can be written as follows:

$$QC_i = QC_L + VK_{max}b_iC_L/(K_s+C_L) + K_{other}\ V\ C_L \qquad (5\text{-}18)$$

where,

Q = flow rate, m^3/s;

K_{other} = sum of apparent first-order rate constants for competing mechanisms, 1/s;

and the other symbols are as previously defined.

Note that Equation (5-18) was written in a general fashion so that, if desired, the rate of removal via adsorption onto

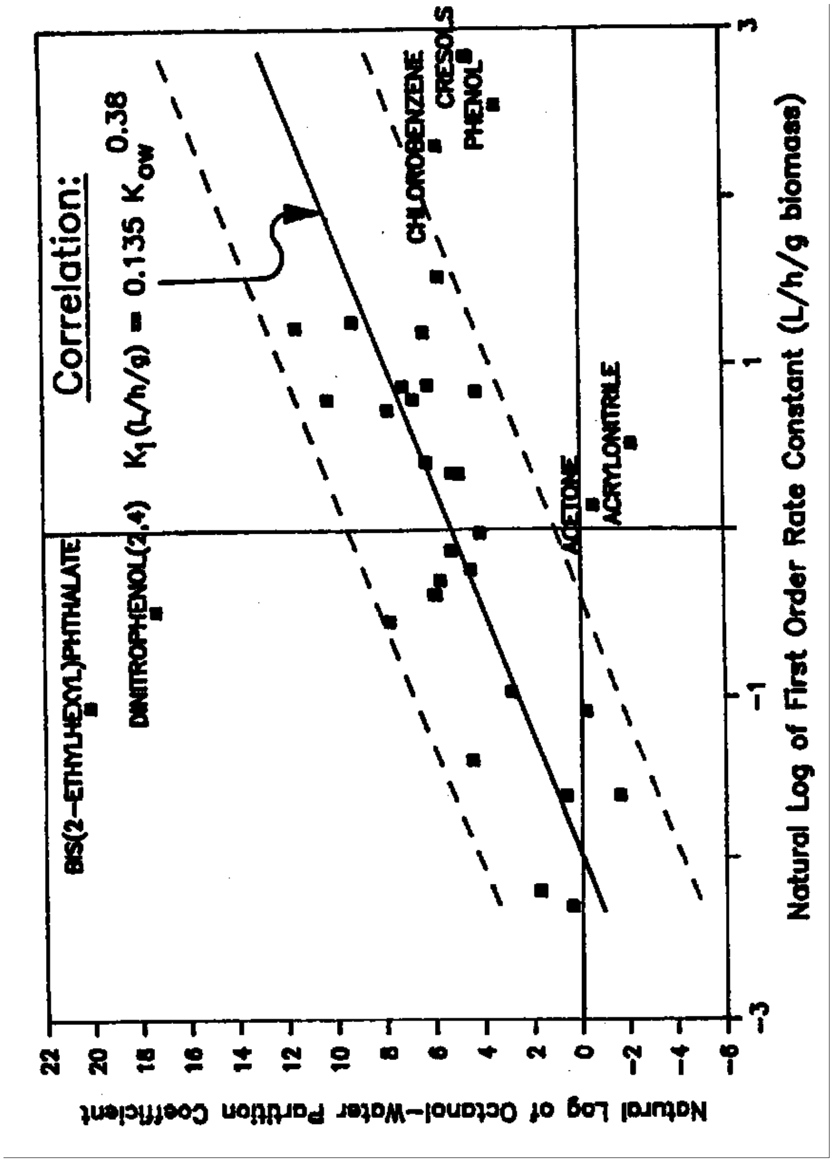

Figure 5.2. Correlation of Octanol-water Partition Coefficient and the first order biorate constant.

biomass solids can be included. For most volatile organics, however, the adsorption pathway is negligible so that K_{other} is dominated by the volatilization rate. Consequently,

$$K_{other} = KA/V \tag{5-19}$$

where,

K = overall mass transfer coefficient, m/s; and

A = area, m^2.

To determine the fraction of the organic compound emitted or biodegraded using the Monod model, one first has to solve for the effluent concentration. The effluent concentration can be determined by rearranging Equation (5-18) as follows:

$$K'C_L^2 + [K_sK' + (V/Q)K_{max}b_i - C_i]C_L - K_sC_i = 0 \tag{5-20}$$

where

$K' = (K_{other})(V/Q) + 1$, dimensionless.

Equation (5-20) is easily solved using the quadratic formula as follows:

$$C_L = [-b + (b^2 - 4ac)^{0.5}]/2a \tag{5-21}$$

where,

$a = K' = (K_{other})(V/Q) + 1$;

$b = K_sK' + (V/Q)K_{max}b_i - C_i$; and

$c = -K_sC_i$.

The plus sign is selected in Equation (5-21) to ensure positive effluent concentrations. Note that, because all of the rate constants and concentrations must have positive values, the constant, c, must be negative so that the quadratic equation always has real, positive roots.

Once the effluent concentration is calculated, the fraction of the component feed emitted to the air (f_{air}) is:

$$f_{air} = K\ A\ C_L/Q\ C_i\ . \tag{5-22}$$

Emissions (E, g/s) are calculated from:

$$E = f_{air}QC_i\ . \tag{5-23}$$

Similarly, the fraction of the component feed biodegraded (f_{bio}) is:

$$f_{bio} = VK_{max}b_i\ C_L/[(K_s+C_L)QC_i]\ . \tag{5-24}$$

If the biological system is operated with plug flow, the treated wastewater does not mix with the influent. The biodegradation rate and air emission rate change as the treatment progresses toward completion. For plug flow, the rate of disappearance of a compound by biodegradation and air emissions is given by:

$$\frac{-d\ C_t\ (V)}{dt} = \frac{VK_{max}b_iC_t}{(K_s + C_t)} + KA\ C \tag{5-25}$$

where,

C_t = concentration at time = t; and
t = time, s.

and with the other symbols as previously defined. Due to the nonlinear nature of the biodegradation rate term, Equation (5-25) cannot be directly integrated. Therefore, it is further assumed that first-order kinetics dominates the system's biodegradation. Equation (5-25) can then be rearranged as follows:

$$\frac{d\ C_t}{C_t} = (-K_1b_i - KA/V)\ dt \tag{5-26}$$

where $K_1 = K_{max}/K_s$, m^3/g biomass.

Integrating Equation (5-26) from $C_t = C_i$ at $t = 0$ to $C_t = C_L$ (effluent concentration) at $t = V/Q$ (one residence time) gives:

$$C_e/C_o = \exp\ (-K_1 b_i V/Q - KA/Q)\quad . \tag{5-27}$$

The ratio C_L/C_i represents the fraction leaving with the effluent; consequently, $1 -{\sim}C_L/C_i$ represents the sum of the fractions that are biodegraded and emitted to the air. The fractions of component feed emitted to the air and biodegraded are calculated from their relative rates:

$$f_{air} = (1 - C_L/C_i)(KA)/(KA + K_1 b_i V) \tag{5-28}$$

$$f_{bio} = (1 - C_L/C_i)(K_1 b_i V)/(KA + K_1 b_i V)\quad . \tag{5-29}$$

The average emissions rate (E, g/s) is:

$$E = f_{air}\ QC_i\quad . \tag{5-30}$$

5.3.3 Example Calculation for Quiescent Impoundments

The application of the biodegradation model to quiescent impoundments is presented in the form of an example calculation. The calculation is based on the quiescent impoundment's operating parameters from Table 5-2. For other types of impoundments, the application of the biodegradation model is illustrated in subsequent sections.

The waste stream for the example calculation is defined as containing benzene at 10 ppm with a total organic content of 250 ppm (0.25 g/L). The resultant organic loading on the impoundment on a daily basis is 12.8 kg/1,000 m^3. The active biomass is assumed to be 0.05 g/L from a reported range from eight quiescent impoundments of 0.0014 to 0.22 g/L.

a. Calculate the effluent concentration of benzene for a well-mixed system from Equation (5-21):

$$C_L = [-b + (b^2 - 4ac)^{0.5}]\ /2a$$

where

$a = K' = (KA/V)\ (V/Q) + 1 = KA/Q + 1$

$b = K_sK' + (V/Q)\ K_{max}\ b_i - C_i$

$c = -K_sC_i$

$K = 4.2 \times 10^{-6}$ m/s (Section 5.2.3, Step c)

$A = 1{,}500\ m^2$

$Q = 0.00156\ m^3/s$

$K_{max} = 19\ mg/g/L = 5.28 \times 10^{-6}\ g/g/s$ (from Appendix C, Table C-2)

$K_s = 13.6\ mg/L = 13.6\ g/m^3$ (from Appendix C, Table C-2), $k_S = k_{MAX}/k_1$

$b_i = 0.05\ g/L = 50\ g/m^3$

$V = 2{,}700\ m^3$

$C_o = 100\ ppm = 100\ g/m^3$

$KA = (4.2 \times 10^{-6}\ m/s)(1{,}500\ m^2) = 6.3 \times 10^{-3}\ m^3/s$

$a = K' = (6.3 \times 10^{-3}\ m^3/s)/(0.00156\ m^3/s) + 1 = 5.0$

$b = (13.6\ g/m^3)(5.0) + (2{,}700\ m^3/0.00156\ m^3/s)$
$(5.28 \times 10^{-6}\ g/g/s)\ (50\ g/m^3) - (100\ g/m^3)$

$b = 425\ g/m^3$

$c = -(13.6\ g/m^3)(100\ g/m^3) = -1{,}360\ g^2/m^6$

$C_L = \{-[425\ g/m^3] + [(425\ g/m^3)^2 - 4(5.0)(-1{,}360\ g^2/m^6)]^{0.5}\}/\ [2(5.0)]$

$C_L = (-425\ g/m^3 + 455.9\ g/m^3)/10$

$C_L = 3.09\ g/m^3$.

b. Calculate the fraction emitted for a well-mixed system from Equation (5-22):

$$f_{air} = KAC_L/(QC_o)$$

where,

$f_{air} = (6.3 \times 10^{-3}\ m^3/s)(3.08\ g/m^3)/$
$[(0.00156\ m^3/s)\ (100\ g/m^3)]$

$f_{air} = 0.124$.

c. Calculate benzene emissions for well-mixed system:

$$
\begin{aligned}
E(g/s) &= f_{air}\ Q\ C_o \\
&= (0.124)(0.00156\ m^3/s)(100\ g/m^3) \\
&= 1.93 \times 10^{-2}\ g/s = 0.61\ Mg/yr.
\end{aligned}
$$

d. For a plug-flow system, calculate fraction removed with the effluent from Equation (5-27):

$$C_L/C_i = \exp\ (-\ K_1\ b_i\ V/Q - KA/Q)$$

where,

K_1 = 1.4 L/g-h = $3.89 \times 10^{-7}\ m^3/g\text{-}s$ (from Appendix C, Table C-1);

b_i = 0.05 g/L = 50 g/m^3;

V = 2,700 m^3;

Q = 0.00156 m^3/s

C_i = 10 ppm = 10 g/m^3;

K = 4.2×10^{-6} m/s; and

A = 1,500 m^2.

$$
\begin{aligned}
K_1 b_i V &= (3.89 \times 10^{-7}\ m^3/s/g\ \text{biomass})(50\ g/m^3)(2,700\ m^3) \\
&= 5.25 \times 10^{-2}\ m^3/s \\
KA &= (4.2 \times 10^{-6}\ m/s)(1,500\ m^2) = 6.3 \times 10^{-3}\ m^3/s
\end{aligned}
$$

$$C_L/C_i = \exp \begin{matrix}*\\*\end{matrix} \frac{-5.25 \times 10^{-2}\ m^3/s}{1.56 \times 10^{-3}\ m^3/s} - \frac{6.3 \times 10^{-3}\ m^3/s}{1.56 \times 10^{-3}\ m^3/s} \begin{matrix}*\\*\end{matrix}$$

$$C_L/C_i = \exp\ (-37.7) = 0.00\ .$$

e. Calculate fraction emitted from Equation (5-28):

$$f_{air} = (1 - C_L/C_i)(KA)/(KA + K_1\ b_i\ V)$$

$$f_{air} = (1 - 0)(6.3 \times 10^{-3}\ m^3/s) / (6.3 \times 10^{-3}\ m^3/s + 5.25 \times 10^{-2}\ m^3/s)$$

$$f_{air} = 0.107\ .$$

f. Calculate benzene emissions for plug flow:

$$
\begin{aligned}
E(g/s) &= f_{air}\ Q\ C_i \\
&= (0.107)(0.00156\ m^3/s)(10\ g/m^3) \\
&= 1.67 \times 10^{-3}\ g/s = 0.053\ Mg/yr.
\end{aligned}
$$

5.4 MECHANICALLY AERATED IMPOUNDMENTS AND ACTIVATED SLUDGE UNITS

Some impoundments and tanks are mechanically agitated to improve mixing or to transfer air to the liquid (e.g., treatment tanks designed for biodegradation). The agitation creates a turbulent liquid surface that enhances mass transfer to the air. A significant difference from the approach for quiescent surfaces discussed in Section 5.2 is the appropriate correlations for the individual mass transfer coefficients.

5.4.1 Emission Model Equations

The calculation of the overall mass transfer coefficient for mechanically aerated systems considers that the liquid surface is composed of two zones, quiescent and turbulent. The individual mass transfer coefficients for the turbulent zone are based on the correlations of Thibodeaux[40] and Reinhardt.[41] Thibodeaux's model was developed from accepted interphase mass transfer concepts, published rate coefficient correlations, and existing operating data on 13 aerated basins at 11 pulp and paper mills. The basins represented a wide range of design and operating parameters, in spite of being from only one industry type. The simulation employed 11 organic chemical species common to industrial wastewater.

Reinhardt absorbed ammonia in aqueous sulfuric acid to measure the gas-phase mass transfer coefficient associated with flat-blade surface agitators in developing his correlation to calculate the gas-phase mass transfer coefficient.[42]

Table 5-6 summarizes the correlations developed by Thibodeaux and Reinhardt. These correlations are used to estimate the individual mass transfer coefficients for the turbulent portion of the liquid surface. The individual coefficients are then used in Equation (5-2) to calculate an overall mass transfer coefficient for the turbulent zone. An overall mass transfer coefficient for the quiescent zone is

TABLE 5-6. EQUATIONS FOR CALCULATING INDIVIDUAL MASS TRANSFER
COEFFICIENTS FOR VOLATILIZATION OF ORGANIC SOLUTES FROM
TURBULENT SURFACE IMPOUNDMENTS

Liquid phase

Thibodeaux:[43,44]

$$k_L=[8.22\ 10^{-9} J(POWR)(1.024)^{t-20}\ O_t\ 10^6\ MW_L\ /(Va_V D_L)]\ (D_w/D_{O_2,w})$$

where,

k_L = mass transfer coefficient based on liquid, (m/s);

J = oxygen transfer rating of surface aerator, lb O_2/h•hp;

POWR = total power to aerators, hp;

T = water temperature, °C;

Ot = oxygen transfer correction factor;

MW_L = molecular weight of liquid;

V = volume affected by aeration, ft^3;

a_V = surface-to-volume ratio of surface impoundment, ft^{-1}

D_L = density of liquid, g/cm^3;

D_w = diffusivity of constituent in water, cm^2/s; and

$D_{O_2,w}$ = diffusivity of oxygen in water = 2.4×10^{-5}, cm^2/s.

Gas phase

Reinhardt:[45,46]

$$k_G = 1.35 \times 10^{-7}\ R_e^{1.42}\ p^{0.4}\ Sc_G^{0.5}\ F_r^{-0.21}\ D_a MW_a/d\ (m/s)$$

where,

$R_e = d^2 w D_a/\mu_a$ = Reynold's number;

d = impeller diameter, cm;

w = rotational speed of impeller, rad/s;

(continued)

TABLE 5-6 (continued)

D_a = density of air, g/cm^3;

μ_a = viscosity of air, g/cm•s;

= 4.568×10^{-7} T(°C) + 1.7209×10^{-4};

p = $P_I\ g_c/(D_L d^{*5} w^3)$ = power number;

P_I = power to impeller, ft•lb$_f$/s

= 0.85 (POWR) (550 ft•lb$_f$/s•hp)/number of aerators, where 0.85 = efficiency of aerator motor;

g_c = gravitation constant, 32.17 lb$_m$•ft/s^2/lb$_f$;

D_L = density of liquid, lb/ft^3;

d* = impeller diameter, ft;

Sc_G = Schmidt number on gas side = $\mu_a/D_a\ D_a$;

F_r = d^*w^2/g_c = Froude number ;

D_a = diffusivity of constituent in air, cm^2/s; and

MW_a = molecular weight of air.

calculated as described in Section 5.2. The two overall coefficients are combined to obtain a single coefficient for the system based on the relative areas of the turbulent and quiescent zones. For example, if 25 percent of the surface of the impoundment is turbulent, the overall coefficient would be the sum of 25 percent of the value for the turbulent area coefficient plus 75 percent of the value for the quiescent zone.

The model for mechanically aerated systems also incorporates biodegradation as a competing mechanism. The extent of biodegradation is difficult to predict in a generally applicable form because it is very dependent upon the constituent of interest, the waste matrix, the design and operation of the biodegradation unit, and the concentrations and properties of the microorganisms.

5.4.2 Model Plant Parameters for Mechanically Aerated Impoundments

The dimensions of the treatment impoundment used as an example to estimate emissions were derived from the Westat data as described in Section 5.2.2 for storage impoundment. A median area of 1,500 m^2 and a depth of 1.8 m were chosen, which yields a total volume of 2,700 m^3. The retention time in treatment impoundments is expected to be less than the retention time in storage impoundments. Two design manuals listed typical retention times for aerated (biologically active) ponds as 7 to 20 days[47] and 3 to 10 days.[48] For the example case, a retention time of 10 days was chosen from the design range of 3 to 20 days. The resulting flow rate is 3.1 L/s (0.0031 m^3/s).

The correlations of Thibodeaux and Reinhardt given in Table 5-6 require values for the parameters that describe the mechanical aeration system. Metcalf and Eddy, Inc.,[49] suggest a range of 0.5 to 1.0 hp/1,000 ft^3 for mixing in an impoundment. However, more power may be needed to supply additional oxygen or to mix certain treatment solutions. A review of trip reports showed power usage as high as 3.5 hp/1,000 ft^3 at a specific TSDF impoundment.[50] For this analysis, a midrange value of 0.75 hp/1,000 ft^3 from Metcalf and Eddy was used to generate an estimate of 75 hp required for mixing in the model unit.

Data from Reference 51 indicated that five aerators with 15-hp motors and 61-cm diameter propellers turning at 126 rad/s would agitate a volume of 441 m^3 (15,590 ft^3). Assuming a uniform depth in the impoundment of 1.8 m, the agitated surface area was estimated as 245 m^2 (441/1.8). The agitated surface is assumed to be turbulent and comprises 16 percent (245/1,500)(100) of the total area. The balance of the surface area of the impoundment (84 percent) is assumed to be quiescent. As a comparison, Thibodeaux reported a turbulent area of 5.22 m^2/hp and investigated a range of 0.11 to 20.2 m^2/hp. The value of 5.22 m^2/hp and a total of 75 hp yields an estimated turbulent area of 392 m^2 (26 percent), which is greater than the 16-percent turbulent area calculated by the above procedure.[52] (Very few data are available on the distribution of turbulent areas for aerated impoundments. The extent of turbulence depends in part on the number, size, and placement of aerators. The example is based on typical aerator requirements to mix the contents of the impoundment.)

Typical values were chosen for the oxygen transfer rating of the aerator and the oxygen transfer correction factor. A value of 3.0 lb O_2/hp/h was chosen for oxygen transfer rating from a range of 2.9 to 3.0.[53] A value of 0.83 was used for the correction factor from a typical range of 0.80 to 0.85.[54] The transfer of power to the impeller was assumed to be 85 percent efficient, yielding an estimate of 64 hp for the impeller power.

The model for biodegradation requires the system's biomass concentration as an input parameter. The concentration of biomass in real systems can be highly variable depending upon the system's design and method of operation. For this analysis, the specified biomass is assumed to be actively degrading the constituent of interest. A value of 250 g/m^3 (0.25 g/L) of biomass was chosen from the values presented in Table 5-5.

The example constituent (benzene) and the meteorological conditions chosen for the example calculation are the same as those chosen for storage impoundments. Input parameters for the mechanically aerated model unit are summarized in Table 5-7.

5.4.3 Example Calculation for Mechanically Aerated Treatment Impoundments

The example calculation for emissions from a mechanically aerated impoundment includes an estimate of the overall mass transfer coefficient for the turbulent zone. The overall mass transfer coefficient for the quiescent zone for storage impoundments is calculated as illustrated in Section 5.2.3 and will not be repeated here. Biodegradation is included as a competing removal mechanism.

a. Calculate turbulent liquid-phase mass transfer coefficient, k_L. Use Thibodeaux (Table 5-6):

$$k_L(m/s)=[8.22\ 10^{-9}\ J(POWR)(1.024)^{T-20}\ O_t 10^{6}\ MW_L/(Va_V D_L)]\left(\frac{D_w}{D_{O_2,w}}\right)^{0.5}$$

where,

J = O_2 transfer rating, use 3.0 lb O_2/h•hp

POWR = 75 hp

T = water temperature = 25 °C

O_t = O_2 transfer correction factor, use 0.83

MW_L = molecular wt of liquid (water) = 18 g/g mol

(Va_V) = agitated area in ft^2 = $240.0\ m^2 \left(\frac{ft^2}{0.0929\ m^2}\right)$

= 2,583 ft^2

D_L = water density = 1 g/cm^3

D_w = 9.8×10^{-6} cm^2/s

$D_{O_2,w}$ = 2.4×10^{-5} cm^2/s

TABLE 5-7. INPUT PARAMETERS--TREATMENT IMPOUNDMENTS (MECHANICALLY AERATED)

Area: 1,500 m^2

Depth: 1.8 m

Volume: 2,700 m^3

Retention time: 10 days

Flow: 0.0031 m^3/s

Turbulent area: 240 m^2 (16%)

Quiescent area: 1,260 m^2

Number of impellers: 5

Total power: 75 hp

Power to impeller: 13 hp

Impeller speed: 126 rad/s

Impeller diameter: 61 cm

O_2 transfer: 3 lb/h/hp

O_2 correction factor: 0.83

Temperature: 25 °C

Windspeed: 4.47 m/s

Viscosity of air: 1.8×10^{-4} g/cm•s

Density of air: 1.2×10^{-3} g/cm^3

Diffusivity of O_2 in water: 2.4×10^{-5} cm^2/s

Density of liquid: 1 g/cm^3

Molecular weight of liquid: 18 g/g•mol

Molecular weight of air: 29 g/g•mol

Constituent: benzene with other biodegradable organics in water

Concentration (benzene): 100 g/m^3 (100 ppm)

Concentration (total organics): 250 g/m^3 (250 ppm)

Henry's law constant (benzene): 5.5×10^{-3} atm•m^3/g mol

(continued)

TABLE 5-7 (continued)

Diffusivity in air (benzene): 0.088 cm^2/s

Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s

Maximum biorate (benzene and other organics):

19 mg/h/g of biomass = 5.28×10^{-6} g/g biomass•s

Limiting first-order biorate constant:

1.4 L/h/g = 3.89×10^{-7} m^3/s/g biomass

Biomass concentration: 0.3 g/L = 300 g/m^3

$$k_L = (8.22 \times 10^{-9})(3)(75)(1.024)^{5}\left[\frac{(0.83)(10^6)(18)}{(2,583)\ (1)}\right]\left[\frac{9.8 \times 10^6}{2.4 \times 10^{-5}}\right]^{0.5}$$

$= 7.7 \times 10^{-3}$ m/s .

b. Calculate turbulent gas-phase mass transfer coefficient, k_G. Use Reinhardt (see Table 5-6):

$$k_G(\text{m/s}) = 1.35 \times 10^{-7}\ Re^{1.42}\ p^{0.4}\ Sc_G^{0.5}\ Fr^{-0.21}\ D_a\ MW_a/d$$

where

Re = Reynold's number = $\dfrac{d^2 w\ D_a}{\mu_a}$

d = impeller diameter = 61 cm

w = impeller speed = 126 rad/s

$D_a = 1.2 \times 10^{-3}$ g/cm^3

$\mu_a = 1.81 \times 10^{-4}$ g/cm•s

$$Re = \frac{(61^2)\ (126)\ (1.2 \times 10^{-3})}{1.81 \times 10^{-4}} = 3.1 \times 10^6$$

p = power number = $\dfrac{P_I\ g_c}{D_L d^{*5} w^3}$

$P_I = 12.8\ \text{hp}\ \dfrac{550\ \text{ft lb}_f}{\text{s•hp}} = 7,040$

$g_c = 32.17\ \dfrac{\text{lb•ft}}{\text{s}^2\ \text{lb}_f}$

$D_L = 62.37$ lb/ft^3

d^* = impeller diameter in feet = 2.0

w = 126 rad/s

$$p = \frac{(7,040)\ \ (32.17)}{(62.37)(2^5)\ (126^3)} = 5.6 \times 10^{-5}$$

Sc_G = 1.71 (from Section 5.2.3, part b)

$$Fr = \text{Froude number} = \frac{d^{*}w^2}{g_c} = \frac{(2)(126)^2}{32.17} = 9.9 \times 10^2$$

D_a = 0.088 cm^2/s (benzene)

MW_a = 29 g/g mol

d = impeller diameter in cm = 61 cm

$$k_G = \frac{(1.35 \times 10^{-7})(3.1 \times 10^6)^{1.42}(5.6 \times 10^{-5})^{0.4}(1.71)^{0.5}(9.9 \times 10^2)^{-0.21}}{(0.088)(29)/61}$$

$k_G = 5.7 \times 10^{-2}$ m/s .

c. Calculate overall mass transfer coefficient for turbulent area, K:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keq\ k_G} = \frac{1}{7.7 \times 10^{-3}} + \frac{1}{(0.225)(5.7 \times 10^{-2})} = 208$$

K = 0.0048 m/s .

d. Calculate overall mass transfer coefficient for combined quiescent and turbulent areas, K:

From Section 5.2.3, K for quiescent area = 4.2×10^{-6} m/s;

From Part C, K for turbulent area = 4.8×10^{-3} m/s;

Turbulent area = 240 m^2; and

Quiescent area = 1,260 m^2.

$$K\ (m/s) = \frac{(4.2 \times 10^{-6})(1{,}260)+(0.0048)\ (240)}{(1{,}260 + 240)} = 7.7 \times 10^{-4}\ m/s.$$

(weighted by area)

e. Calculate the effluent concentration for benzene for a well-mixed system from Equation (5-21):

$$C_L = [-b + (b^2 - 4ac)^{0.5}]\ /2a$$

where

$a = K' = \quad (KA/V)\ (V/Q) + 1 = KA/Q + 1$

$b \quad = \quad K_sK' + (V/Q)\ K_{max}\ b_i - C_o$

$c \quad = \quad -K_sC_o$

$K \quad = \quad 7.7 \times 10^{-4}$ m/s

$A \quad = \quad 1{,}500$ m^2

$Q \quad = \quad 0.0031$ m^3/s

$K_{max} \quad = \quad 5.28 \times 10^{-6}$ g/s/g biomass

$b_i \quad = \quad 0.3$ g/L = 300 g/m^3

$V \quad = \quad 2{,}700$ m^3

$C_o \quad = \quad 100$ ppm = 100 g/m^3

$K_s \quad = \quad K_{max}/K_1$

$K_s \quad = (5.28 \times 10^{-6}$ g/s/g)/(3.89 $\times 10^{-7}$ m^3/s/g)

$K_s \quad = \quad 13.6$ g/m^3

$KA \quad = (7.74 \times 10^{-4}$ m/s)(1,500 m^2) = 1.16 m^3/s

$a = K' =$(1.16 m^3/s)/(0.0031 m^3/s) + 1 = 375

$b =$ (13.6 g/m^3)(373) + (2,700 m^3/0.0031 m^3/s)

(5.28 x 10^{-6} g/s/g) (300 g/m^3) - (100 g/m^3)

$b =$ 6,352 g/m^3

$c =$ -(13.6 g/m^3)(100 g/m^3) = -1,360 g^2/m^6

$C_L \quad = \quad$ {-[6,352 g/m^3] + [(6,352 g/m^3)^2

- 4(373) (-136 g^2/m^6)]$^{0.5}$}/ [2(373)]

$C_L \quad = \quad$ (-6,352 g/m^3 + 6,509 g/m^3)/746

$C_L \quad = \quad$ 0.021 g/m^3 .

f. Calculate the fraction emitted for a well-mixed system from Equation (5-22):

$$f_{air} = KAC_L/(QC_o)$$

where

f_{air} = (1.15 m^3/s)(0.21 g/m^3)/[(0.0031 m^3/s)(100 g/m^3)]

f_{air} = 0.78 .

g. Calculate benzene emissions for well-mixed system:

$E(g/s) \quad = f_{air}\ Q\ C_o$

$$= (0.79)(0.0031\ \text{m}^3/\text{s})(100\ \text{g/m}^3)$$

$$= 0.24\ \text{g/s} = 7.7\ \text{Mg/yr} \quad .$$

h. For a plug-flow system, calculate the fraction removed with the effluent from Equation (5-27):

$$C_L/C_i = \exp\ (-K_1\ b_i\ V/Q - KA/Q)$$

$K_1 = 3.89 \times 10^{-7}\ \text{m}^3/\text{s/g biomass}$

$b_i = 0.3\ \text{g/L} = 300\ \text{g/m}^3$

$V = 2{,}700\ \text{m}^3$

$Q = 0.0031\ \text{m}^3/\text{s}$

$C_i = 10\ \text{ppm} = 10\ \text{g/m}^3$

$K = 1.0 \times 10^{-3}\ \text{m/s}$

$A = 1{,}500\ \text{m}^2$

$$K_1b_iV = (3.89 \times 10^{-7}\ \text{m}^3/\text{s/g biomass})(300\ \text{g/m}^3)(2{,}700\ \text{m}^3)$$

$$= 0.315\ \text{m}^3/\text{s}$$

$$KA = (7.7 \times 10^{-4}\ \text{m/s})(1{,}500\ \text{m}^2) = 1.15\ \text{m}^3/\text{s}$$

$$C_L/C_i = \exp\ \frac{-0.315\ \text{g/s}}{0.0031\ \text{m}^3/\text{s}} - \frac{1.15\ \text{m}^3/\text{s}}{0.0031\ \text{m}^3/\text{s}} = 0\ .$$

i. Calculate fraction emitted from Equation (5-28):

$$f_{air} = (1 - C_L/C_i)(KA)/(KA + K_1b_iV)$$

$$f_{air} = (1 - 0)(1.15\ \text{m}^3/\text{s})/(1.15\ \text{m}^3/\text{s} + 0.315\ \text{m}^3/\text{s})$$

$$f_{air} = 0.78 \quad .$$

j. Calculate benzene emissions for plug flow:

$$E(\text{g/s}) = f_{air}\ Q\ C_i$$

$$= (0.78)(0.0031\ \text{m}^3/\text{s})(100\ \text{g/m}^3)$$

$$= 0.24\ \text{g/s} = 7.7\ \text{Mg/yr} \quad .$$

5.4.4 Example Calculation for Activated Sludge Unit

As discussed in Section 5.2, an activated sludge unit usually consists of a concrete tank that is aerated and contains a relatively high concentration of active biomass. A model unit is defined in this section for this process, and the results of intermediate and final calculations are given. Detailed example calculations are not presented because the approach is exactly the same as that used for the mechanically aerated impoundment. The only significant difference in the method of operation is the recycle of solids back to the activated sludge unit, which results in a higher biomass concentration. For this model unit, a biomass concentration of 4 g/L (4,000 g/m^3) was chosen from the range of 1.5 to 6 g/L in Table 5-3 and the recommended values in Table 5-5. Other differences between the aerated impoundment and activated sludge tank include, for the tank, a smaller surface area, a shorter retention time, a greater turbulent area, and a smaller F/D ratio. 70 percent of the unit surface is assumed to be turbulent. The aerated surface area was estimated as described in Section 5.4.2. An aerator with a 7.5-hp motor will agitate a volume of 56.9 m^3 (2,010 ft^3). For a uniform depth of 4 m, the agitated volume yields an agitated surface area of 14.2 m^2 (56.9 m^3/4 m). The input parameters are defined for this model unit in Table 5-8, and the results of the calculations are presented in Table 5-9.

5.5 DISPOSAL IMPOUNDMENTS WITH QUIESCENT SURFACES

5.5.1 Emission Model Equations

A disposal impoundment is defined as a unit that receives a waste for ultimate disposal rather than for storage or treatment. This type of impoundment differs from the storage and treatment impoundments in that there is no liquid flow out of the impoundment (seepage into the ground is neglected). For this case, the well-mixed system with a bulk concentration that is at equilibrium (i.e., the bulk concentration does not change

TABLE 5-8. INPUT PARAMETERS--MECHANICALLY AERATED ACTIVATED SLUDGE UNIT

Area: 27 m^2
Depth: 4 m
Volume: 108 m^3
Retention time: 4 h
Flow: 0.0075 m^3/s
Turbulent area: 19 m^2 (70%)
Quiescent area: 8.0 m^2

Total power: 7.5 hp
Power to impeller: 6.4 hp
Impeller speed: 126 rad/s
Impeller diameter: 61 cm
O_2 transfer: 3 lb/h/hp
O_2 correction factor: 0.83

Temperature: 25 °C
Windspeed: 4.47 m/s

Viscosity of air: 1.8×10^{-4} g/cm•s
Viscosity of water: 9×10^{-3} g/cm•s
Density of air: 1.2×10^{-3} g/cm^3
Diffusivity of O_2 in water: 2.4×10^{-5} cm^2/s
Density of liquid: 1 g/cm^3
Molecular weight of liquid: 18 g/g•mol
Molecular weight of air: 29 g/g•mol

Constituent: benzene with other biodegradable organics in water
Concentration (benzene): 10 g/m^3 (10 ppm)
Concentration (total organics): 250 g/m^3 (250 ppm)

Henry's law constant (benzene): 5.5×10^{-3} atm•m^3/g•mol
Diffusivity in air (benzene): 0.088 cm^2/s
Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s
Maximum biorate (benzene and other organics): 5.28×10^{-6} g/s/g biomass
Limiting first-order biorate constant = 3.89×10^{-7} m^3/s/g biomass
Biomass concentration: 4.0 g/L = 4,000 g/m^3

TABLE 5-9. INTERMEDIATE AND FINAL CALCULATION RESULTS FOR ACTIVATED SLUDGE MODEL UNIT

Quiescent zone:

$k_L = 6.5 \times 10^{-6}$ m/s
$k_g = 8.9 \times 10^{-3}$ m/s
$K = 6.5 \times 10^{-6}$ m/s

Turbulent zone:

$k_L = 9.7 \times 10^{-2}$ m/s
$k_g = 4.3 \times 10^{-2}$ m/s
$K = 4.88 \times 10^{-3}$ m/s

Overall mass transfer coefficient = 3.4×10^{-3} m/s

For well-mixed system:

$C_L = 3.17$
$f_{air} = 0.391$
Emissions = 0.30 g/s = 9.3 Mg/yr

For plug-flow system:

$f_{air} = 0.391$

Emissions = 0.30 g/s = 9.3 Mg/yr

with time) is not applicable. The quantity of a constituent in a disposal impoundment will decrease with time after the waste is placed in the impoundment because of the loss of volatiles to the air.

The calculation of the overall mass transfer coefficient is the same as that presented for impoundments with quiescent surfaces. If the disposal impoundment is aerated, K is calculated as described for aerated impoundments in Section 5.4. The emission estimating procedure differs in the calculation of the liquid-phase concentration that is the driving force for mass transfer to the air. For a disposal impoundment that is filled with a batch of waste, the rate of disappearance of a compound by biodegradation and air emissions is described by Equation (5-26).

Integrating Equation (5-26) from $C_t = C_i$ at t = 0 to $C_t = C_t$ at t = t gives:

$$C_t/C_i = \exp\,(-K_1 b_i t - KAt/V) \quad . \tag{5-31}$$

For an impoundment with a uniform depth, V/A = D. Substituting V/A = D into Equation (5-31) yields:

$$C_t/C_i = \exp\,(-K_1 b_i\ t - Kt/D) \tag{5-32}$$

When Equation (5-32) is evaluated after some fixed time t, the ratio C_t/C_i represents the fraction of the compound remaining in the impoundment; consequently, $1 - C_t/C_i$ represents the fraction that has been removed by biodegradation and air emissions. The fractions emitted to the air and biodegraded after some time (t) are calculated from their relative rates:

$$f_{air} = (1 - C_t/C_i)(KA)/(KA + K_1 b_i V) \tag{5-33}$$

$$f_{bio} = (1 - C_t/C_i)(K_1 b_i V)/(KA + K_1 b_i V) \tag{5-34}$$

The quantity emitted after some time (t) is given by:

$$\text{Emitted quantity (g)} = f_{air}\ V\ C_i. \tag{5-35}$$

The average emission rate over the period of time = t is:

$$E\ (g/s) = f_{air}\ V\ C_i/t\ . \qquad (5\text{-}36)$$

Alternatively, a simplifying assumption may be made that, because the impoundment is designed for disposal, all significantly volatile compounds are eventually emitted to the air. Emissions under this assumption would simply be QC_i where Q equals the disposal rate in cubic meters/second. This assumption is probably valid for volatile compounds; however, compounds that are relatively nonvolatile may be removed slowly and the assumption may result in an overestimate of emissions.

5.5.2 Model Plant Parameters for Disposal Impoundments

The Westat data summary for impoundments indicated that disposal impoundments generally have higher surface areas and shallower depths than storage and treatment impoundments. The median surface area for disposal impoundments was approximately 9,000 m^2 (compared to 1,500 m^2 for storage impoundments), and the median depth was approximately 1.8 m. The disposal impoundment is assumed to be filled with waste every 6 months (two turnovers per year).

The meteorological conditions and type of waste (water containing benzene and other organics for the example calculation are the same as those used for quiescent and aerated impoundments with biodegradation. The inputs for the example calculation of emissions from disposal impoundments are summarized in Table 5-10.

5.5.3 Example Calculations for Disposal Impoundments

Example calculations are presented below for the model unit defined to represent disposal impoundments.

a. Calculate liquid-phase mass transfer coefficient, k_L. Use Springer's model (see Table 5-1):

$$\text{Effective diameter} = \left[\frac{\text{Area}}{B}\right]^{0.5} \times 2 = \left[\frac{9{,}000}{B}\right]^{0.5} \times 2 = 107 \text{ m}$$

$$\text{F/D} = \text{Effective diameter/depth} = \frac{107}{1.8} = 59.5 \quad .$$

Windspeed = 4.47 m/s ($U_{10} \geq 3.25$ m/s)

$$k_L = 2.611 \times 10^{-7}\, U_{10}^2 \left[\frac{D_w}{D_{ether}}\right]^{0.67} \text{ m/s}$$

TABLE 5-10. INPUT PARAMETERS--DISPOSAL IMPOUNDMENTS

Area: 9,000 m^2
Depth: 1.8 m
Volume: 16,200 m^3
Turnovers per year: 2

Temperature: 25 °C
Windspeed: 4.47 m/s

Diffusivity in water (ether): 8.5×10^{-6} cm^2/s
Viscosity of air: 1.81×10^{-4} g/cm•s
Density of air: 1.2×10^{-3} g/cm^3

Constituent: benzene with other biodegradable organics in water
Concentration (benzene): 100 g/m^3 (100 ppm)
Concentration (total organics): 250 g/m^3 (250 ppm)
Henry's law constant (benzene): 5.5×10^{-3} atm•m^3/g mol
Diffusivity in air (benzene): 0.088 cm^2/s
Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s
Limiting first-order biorate constant: 3.89×10^{-6} m^3/s/g biomass
Biomass concentration: 0.05 g/L = 50 g/m^3

TABLE 5-11. INPUT PARAMETERS--DIFFUSED AIR ACTIVATED SLUDGE UNIT

Area: 27 m^2
Depth: 4 m
Volume: 108 m^3
Retention time: 4 h
Flow: 0.0075 m^3/s
Quiescent area: 8.0 m^2
Diffused air rate: 0.04 m^3/s

Temperature: 25 °C
Windspeed: 4.47 m/s

Viscosity of air: 1.81×10^{-4} g/cm•s
Density of air: 1.2×10^{-3} g/cm^3
Diffusivity of O_2 in water: 2.4×10^{-5} cm^2/s
Density of liquid: 1 g/cm^3
Molecular weight of liquid: 18 g/g•mol
Molecular weight of air: 29 g/g•mol

Constituent: benzene with other biodegradable organics in water
Concentration (benzene): 100 g/m^3 (100 ppm)
Concentration (total organics): 250 g/m^3 (250 ppm)

Henry's law constant (benzene): 5.5×10^{-3} $atm•m^3$/g•mol
Diffusivity in air (benzene): 0.088 cm^2/s
Diffusivity in water (benzene): 9.8×10^{-6} cm^2/s
Maximum biorate (benzene and other organics): 5.28×10^{-6} g/s/g biomass
Limiting first-order biorate constant: 3.89×10^{-7} m^3/s/g biomass
Biomass concentration: 4.0 g/L = 4,000 g/m^3

where,

U_{10} = windspeed = 4.47 m/s;

$D_w = 9.8 \times 10^{-6}$ cm^2/s (benzene); and

$D_{ether} = 8.5 \times 10^{-6} =$ cm^2/s (ether).

Then,

$$k_L = 2.611 \times 10^{-7} (4.47)^2 \left(\frac{9.8 \times 10\text{-}6}{8.5 \times 10^{-6}} \right)^{0.67}$$

$$k_L = 5.7 \times 10^{-6} \text{ m/s} \quad .$$

b. Calculate gas-phase mass transfer coefficient, k_g. Use MacKay and Matasugu (see Table 5-1):

$$k_G = 4.82 \times 10^{-3}\, U^{\,0.78} Sc_G^{\,-0.67}\, d_e^{\,-0.11} (\text{m/s})$$

where,

U = windspeed = 4.47 m/s

$$Sc_G = \begin{array}{l}\text{Schmidt No.}\\ \text{for gas}\end{array} = \frac{\text{viscosity of gas}}{(\text{gas density})(\text{diffusivity of i in gas})}$$

Gas = air

Viscosity (air) = 1.81×10^{-4} g/cm•s

Density (air) = 1.2×10^{-3} g/cm^3

Diffusivity (benzene in air) = 0.088 cm^2/s

$$Sc_G = \frac{1.81 \times 10^{-4} \text{ g/cm•s}}{(1.2 \times 10^{-3} \text{ g/cm}^3)\ (0.088 \text{ cm}^2\text{/s})} = 1.71$$

d_e = effective diameter = 107 m .

Then,

$$k_G = (4.82 \times 10^{-3})\ (4.47)^{0.78}\ (1.71)^{-0.67}\ (107)^{-0.11}$$

$$= 6.5 \times 10^{-3} \text{ m/s} \quad .$$

c. Calculate overall mass transfer coefficient, K:

$$\frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keq\ k_G}$$

where,

$$Keq = \frac{H}{RT} = \frac{5.5 \times 10^{-3}\ m^3 \bullet atm/mol}{(8.21 \times 10^{-5}) \left| \frac{atm\ m^3}{mol\ K} \right| (298\ K)} = 0.225.$$

Then

$$\frac{1}{K} = \frac{1}{5.7 \times 10^{-6}} + \frac{1}{(0.225)(6.5 \times 10^{-3})} = 1.76 \times 10^5$$

$$K = 5.7 \times 10^{-6}\ m/s \quad .$$

d. Calculate the fraction remaining from Equation (5-32). The impoundment is filled with waste initially, and 6 month later it will be filled again. Calculate the fraction remaining after the initial 6-month period:

C_t/C_i = exp $(-K_1 b_i\ t - Kt/D)$;

$K_1 = 3.89 \times 10^{-7}\ m^3/s/g$ biomass;

$b_i = 50\ g/m^3$;

$t = 6$ mo $= 1.58 \times 10^7$ s;

$C_i = 100\ g/m^3$;

$K = 5.7 \times 10^{-6}$ m/s;

$D = 1.8$ m;

$K_1 b_i t = (3.89 \times 10^{-7}\ m^3/s/g\ \text{biomass})(50\ g/m^3)(1.58 \times 10^7\ s)$;

$= 307$;

$Kt/D = (5.7 \times 10^{-6}\ m/s)(1.58 \times 10^7\ s) / 1.8\ m = 50.0$; and

$C_t/C_i = \exp(-307 - 50) = 0$.

f. Calculate the fraction emitted from Equation (5-33):

$$f_{air} = (1 - C_t/C_i)(KA) / (KA + K_1 b_i V)$$

$$C_t/C_i = 0$$

$$KA = (5.7 \times 10^{-6}\ m/s)(9{,}000\ m^2) = 0.051/m^3/s$$

Since the concentration is high enough for zero-order kinetics, $K_1 b_i V$ is replaced with K_{max}

$$f_{air} = (1 - 0)(0.051\ m^3/s) / (0.051\ m^3/s + 0.315\ m^3/s)$$

$$f_{air} = 0.14 \quad .$$

g. Calculate the average emission rate over the 6-mo period from Equation (5-36):

$$E\ (g/s) = f_{air}\ V\ C_i/t$$

$$= (0.14)(16{,}200\ m^3)(100\ g/m^3)/1.58 \times 10^7\ s$$

$$= 1.4 \times 10^{-2}\ g/s.$$

5.6 DIFFUSED AIR SYSTEMS

5.6.1 Emission Model Equations

Some impoundments and open tanks (e.g., activated sludge units) are sparged with air to promote biodegradation or air stripping. To estimate emissions from diffused air systems, the model assumes that the air bubbling through the liquid phase reaches equilibrium with the liquid-phase concentration of the constituent. The emissions leaving with the diffused air are estimated by:

$$E = Q_a K_{eq} C_L \qquad (5\text{-}37)$$

where,

E = emissions, g/s;

Q_a = air flow rate, m^3/s;

K_{eq} = equilibrium constant; and

C_L = concentration in the liquid phase, g/m^3.

Emissions can also occur from wind blowing across the surface. If the air sparging creates a very turbulent surface similar to the surface of mechanically aerated systems, then the emission rate should be based on values of K typical for mechanically aerated systems. If the air sparging rate does not result in a turbulent surface, then K can be estimated from the correlations given for quiescent surfaces in Section 5.2.

The approach to estimate total emissions for flowthrough tanks and impoundments sparged with diffused air is similar to that described for quiescent and aerated systems. Because the unit is sparged with air, the liquid phase is assumed to be well mixed and the plug-flow model is not used. A material balance around this well-mixed system is identical to Equation (5-18) in Section 5.3.2, but now K_{other} is:

$$K_{other} = (KA + Q_a Keq)/V \tag{5-38}$$

where all of the symbols have been previously defined. The steady-state liquid phase concentration (C_L) is then calculated using Equation (5-21). Air emissions are estimated as the sum from wind blowing across the surface and from the diffused air:

$$E = KAC_L + Q_a \; Keq \; C_L \; . \tag{5-39}$$

The fraction of the component feed emitted to the air (f_{air}) is:

$$f_{air} = (KC_L A + Q_a KeqC_L)/QC_i. \tag{5-40}$$

For disposal impoundments with diffused air systems, the steady-state assumptions of the flowthrough models do not apply. Emissions are greatest when the waste is first placed in the impoundment and gradually decrease with time. To incorporate the contribution to mass transfer from diffused air, an equivalent mass transfer coefficient is defined:

$$K_D = KeqQ_a/A \tag{5-41}$$

where

K_D = equivalent mass transfer coefficient for diffused air, m/s and all of the other symbols are as previously defined.

The mass transfer coefficient for wind blowing across the surface (K) is calculated as described previously for flowthrough systems. A combined overall mass transfer coefficient (K_C) is defined as:

$$K_C = K_D + K \quad . \tag{5-42}$$

The overall mass transfer coefficient (K_C) is used in the equations for disposal impoundments (Section 5.5.1) to estimate the fraction emitted (Equation 5-33) and the average emission rate (Equation 5-36). The combined overall mass transfer coefficient defined above includes the mass transfer effects from both removal mechanisms (wind and diffused air).

5.6.2 Model Unit Parameters for Activated Sludge Unit with Diffused Air

A model unit for the activated sludge process was defined in Section 5.4.4 and Table 5-8. The same dimensions are used here to define an activated sludge unit that uses diffused air instead of mechanical aeration. The only additional parameter that must be specified is the diffused air rate, which typically ranges from 0.3 to 0.5 m^3/s per 1,000 m^3 of volume (20 to 30 ft^3/min per 1,000 ft^3 of volume).[55] For the model unit with a volume of 108 m^3, an estimate of 0.04 m^3/s is recommended based on the mid-point of the design range. The model unit input parameters are summarized in Table 5-11.

5.6.3 Example Calculation for Diffused Air Activated Sludge Unit

An example calculation is presented below for the model unit defined in Table 5-11.

a. Calculate the liquid-phase, gas-phase, and overall mass transfer coefficients. This procedure was illustrated for quiescent surfaces and the results for this model unit are given in Table 5-9:

$k_L = 6.5 \times 10^{-6}$ m/s;

$k_g = 8.7 \times 10^{-3}$ m/s; and

$K = 3.42 \times 10^{-3}$ m/s (weighted by area).

b. Calculate the equilibrium constant, Keq. The compound is benzene in water, and Keq has been presented as 0.225 in the previous sample calculations (from Equation 5-5).

c. Calculate the equilibrium liquid concentration in the unit (C_L) from Equation (5-21):

$Q = 0.0075\ m^3/s$

$C_i = 100\ g/m^3$

$K = 3.42 \times 10^{-3}\ m/s$

$A = 27\ m^2$

$Qa = 0.04\ m^3/s$

$Keq = 0.225$

$K_{max} = 5.28 \times 10^{-6}$ g/s/g biomass

$K_s = K_{max}/K_1 = (5.28 \times 10^{-6}\ g/s/g)/(3.89 \times 10^{-7}\ m^3/s/g)$

$= 13.6\ g/m^3$

$b_i = 4{,}000\ g/m^3$

$V = 108\ m^3$

$QC_i = (0.0075\ m^3/s)(100\ g/m^3) = 0.75\ g/s$

$KA = (3.42 \times 10^{-3}\ m/s)(27\ m^2) = 9.23 \times 10^{-2}\ m^3/s$

$QaK_{eq} = (0.04\ m^3/s)(0.225) = 9.0 \times 10^{-3}\ m^3/s$

$K_{other} = (KA + Q_aKeq)/V$ (from Equation 5-38)

$= [(9.23 \times 10^{-2}\ m^3/s) + (9.0 \times 10^{-3}\ m^3/s)]/(108\ m^3)$

$= 9.39 \times 10^{-4}\ 1/s$

$V/Q = (108\ m^3)/(0.0075\ m^3/s) = 14{,}400\ s$

$a = K' = (9.29 \times 10^{-4}\ 1/s)(14{,}400\ s) + 1 = 14.5$

$$b = (13.6\ g/m^3)(14.5) + (14{,}400\ s)(5.28 \times 10^{-6}\ g/s/g)$$
$$(4{,}000\ g/m^3) - 100\ g/m^3$$
$$= 401\ g/m^3$$
$$c = -(13.6\ g/m^3)(100\ g/m^3) = -1{,}360\ g^2/m^6$$
$$C_L = \{[-401\ g/m^3] + [(401\ g/m^3)^2 - 4(14.5)$$
$$(-1{,}360\ g^2/m^6)]^{0.5}\}/[2(14.5)]$$
$$= [(-401\ g/m^3) + (490\ g/m^3)]/29$$
$$= 3.06\ g/m^3\ .$$

d. Calculate air emissions from Equation (5-39).

$$E = (9.23 \times 10^{-2}\ m^3/s)(3.06\ g/m^3) + (9.0 \times 10^{-3}$$
$$m^3/s)(3.06\ g/m^3)$$
$$= 0.31\ g/s = 9.7\ Mg/yr.$$

5.7 OIL FILM SURFACES

Some wastes discharged into impoundments may contain volatile organics and oil. Many volatile organics will partition mostly into the oil, so the oil phase can contain most of the volatiles. The oil phase will rise to the surface of the impoundment where it is exposed to the atmosphere.

Some impoundments may have a floating film of oil on the surface. A rigorous approach to estimating emissions from this type of source would consider three resistances acting in series:

- From the aqueous phase to the oil
- Through the oil
- From the oil to the air.

Such an approach would require estimates of these three resistances and estimates of the equilibrium partitioning between both the aqueous and oil phases and the oil and air phases. Because these estimates are not generally available, a simplifying assumption is that the oil film is relatively thin, that the oil originally contains the volatile constituents, and that mass transfer is controlled by the gas-phase resistance. For this case, Equation (5-2) reduces to:

$$K = k_G \, Keq \qquad (5\text{-}43)$$

where k_G is calculated from the correlation of MacKay and Matasugu (Table 5-1) and Keq is calculated from Raoult's law by:

$$Keq = P^* D_a \, MW_{oil}/(D_L MW_a P_o) \qquad (5\text{-}44)$$

where

Keq = dimensionless equilibrium constant
P^* = vapor pressure of the volatile compound of interest, atm
P_o = total pressure, 1 atm
D_a = density of air, g/cm^3
D_L = density of oil, g/cm^3
MW_{oil} = molecular weight of oil, g/g mol
MW_a = molecular weight of air, 28.8 g/g mol.

The value of K calculated above is substituted into the equations for flow-through systems to estimate emissions. For the well-mixed flow models, C_i and C_L in Equations (5-1) and (5-6) represent the organic compound concentration in the oil phase (entering and leaving the impoundment, respectively), and the flowrate Q is the volumetric flow rate of oil. Biodegradation is neglected because the oil film inhibits the transfer of oxygen.

The procedure described above assumes that the oil layer in the impoundment is well mixed. For example, changes in wind direction in units with retention times on the order of days may tend to move the oil layer in different directions and result in mixing. However, some systems may be designed for or characterized by plug flow. This flow model assumes that the oil film moves across the impoundment's surface without backmixing. For plug flow of the oil film in flowthrough impoundments and tanks, the fraction of organic compound in the oil layer emitted to the air is given by Equation (5-11), and air emissions are estimated from Equation (5-12). In these equations, C_L is the organic compound concentration in the oily effluent, C_i is the initial concentration in the oil layer entering the impoundment, J is the residence time, D is the oil-film thickness, and Q is the volumetric flowrate of oil.

For an oil film on a disposal impoundment, emissions are calculated as described in Section 5.5. However, biodegradation is neglected and Equation (5-32) reduces to:

$$C_L/C_i = \exp\ (-Kt/D) \tag{5-45}$$

and the fraction emitted to the air is:

$$f_{air} = 1 - \exp\ (-Kt/D) \tag{5-46}$$

where,

C_t = concentration in the oil film at time = t;
C_L = initial concentration in the oil film; and
D = oil-film thickness.

and with the other symbols as previously defined. The average emission rate E, in units of g/s, over the period of time equal to t is:

$$E = f_{air}\ V\ C_i/t \tag{5-47}$$

where V = volume of oil in the impoundment, m^3 and with the other symbols as previously defined. An example calculation of this approach is given in Section 7.0 for applying an oil film to soil, which is analogous to an oil film on a disposal impoundment because there is no flow out in either case and emissions are a function of the time since disposal.

5.8 DISCUSSION OF ASSUMPTIONS AND SENSITIVITY ANALYSIS

5.8.1 Removal Mechanisms

The organic constituents present in wastes that are treated, stored, or disposed of in surface impoundments and open tanks may leave the unit by any of several mechanisms. Because of the large open surface area and relatively high volatility of many organic constituents, emissions to the air may be a primary removal mechanism for certain constituents. Other constituents may be destroyed in impoundments and tanks specifically designed for biodegradation. Aeration is often used to supply oxygen to biologically active systems. Unfortunately, aeration also greatly enhances the mass transfer of organic constituents to the air. Other removal mechanisms include adsorption on solids, seepage through the ground, or degradation (e.g., by photolysis or hydrolysis). For flowthrough systems, the organic constituents may leave the unit with the effluent that will subsequently be treated, stored, or disposed of.

Initial studies suggest that emission to air is a primary removal mechanism, especially for volatile constituents. Biodegradation in specific systems, particularly for semivolatiles, may also be significant. For flowthrough systems, the removal of semivolatiles with the effluent may also be a primary removal mechanism. Other forms of degradation, adsorption, and seepage are neglected in this analysis for several reasons. These mechanisms are not believed to be significant for most systems and most constituents; however, they may be removal routes in a specific system or for a specific constituent. For example, an open tank may be designed specifically for liquid-phase carbon adsorption. These mechanisms are also difficult to model in a manner that is generally applicable considering the relatively sparse data on such removal mechanisms, especially in hazardous waste impoundments and tanks. Consequently, the modeling effort focuses on mass transfer to the air and some consideration of biodegradation.

Numerous studies have been conducted to assess mass transfer to the air; these include theoretical assessments, correlations based on laboratory and bench-scale measurements, and field measurements at actual sources. Additional data on specific wastes have been collected in air- stripping studies as more air-stripping columns have been used to remove organic constituents from water. The result is that the state of knowledge of mass transfer from the liquid to the gas phase (e.g., ambient air) is probably advanced compared to the state of knowledge of other removal mechanisms. The level of confidence in the air emission models is probably highest for the volatile constituents because of very high mass transfer rates. The level of confidence is somewhat lower for the relatively nonvolatile constituents because of potentially significant rates of removal by other mechanisms.

Much of the data on the performance of systems designed for biodegradation are reported as total removal from measurement of the influent and effluent concentrations. This total would include removal to the air and biodegradation. Some studies have been conducted in closed systems in which the biodegradation rate may be measured directly (loss to the air is deliberately prevented). These data are useful for comparing the relative rates of removal by biodegradation among constituents and make possible a ranking of these constituents with respect to biodegradability. In addition, the estimated rate of biodegradation may be compared to the estimated rate of air emissions to assess the relative extent of each.

The biodegradation model has not been validated and is used in this report as an approximate measure of the extent of biodegradation. For any specific treatment system, measurements of actual biodegradation rates should be used if available. Any user of the biodegradation model should be aware that the predicted rate is very sensitive to the choice of values for the biorate, biomass concentration, and the concentration of organic constituents in the waste. An environmentally conservative approach with respect to air emissions would be to neglect biodegradation (assume the rate is zero). This approach is probably valid for volatile constituents in aerated systems; however, the approach may tend to overestimate emissions of relatively nonvolatile constituents that are destroyed in treatment systems specifically designed for biodegradation.

5.8.2 Major Assumptions

An inherent assumption in the emission estimating procedure is that the mass transfer correlations chosen earlier are generally applicable. A paper that compares several different models concludes that, in most cases, many different models yield comparable results for volatile constituents.[56] The choice of models may affect the estimated mass transfer coefficients for semivolatiles more than those for volatiles. The calculations indicate that emissions of volatiles are controlled by the liquid-phase resistance. Consequently, the value for the overall mass transfer coefficient (K) is primarily determined by the correlation used for the liquid-phase mass transfer coefficient (k_L). For constituents with decreasing volatility, both the liquid-phase and gas-phase resistance begin to contribute to the overall resistance to mass transfer. For these constituents, the choices of correlations for both k_G and k_L become important, and the choice of correlations may significantly affect the emission estimates.

The flow model chosen for storage and treatment impoundments assumes that the impoundment's contents are well mixed and that the system is operated at steady-state conditions. The flow for specific facilities may be better represented by plug flow or a model that accounts for axial dispersion. The choice of flow model does not make a significant difference in the estimated emissions. However, if the loading of the impoundment is cyclical or intermittent instead of continuous, the emissions from the impoundment are likely to be cyclical or intermittent. Estimates of short-term emission rates are very dependent upon the method of operation of the system. For disposal impoundments, peak emissions occur when the waste is first placed in the impoundment and then decrease with time. The approach used in this report estimates the average emission rate over a given period of time and does not provide an estimate of the initial peak emissions.

The calculation of Henry's law constant also contains inherent assumptions. The approach is valid for dilute solutions and has been applied successfully in the design of air-stripping columns. However, specific mixtures may deviate from Henry's law because of component interactions or because of concentrations outside the range of applicability. Errors in applying Henry's law are generally environmentally conservative; i.e., the actual gas-phase concentration is not likely to be underestimated.

For concentrated mixtures of organics in a separate oil layer, the use of Raoult's law is recommended. This approach is valid for mixtures of constituents with similar properties, especially when the concentration of the component of interest is very high. A preferred approach would be to avoid the use of Henry's law or Raoult's law and actually measure the equilibrium partitioning between the liquid and gas phase of a waste. However, very few data are available for equilibrium partitioning that can be applied generally to hazardous waste mixtures.

5.8.3 Sensitivity Analysis

The emission correlations were evaluated for sensitivity to each of the input parameters.[57] In the analysis, each input parameter was varied individually over the entire range of reasonable values. The effect on emissions was noted, and the most sensitive parameters were identified.

Detention time is an important parameter that affects emissions from the impoundment. The emission estimates for volatile constituents are sensitive to short detention times, and the estimates for semivolatiles are sensitive to long detention times. Essentially all of the volatile constituents are emitted for longer detention times (several days), and very little of the semivolatiles are emitted for short detention times (a few days). However, significant emissions of the semivolatiles may occur for long detention times in storage impoundments or in disposal impoundments.

The value of Henry's law constant was not important for volatile constituents. The correlations indicated that these constituents are controlled by the liquid-phase resistance, which is not affected by Henry's law constant. The value of Henry's law constant has a direct effect on the emissions of semivolatiles (such as phenol), and the greatest effect is on those relatively nonvolatile compounds for which mass transfer is controlled by the gas-phase resistance.

Windspeed has a direct effect on the emission estimates for quiescent surfaces and has little effect on those from aerated systems. The results showed that a standard windspeed of 5.5 m/s was reasonable compared with the results for windspeed distributions at actual sites.

Temperature did not affect the emission estimates for the volatile constituents. However, temperature did affect the emission estimates for nonvolatile constituents with mass transfer controlled by the gas phase. The temperature dependence of Henry's law constant accounts for this effect.

The diffusivity in air and water for a wide variety of constituents spans a relatively narrow range of values. The analysis showed that the emission estimates were not sensitive to the choice of values for diffusivity.

For mechanically aerated systems, the choice of values for impeller diameter, impeller speed, oxygen transfer rate, and oxygen correction factor did not affect the emission estimates significantly. The total horsepower and turbulent area had a direct effect on emissions of semivolatiles (e.g., phenol). However, there was no significant effect on emissions of volatile constituents because the models predicted that they would be stripped almost completely from the water over the full range of aeration values.

The biodegradation model was very sensitive to all parameters investigated. The sensitive parameters include organic concentration, biomass concentration, and biorate.

Two meteorological parameters required in the models are temperature and windspeed. The emission estimates are based on a standard temperature of 25 °C and a windspeed of 4.47 m/s (10 mi/h). These standard values were evaluated by estimating emissions for windspeed/temperature combinations at actual sites based on their frequency of occurrence. Over a 1-yr period, the results from site-specific data on windspeed and temperature were not significantly different from the results using the standard values. Consequently, the standard values were judged adequate to estimate annual emissions. For short-term emissions, the actual temperature and windspeed over the short-term interval should be used to avoid underestimating emissions during high-windspeed /high-temperature conditions.

A sensitivity analysis was performed for three impoundment model units (storage, mechanically aerated, and disposal) presented in the example calculations in this section. Three compounds were chosen to represent relatively nonvolatile compounds (p-cresol), moderately volatile compounds (acetone), and relatively volatile compounds (benzene). Each of these compounds can be biodegraded. The results are given in Tables 5-12, 5-13, and 5-14. The key input parameters identified in the tables were increased by 50 percent from the base case to determine the effect on the percent of the compound in the waste that is emitted to the air.

For each of the different types of impoundments, the volatility appears to be important only for the low volatility category. As discussed previously, the windspeed (air turbulence) has a direct effect for each of the compounds in a storage impoundment and does not affect the mechanically aerated unit's results. The low volatility compounds are the most sensitive to changes in depth and biomass concentration for all three types of impoundments. An assumption of no biodegradation also has the most dramatic effect on the low volatility compound with smaller effects observed for the higher volatility compounds. The effects of retention time are small except for the results shown for the disposal impoundment after 5 days. The disposal impoundment results show that for short times, the time since disposal is an important parameter affecting emissions.

TABLE 5-12. RESULTS OF SENSITIVITY ANALYSIS FOR QUIESCENT STORAGE IMPOUNDMENT

	Percent emitted for given Henry's law constant, atm•m^3/mole		
Key emission model inputs	10^{-7}	10^{-5}	10^{-3}
Base case[a]	2.9	58	59
50-percent increase from base case[b]			
Volatility	4.2 (45)[c]	61 (5)	59 (0)
Air turbulence	4.0 (38)	72 (24)	76 (29)
Retention time	3.2 (10)	62 (7)	62 (5)
Depth	2.1 (-28)	50 (-14)	49 (-17)
Biomass concentration	2.1 (-28)	52 (-10)	52 (-12)
No biodegradation[d]	10 (245)	74 (28)	80 (36)

[a] This corresponds to the model unit for storage impoundments used in the example calculation.

[b] Each parameter is increased individually by 50 percent from its base case value.

[c] Values in parentheses are percent change from the base case.

[d] Base case with no biodegradation.

TABLE 5-13. RESULTS OF SENSITIVITY ANALYSIS FOR MECHANICALLY AERATED IMPOUNDMENTS

Key emission model inputs	Percent emitted for given Henry's law constant, atm•m^3/mole 10^{-7}	 10^{-5}	 10^{-3}
Base case[a]	2.7	79	99
50-percent increase from base case[b]			
Volatility	3.9 (44)[c]	85 (8)	99 (0)
Air turbulence	2.8 (4)	80 (1)	99 (0)
Water turbulence	3.6 (33)	85 (8)	99 (0)
Retention time	2.7 (0)	80 (1)	99 (0)
Depth	1.8 (-33)	73 (-8)	98 (-1)
Biomass concentration	1.8 (-33)	73 (-8)	98 (-1)
No biodegradation[d]	20 (640)	94 (28)	100 (1)

[a] This corresponds to the model unit for mechanically aerated impoundments used in the example calculation.

[b] Each parameter is increased individually by 50 percent from its base case value.

[c] Values in parentheses are percent change from the base case.

[d] Base case with no biodegradation.

TABLE 5-14. RESULTS OF SENSITIVITY ANALYSIS FOR DISPOSAL IMPOUNDMENTS

Key emission model inputs	Percent emitted for given Henry's law constant, atm•m³/mole		
	10^{-7}	10^{-5}	10^{-3}
Base case[a]	13	93	92
50-percent increase from base case			
Volatility	18 (38)[b]	94 (1)	92 (0)
Air turbulence	17 (31)	96 (3)	96 (4)
Retention time[c]	2.3 (-82)	55 (-41)	72 (-22)
Depth	9 (-31)	89 (-4)	88 (-4)
Biomass	9 (-31)	89 (-4)	89 (-3)
No biodegradation[d]	84 (550)	100 (8)	100 (9)

---

[a] Based on the dimensions given in the example calculation, 100 mg/L of the constituent in 1,000 mg/L total organics, and a time since disposal of 12 months.

[b] Values in parentheses are percent change from base case.

[c] A retention time of 5 days was selected here to show the sensitivity to retention time soon after disposal.

[d] Base case with no biodegradation.

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6.0 WASTEWATER TREATMENT MODELS (WATER8)

This section describes a series of wastewater models that can be used to estimate air emissions from miscellaneous wastewater treatment units. Many of the models presented in this section are not included with CHEMDAT8 due to the nature of the calculations that are required. Section 6.1 presents an overview of the models that are included in WATER8 and some general guidance for the use of these models. Section 6.2 presents a discussion of trickling filters and a proposed model for trickling filters. Section 6.3 discusses a cooling tower model. Section 6.4 discusses a model for an API separator. Table 6-1 lists selected units and the appropriate models.

6.1 UNITS FOR MODELING EMISSIONS OF VOLATILE COMPOUNDS

Although presented as discrete units, it should be noted that these units are present in a number of different treatment plants, and that most treatment plants can be composed of unit processes that fit into the broad categories of the units defined here. For example, a trickling filtration unit could be used in the treatment train ahead of an activated sludge unit. In this capacity, the trickling filter operates as a roughing filter to pretreat wastewater prior to secondary treatment and not as a secondary treatment process.

It should be emphasized that treatment systems vary widely depending on the nature of the wastewater, the availability of land, prior regulatory pressure, the composition and flow rate

TABLE 6-1. REFERENCE TABLE FOR THE LOCATION OF WASTEWATER TREATMENT UNITS MODELS AND RELATED DISCUSSION.

Unit Description	WATER8	CHEMDAT8	THIS REPORT
Collection system	YES	NO	Section 4
Sump	YES	NO	Section 4
Cooling tower	YES	NO	Section 6
Wastewater separator	YES	NO	Section 6
Trickling filters	YES	NO	SECTION 6
mix tanks	YES	YES	SECTION 5
Activated sludge	YES	YES	SECTION 5
Agitated impoundment	YES	YES	SECTION 5
Disposal impoundment	YES	YES	SECTION 5
Plug flow system	YES	NO	SECTION 5
Trench	YES	NO	SECTION 4
Clarifier	YES	NO	SECTION 4
Storage tank	YES	NO	SECTION 9
Waterfall or weir	YES	NO	SECTION 4
Pretreatment	YES	NO	SECTION 6
Oil film surface	YES	YES	SECTION 5

that may have existed at the time the system was designed, and many other factors. The units that follow do not represent a "typical" system. The unit parameters can be defined as those of a specific system component parameters to estimate the air emissions from that specific system component.

6.1.1 Conventional Activated Sludge System

A typical configuration of an activated sludge system is pretreatment, optional primary sedimentation (primary clarifier) followed by the aeration process including secondary clarification, and post treatment. The principal treatment process is the aeration tank. This is a continuous flow, biological treatment process characterized by the turbulent suspension of microscopic aerobes. The turbulence promotes mixing and induces a relatively homogenous state in which the microbes are able to absorb and oxidize soluble and colloidal organics. The process involves an aeration step followed by a solid-liquid separation step in which part of the separated sludge is recycled back to the system for mixing with the raw influent.

There are many variations of the activated sludge process; however, they generally can be reduced to looking at either the loading rates in terms of BOD or the physical arrangement of the process train. The loading is typically one of three basic types. High rate takes advantage of the settleability of sludge when the system is loaded at a rate of 0.80-1.15 g of BOD/g of mixed liquor suspended solids per day. Conventional rate is of the range 0.2 to 0.5 g BOD/g mixed liquor volatile suspended solids per day. This rate is typical for most larger municipal treatment plants. Extended aeration rate is the lowest range of process loading and is used in those plants which are small in size and do not receive 24 hour supervision. As such they are generally conservatively designed and operate in the range of 0.05-0.15 g of BOD applied/g of MLVSS/day; industrial wastewaters vary widely in terms of influent concentration and biodegradability. Thus, a wide range of loading rates are used depending on individual circumstances.

Physical arrangements are of three types; the complete mix activated sludge, plug flow activated sludge, and activated sludge with reaeration. In the complete mix arrangement, the return sludge and the wastewater are uniformly introduced into the aeration basin through several points in order to obtain a homogeneous mixture. In a plug flow arrangement both the untreated wastewater and the return sludge are introduced at the head of the plant and flow through the plant in a modified plug flow. Such plants are often compartmentalized to maintain the plug flow regime. Activated sludge with sludge reaeration constitutes a rearrangement of process streams. In this instance the sludge is compartmentalized and aerated prior to its contact with the untreated waste.

6.1.2 Sludge handling

Sludge handling involves the stabilization of the solid-water mixtures derived from the primary and secondary clarifier as well as the excess biomass from the activated sludge process and chemical reactions. These mixtures undergo thickening, anaerobic or aerobic digestion and dewatering prior to ultimate disposal. Anaerobic digestion is designed for minimal air/sludge contact. Emissions from the other processes are likely to be insignificant because the upstream processing units will have provided extensive opportunities for volatilization prior to the sludge handling operations.

6.1.3 Conventional Activated Sludge (Mechanical Aeration)

The principle component of the mechanical aeration system is the aerator. There are two types in general use today, surface aerators and turbine aerators. The surface aerator is highly developed and widely used, particularly in the treatment of industrial waste. The surface aerators may either float or be mounted on supports in the aeration basin. They enhance the entrainment of atmospheric air in the aeration basin by producing a region of high turbulence around the periphery of the aerator. Oxygen transfer efficiency of these aerators increases with the depth of submersion, as does power cost; consequently, there is a trade off between efficiency and cost.

Since 1950, the submerged turbine has been widely used in the chemical industry. It offers an attractive means of upgrading existing facilities to handle increased loads. These aerators are used because of improved oxygen transfer efficiency and lower horsepower requirements. Oxygen transfer efficiency for aerators, as rated in terms of mass of oxygen transferred per energy input, is typically on the order of 1.2 Kg 02/KW-hr (2 lb 02/hp.hr). Air and energy requirements for an aeration system are typically on the order of 50-90 m^3/kg BOD removed and 0.040 to 0.26 Kw/m^3 of basin volume.[1]

The mechanical aerator approach is found in large open basins particularly in those plants operating in a complete mix, conventional activated sludge mode. The turbulence introduced by the rotary action of the aerator blades promotes a homogeneous mixing and enhances the overall complete mix mode of operation.

6.1.4 Conventional Activated Sludge (Diffused Air: Coarse and Fine Bubble)

A second approach to aeration is the use of diffuser systems which are generally used in plug flow systems and sludge reaeration systems, the most common types of aeration systems used in activated sludge plants. The distribution system consists of an array of diffusers situated near the bottom of the basin. These diffusers are designed to produce either coarse or fine bubbles and are supplied with air by compressors. In the period from 1950 to 1978, the fine bubble systems were in wide use. At that time, it was felt that the increase in oxygen transfer efficiency of the smaller bubble diameter (8 percent vs.

5 percent for the coarse bubble) was important. Later, however, inefficiencies such as clogging decreased the overall attractiveness of these systems.

The most common type of fine bubble diffusers are nylon or Dacron socks and saran wrapped tubes. Other systems include porous ceramic plates that generate small diameter bubbles. Coarse bubble diffusers can be tubes covered with synthetic fabric or wound with filaments, and sprayers with multiple openings created by drilling holes in pipes or loosely attaching plates or discs to a supporting piece of pipe. Although the oxygen transfer efficiency is lower, coarse bubble diffusers do not suffer from clogging and have lower initial cost and maintenance. Many treatment plants are reported to have switched to the coarse bubble systems in order to take advantage of these features.[2]

6.1.5 Aerated Lagoons (Mechanical Air)

Aerated lagoon systems are medium depth basins designed for biological treatment on a continuous flow basis. They are equipped with surface aerators and are primarily used to treat wastes of low-medium strength in areas where land is inexpensive. They are not as widely used as stabilization ponds, but their feasibility has been fully demonstrated and they may represent an upgrading of an oxidation pond.

Aerated lagoons have detention times on the order of 3-10 days. Aerated lagoons are staged in series and are designed to achieve partial mixing. Consequently, aerobic and anaerobic stratification can occur. A large fraction of the incoming solids may in fact settle out near the head of the plant.[3]

6.1.6 Spray Evaporation Ponds

Spray evaporation ponds are used primarily to reduce the amount of water contained in a waste. These are basically ponds equipped with submersible pumps attached to vertical pipes ending in standard irrigation spray headers. Water is pumped through this system and dispersed in the air. As the droplets fall back to the pond they are enriched with oxygen and subjected to evaporative processes. These ponds occur primarily in waste treatment systems involving large quantities of recycled water. Evaporation ponds without spray headers are termed solar evaporation ponds and are not intentionally aerated.

6.1.7 Dissolved Air Flotation (DAF)

Dissolved air flotation is widely used in industry to remove suspended solids by flotation. The flotation of the particulate is induced by microscopic air bubbles attaching to the particulate or agglomerate and giving it buoyancy. Particles are floated to the surface where they are removed by skimmers for further treatment.

The DAF system generates a supersaturated solution of wastewater and air by pressurizing either the influent wastewater (or a side stream of the influent wastewater) and introducing compressed air. The pressure is then released in the detention tank generating the numerous microscopic bubbles which adhere to particulates or are trapped by any floc which may be present.

6.1.8 Neutralization (Equalization) Process

Although neutralization and equalization units perform different functions, i.e., pH neutralization vs. flow equalization, these operations can be considered together as they permit similar modes of air/water contact. Primarily, these units are open basins or tanks with varying size depending upon the desired retention time. Mechanical agitation by stirrers is used to assure a homogeneous mixture. The design criteria for these processes are dependent on the variation in influent composition. For example, when the objective is equalization, more erratic fluctuations in the influent composition necessitates longer residence times.

6.1.9 Miscelaneous Physical-Chemical Treatment Systems

Physical-chemical processes are generally defined as those operations which effect the removal and/or destruction of undesirable constituents in wastewater by means other than biological degradation or biological conversion.

Physical-chemical processes include a wide array of traditional and innovative processes. These processes include dissolved air flotation, and mechanically agitated equalization/neutralization basins. These processes can be used as adjuncts to the model plant flow charts presented in this section. If appropriate, an open agitated tank model can be used to characterize some of the miscelaneous wastewater treatment operations.

6.2 AIR EMISSIONS OF VOLATILE COMPOUNDS FROM TRICKLING FILTERS

The typical trickling filter plant consists of the following units: pretreatment, primary clarifier, trickling filter, secondary clarifier and post-treatment unit (see Figure 6-1). The heart of the system is the trickling filter itself, which consists of a circular basin 1-2.4 m deep packed with a bed of either rock or plastic media, over which wastewater is sprayed. A zoogleal slime which attaches to the media assimilates and oxidizes the organics in the wastewater. Oxygen and organic matter diffuse into the zoogleal mass and end products of oxidation counter-diffuse back into the flowing liquid or to the void spaces. The treated water and any particulates from the filter bed are collected in an underdrain system and sent to secondary clarifiers for sedimentation.

The packing media is typically dosed with a rotary distributor which sprays the waste over the media. The media may be either plastic or rock. The rock medium represents a traditional approach; the plastic however, offers advantages such as lower specific weights and higher void spaces and is amenable to above ground installation.

The performance of the unit is affected by many factors such as hydraulic and organic loadings, depth and physical characteristic of the media, the method of wastewater distribution, ventilation, and characteristics of the applied wastewater.[2] Municipal wastewater and a wide variety of industrial wastewaters are amenable to treatment in trickling filters.

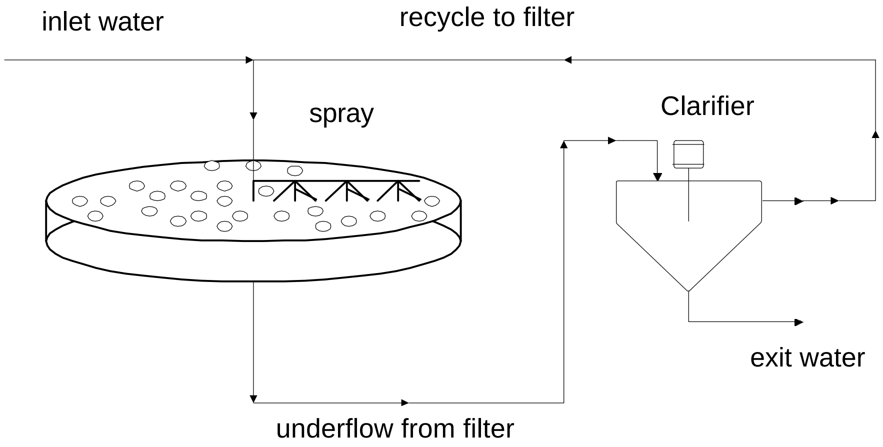

Figure 6-1. Illustration of a trickling filter.

The principal components of the trickling filter process are:

1. The distribution system
2. The filter media
3. The underdrain
4. Final sedimentation.

The rotary distributor consists of two or more horizontal arms mounted on a turntable assembly anchored to a center column. The wastewater is uniformly distributed over the media through orifices located in the arms. The principal drive mechanism for these arms is the reaction force from the spray on the radial arms. The arms are sized to limit velocities to 1.2 m/sec at maximum flow. The rotation speed of the arms varies with flow rate in the range of 0.1-2 rpm.

Ventilation is extremely important in achieving efficient filter operation. Usually, if the underdrain is properly sized, the differences in air and water temperature will provide a natural driving force for ventilation. An air flow rate of approximately 0.03 m^3/m^2 filter area per minute is required to sustain aerobic conditions within the bed. When forced ventilation systems are required, they are typically designed to provide an air flow of 0.3 m^3/m^2 of filter area per minute.

Organic and hydraulic loading determines the classification of the filters: low-rate, high-rate, or roughing-rate. Low-rate filters are generally not equipped with recirculation an are rarely used. High-rate filters use recirculation to dilute the influent organic strength and to flush the media voids. This permits higher BOD loadings per volume of media and promotes the return of activated organisms as a seed. The high-rate filters are generally designed to accept a continuous flow of wastewater and may be either single stage or two staged. High-rate filters also have a number of modifications of the basic recirculation scheme.

Roughing rate trickling filters provide an intermediate stage of treatment and are used frequently to precede activated sludge units or second stage filters. The purpose of this operation is to reduce high organic loadings prior to further treatment. This intermediate stage is typical for industrial systems.

The trickling filter model is based on a design currently in operation in a U.S. municipality.[2] It represents a single train of a multi-train high rate process. The operating conditions and specifications fall within the range expected for industrial waste treatment. The design parameters are given in Table 6-2.

6.3 AIR EMISSIONS OF VOLATILE COMPOUNDS FROM COOLING TOWERS

Cooling towers are used in the chemical industry and in the pulp and paper industry to cool the wastewater before biological treatment. Excessively high wastewater temperatures can cause the biological treatment plant to fail to perform as designed. Cooling towers have been used in pulp mills, even in the cooler climate of the north central United States. Part of the wastewater evaporates, cooling the wastewater. An illustration of a cooling tower is presented in Figure 6-2.

Cooling towers may not be needed to cool high temperature wastewater if aeration basins are located before the biological units. It has been observed in several plants that only part of the wastwater has been diverted to the cooling tower. The overall temperature of the combined wastewater should be less than 50 °C. A cooling tower is typically a forced air cooling tower where the wastewater is contacted with ambient air. In the mass transfer with the ambient air, volatile organics can transfer to the air along with the water.

TABLE 6-2. MODEL PLANT OPERATIONAL PARAMETERS: TRICKLING FILTER

Parameter	Value	
Plant Flow	6.4 MGD (0.28 m^3/s)	
Plant Performance	85 percent BOD Removal 75 percent Suspended Solids Removal	
Influent BOD	183 mg/1	
Influent Suspended Solids	188 mg/1	
Trickling Filter	Diameter	190 ft (58 m)
	Depth	5 ft (1.5 m)
	Area	28353 ft^2 (2640 m^2)
	Volume	141764 ft^3 (3960 m^3)
	Hydraulic loading	29 MGD/acre (1.1 m3/m^2-hr)
	Recirculation	190 percent
Clarifiers	Diameter	100 ft (30 m)
	Depth	9.2 ft (2.8 m)
	Area	7854 ft^2(730 m^2)
	Weir height	1 ft (30 cm)
	Surface loading	1350 gal/ft^2/day (0.47 m^3/m^2-day)
	Detention time	1.2 hours

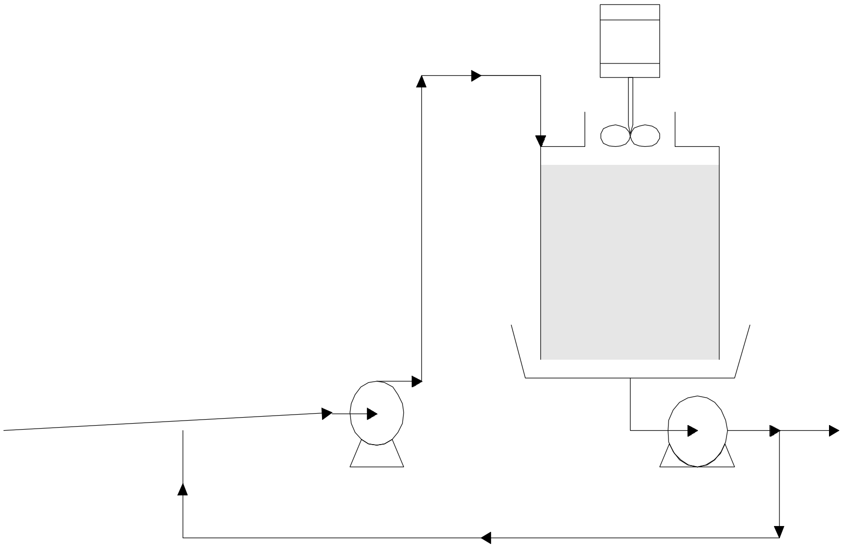

Figure 6-2. Cooling tower.

6.3.1 Cooling Tower Default Parameters

The typical operating conditions of cooling towers at pulp and paper mills are presented in Table 6-3.[3]

6.3.2 Performance Data of Cooling Towers

Reference 3 indicates in the abstract that 25 percent to 30 percent BOD reduction (presumably predominantly methanol) can be achieved by cooling tower treatment. This corresponds to physical stripping of volatile components at a rate of 60,000 lb BOD/day or 11,000 tons BOD/year from a Kraft linerboard mill of 850 ton/day. The wastes treated included the pulp mill condensates, the decker filtrate, turpentine decanter underflow, and the condenser waters from a barometric type evaporator.

The BOD removal in a laboratory cooling tower was related to the liquid to gas ratio. Lower liquid rates permitted a cooling tower to remove up to 70 percent of the BOD. There was some evidence of biodegradation contributing to the removal of BOD in the cooling tower, up to 15 percent of the total BOD removal. It was demonstrated that the main removal mechanism was air stripping.

Figure 6-1 illustrates a cooling tower with recycle. Some of the cooled water is recycled to the entrance of the cooling tower. This permits multiple passes of part of the wastewater being treated with the cooling tower. basins are located before the biological units. It has been observed in several plants that only part of the wastwater has been diverted to the cooling tower.

6.3.3 Air Emission Modeling for Cooling Tower

The method selected for the modeling of air emissions from a cooling tower is to model both the mass transfer of water and the mass transfer of methanol by the same mechanism. The predicted performance of the cooling tower would then be subject to

TABLE 6-3 TREATMENT OF SELECTED INTERNAL KRAFT MILL WASTES IN A COOLING TOWER.

Parameter	Value
Air velocity	200-600 ft/min
Waste loading	1-4 gal/min-ft^2
Inlet temperature	50 C
Exit temperature	32 C
Recycle ratio for treatment	0.8 gal recycled/gal leaving the tower
Blowdown	15 percent to 20 percent of tower flow
Recycle ratio for cooling	none, assumed for current case

verification and model parameter adjustment by temperature measurements. The overall mass transfer of the methanol in the cooling tower is given by the two resistance model. In the case of water, the resistance of the liquid phase is negliable.

$$K_{ol} = \left(\frac{1}{K_l} + \frac{1}{40.9K_g\ H} \right)^{-1} \tag{6-1}$$

where, the above equation has the following variables and units:

K_{ol}	cm/s	overall mass transfer coefficient;
K_l	cm/s	liquid phase mass transfer coefficient;
K_g	cm/s	gas phase mass transfer coefficient;
H	atm-m3/mol	Henry's law constant; and
40.9	mol/atm-m3	1/RT (at 25C, R is the gas constant).

For computational purposed, the cooling tower is divided into ten equal sections by partitioning with imaginary horizontal planes. The number of moles transferred in each volume element of the cooling tower is given by the following equation:

$$\frac{dm}{dt} = \frac{K_{ol}}{18} A \left(x_{lL} - \frac{Y}{K} \right) \tag{6-2}$$

where, the above equation has the following variables and units:

dm	mols	mols transferred to the gas phase;
t	sec	time;
K_{ol}	cm/s	overall mass transfer coefficient;
A	cm2	wetted surface area in tower section;
x_{lL}		mol fraction methanol in water;
18	cm/s per mol/cm2-s-mol fraction;	
K	y/x	Henry's law constant; and
y		mol fraction methanol in the gas.

The mass transfer is calculated for each of the ten segments in the cooling tower. The values of the temperature of the gas, the temperature of the liquid, the equilibrium concentration of water vapor, the flow rate of the gas phase, and the Henry's law value is calculated separately for each of the segments in the cooling tower.

6.3.4 Material Balance with Recycle

The following terms describe the cooling tower recycle concentrations:

x_i = the inlet mol fraction of the wastewater;
x_{out} = the outlet mol fraction of the treated wastewater;
f = the fraction of the component removed each treatment pass;
r = the recycle fraction of the cooling tower water;
c = the ratio of x_{out} to x_i; and
F = the overall fraction removed by the cooling tower.

The overall removal may be written as follows:

$$C = (1 - F) \tag{6-3}$$

$$F = \frac{(x_i - x_{out})}{x_i} \tag{6-4}$$

On a single pass the removal is a function of the inlet and outlet concentrations:

$$f = (x_i (1-r) + x_{out} (r) - x_{out}) / (x_i (1-r) + x_{out} (r)) \tag{6-5}$$

or,

$$f = (1-r + c\ r - c) / (1-r + c\ r) \tag{6-6}$$

Rearranging the previous equation,

$$f - fr + fcr = 1 - r + cr - c \tag{6-7}$$

Substituting the equation for c into the above equation,

$$f - fr + fr(1 - F) = 1 - r + (r - 1)(1 - F) \qquad (6\text{-}8)$$

Solving for f, an equation is obtained which relates the single pass removal to the removal with recycle:

$$f = \frac{(1 - r)F}{1 - r + r(1 - F)} \qquad (6\text{-}9)$$

Reference 3 reported 20 to 30 percent removal of methanol with a recycle ratio of r = 0.8. Assuming an average value of 25 percent removal, F = 0.25. Substituting the values of r and F into the above equation, the single pass removal fraction f is estimated as 0.0625.

$$0.0625 = \frac{(1 - 0.8)0.25}{1 - 0.8 + 0.8(1 - .25)}$$

With 15 percent removal under the same conditions, the single pass removal fraction f is estimated as 0.034. From the available data from Table 6-3, it is concluded that the removal of methanol in the wastewater treated in a cooling tower is between 3 and 6 percent. Greater removal of methanol is expected with cooling tower recycle.

6.4 ESTIMATION OF AIR EMISSIONS FROM API SEPARATOR UNITS

This section presents the model for the API separator and illustrates the use of the model with a sample calculation. The API separator model is composed of three regions: the flow distribution region, the separation region, and the exit region that may have flow over a weir. The total air emissions are the sum of the air emissions from the three regions.

6.4.1 API Separator Model Elements

The API separator is modeled as the unit which separates oil from the wastewater. If additional units are used to treat the wastewater before separation in the API unit, those additional units should be modeled separately. Also, if additional units are used to dewater the oil by heating or other methods, those additional oil units should be modeled separately.

6.4.1.1 <u>Region 1 flow distribution</u>. The mass transfer from the wastewater in the flow distribution region is characterized by the resistance of two phases, the liquid phase resistance and the gas phase resistance. The overall mass transfer from this two-resistance model, K , is a combination of the gas and the liquid mass transfer coefficients:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\ K_g\ K\ f_p} \right)^{-1} \qquad (6\text{-}10)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s);

f_p = the fraction of the compound in the water phase; and

K = the partition coefficient (atm-m^3/mol).

K_g is estimated by:

$$K_g = 0.00482 \left(\frac{V}{100} \right)^{.78} \left(\frac{dia}{100} \right)^{-.11} \left(\frac{0.0012\ \ D_g}{0.000181} \right)^{.67}$$

K_l is estimated by:

$$K_l = 2.61\ 10^{-7} \left(\frac{V}{100} \right)^{2} \left(\frac{D_l}{0.0000085} \right)^{.67}$$

where,

V = the wind velocity at 10 meters over the surface (cm/s);

dia = the width of the region (cm);

D_g = the gas phase diuffusivity (cm^2/s); and

D_l = the liquid phase diffusivity (cm^2/s).

The fraction of the compound in the water phase is used to correct the partitioning in the gas phase. The fraction of the compound in the water phase is estimated from the octanol-water partition coefficient.

$$OWR = \frac{OWPC \;\; oilfract}{1 - oilfract} \qquad (6-11)$$

$$f_o = \frac{OWR}{1 + OWR} \qquad (6-12)$$

$$F_p = 1 - f_o \qquad (6-13)$$

where,

OWPC = the octanol water partition coefficient;

oilfract = the fraction of the waste that is oil and insoluble in water;

OWR = the ratio of the amount in oil to the amount in the water;

f_o = the fraction of the component in the oil phase; and

f_p = the fraction of the component in the water phase.

The air losses, f_{air1}, from the two-resistance model are as follows:

$$f_{air1} = 1 - EXP\left(- \frac{K_o\ A}{q} \right) \qquad (6-14)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate (m^3/s);

A = the surface area of the region (m^2); and

f_{air1} = the liquid flow rate (m^3/s),

6.4.1.2 Region 2 oil film separation. The mass transfer from the floating oil on the wastewater surface is characterized by a resistance of only one phase, the gas phase resistance. The overall mass transfer from this one resistance model, K_o, is estimated as follows:

$$K_o = 240\ K_g\ K_{eq} \tag{6-15}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_g = the gas phase mass transfer coefficient (identical to region 1, m/s);

K_{eq} = the partition between the gas phase and the oil phase; and

K = the partition coefficient ($atm\text{-}m^3/mol$).

The fraction of the compound in the water phase is used to correct the partitioning in the gas phase. The fraction of the compound in the water phase is estimated from the octanol-water partition coefficient as described above.

The partition between the gas phase and the oil phase is estimated as follows:

$$K_{eq} = \frac{0.0012\ \ V_p\ \ mwt}{\rho\ \ 28.8\ \ 760} \tag{6-16}$$

where,

V_p = the vapor pressure of the pure component at the surface temperature (mm Hg);

mwt = the molecular weight of the compound (g/g-mol); and

D = the liquid density (g/cm^3).

The air losses, f_{air2}, from the one-resistance model are as follows:

$$f_{air2} = 1 - EXP\left(\frac{-f_o\ K_o\ A}{q}\right) \tag{6-17}$$

where

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate (m^3/s);

f_o = the fraction of the compound in the oil phase;

A = the surface area of the region (m^2); and

f_{air2} = the liquid flow rate (m^3/s).

The concentration in the oil phase on the surface is assumed to be in equilibrium with the concentration in the aqueous phase. The exponential form of the estimation of f_{air2} prevents the possibility of estimating air emissions that are in excess of the total amount present.

Some of the component will be removed with the oil that is removed from the surface. The fraction in the oil is estimated with the following equation. Components removed with the oil are not available for contributing to air emissions in region 3.

$$f_{roil} = \left(1 - f_{air1}\right)\left(1 - f_{air2}\right) f_o \tag{6-18}$$

6.4.1.3 Region 3 weir overflow. The air emissions from the weir outfall of the API separator are estimated by a modification of the weir model presented by Nakasone.[4] The equations used in this method are presented in this section.

$$\ln(r) = 0.0785\ Z^{1.31}\ q^{0.428}\ h^{0.310} \qquad (6\text{-}19)$$

where,

r = Cs/(Cs-Co) deficit ratio, assumes that there is no oxygen before the weir;

Cs = saturated oxygen concentration;

Co = outlet oxygen concentration;

Z = distance of fall (m), includes 1.5 times the distance from the weir top to the critical depth above the weir;

q = flow rate per length of weir (m3/h-m); and

h = the tailwater depth (m).

It is assumed that the rate limiting step for the diffusion of oxygen is the mass transfer in the liquid phase (oxygen is only slightly soluble in the water). From the following equation, a value of the liquid phase mass transfer coefficient can be estimated for volatile organics, after correcting for the relative diffusion coefficient of the organic and oxygen in water.

$$K_l\left(\frac{m}{s}\right) = \frac{q}{Z}\left(\frac{D_{lv}}{D_{lo}}\right)^{0.66} \ln(r)\left(\frac{hr}{3600\ s}\right) \qquad (6\text{-}20)$$

where,

K_l = the mass transfer coefficient of the volatile organic in water (m/s);

ln(r) = the natural log of the deficit ratio for oxygen in the water flowing over the weir;

D_{lv} = the diffusion coefficient of the volatile organic in water (cm^2/s);

D_{lo} = the diffusion coefficient of oxygen in water (0.000024 cm^2/s);

Z = distance of fall (m), includes 1.5 times the distance from the weir top to the critical depth above the weir; and

q = flow rate per length of weir (m^3/h-m).

The gas phase mass transfer coefficient of the flow at the weir is estimated as 0.05 m/s for benzene. This is approximately the magnitude for mechanically aerated systems. The assumption of a gas phase mass transfer coefficient of this magnitude will lower the estimate of the oxygen transfer from the correlation by only a few percent. Significantly lower gas phase mass transfer coefficients will lower the predicted oxygen transfer to an extent not predicted by the correlation.

$$k_g \left(\frac{m}{s} \right) = 0.05 \left(\frac{D_{gv}}{D_{go}} \right)^{0.66} \qquad (6\text{-}21)$$

where,

k_g = the mass transfer coefficient of the volatile organic in air (m/s);

D_{gv} = the diffusion coefficient of the volatile organic in air (cm^2/s);

D_{go} = the diffusion coefficient of the reference material in air (0.088 cm^2/s); and

0.05 = the assumed mass transfer coefficient of a turbulent surface.

The value of the overall mass transfer coefficient is estimated by combining the liquid and gas mass transfer coefficients.

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\ K_g\ K} \right)^{-1} \qquad (6\text{-}22)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s); and

K = the partition coefficient (atm-m^3/mol).

The fraction of the volatile components that are emitted to the air is estimated by the following relationship:

$$f_{air} = 1 - \mathrm{EXP}\left(- \frac{K_o\ Z}{q} \frac{3600\ \mathrm{sec}}{\mathrm{hr}} \right) \qquad (6\text{-}23)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate per length of the weir(m^3/h-m);

Z = the distance of fall (m); and

f_{air} = the fraction of the volatile component emitted to the air.

6.4.2 Example Calculation

It is assumed that an aqueous stream with 1 percent dispersed oil is cleaned in an open API separator. The oil stream is stored in a heated fixed roof tank to remove the water from the oil. The heated tank is vented without a condenser to the atmosphere. In this example the air emissions of benzene is estimated from the separator unit.

The open API oil/water separator used for the example calculations was characterized as having three regions, an entrance distribution region of 20 m^2, a separation region where the floating oil was removed, and a third region with a weir.

Since the concentration of benzene in the wastewater is not specified, the estimates of air emissions should be expressed in fraction of inlet benzene that is lost to the atmosphere.

6.4.2.1 <u>Properties of benzene and unit specifications</u>. Properties of benzene as well as the constants needed for the sample calculations are presented in Tables 6-4 and 6-5.

6.4.2.2 <u>Region 1 Calculations.</u> The fraction of the compound in the water phase is used to correct the partitioning in the gas phase. The fraction of the compound in the water phase is estimated from the octanol-water partition coefficient:
where,

$$OWR = \frac{OWPC \quad oilfract}{1 - oilfract} \qquad (6-24)$$

$$0.412 = 1 - 0.588$$

$$1.4268 = \frac{141.25\,(0.01)}{1 - 0.01}$$

$$F_o = \frac{OWR}{1 + OWR}$$

$$0.588 = \frac{1.4268}{1 + 1.4268}$$

TABLE 6-4. PROPERTIES OF BENZENE USED FOR SAMPLE CALCULATIONS

Variable	Symbol	Number and units
Diffusivity in water	Dl	0.98 x 10^{-5} cm^2/s
Diffusivity in air	Dv	.088 cm^2/s
Molecular weight	Mwt	78 g/g-mol
Henry's law constant	H	0.00555 atm-m^3/mol
Diffusivity O_2 in water	Do	2.5 x 10^{-5} cm^2/s
Vapor pressure benzene	vp	95.2 mm Hg
Octanol water partition coefficient	owpc	141.25

TABLE 6-5. UNIT PARAMETER NAMES AND SPECIFICATIONS FOR EXAMPLE CALCULATIONS.

Unit Specification	Symbol	Variable Name	Value
Wastewater flow rate	q	q	0.10 m^3/s
Wind speed	v	v	447 cm/s
Number of units	n	n%	1
Temperature	T	T	25 deg. C
Region 1 area		area.enter	20 m^2
Region 2 area		area.oil	50 m^2
Oil in waste	fo	oilfract	0.01
Density of oil	do	densoil	0.7 g/cm^3
Oil molecular weight	mwt	mwtoil	180
Waterfall drop height	h	drop	20 cm
Waterfall width	w	widthfall	4 m

OWPC = the octanol water partition coefficient;

oilfract = the fraction of the waste that is oil and insoluble in water;

OWR = the ratio of the amount in oil to the amount in the water;

f_o = the fraction of the component in the oil phase; and

f_p = the fraction of the component in the water phase.

$$f_p = 1 - f_o$$

The effective diameter of the region 1 surface is estimated with the following general equations:

$$\text{dia} = \sqrt{\frac{\text{Area}\,(4)}{\pi}} \qquad (6\text{-}25)$$

$$505\ \text{cm} = \sqrt{\frac{20\ \text{m}^2\,(4)}{\pi}}\left(100\ \frac{\text{cm}}{\text{m}}\right)$$

In region 1, the area is 20 m^2 (see Table 6-5). The mass transfer from the wastewater in the flow distribution region is characterized by two phases, the liquid phase resistance and the gas phase resistance. The overall mass transfer from this two-resistance model, K, is a combination of the gas K_g and the liquid mass transfer coefficients K_l. K_g is estimated by:

$$K_g = 0.00482\ \left(\frac{V}{100}\right)^{.78}\ \left(\frac{\text{dia}}{100}\right)^{-.11}\ \left(\frac{0.0012\quad D_v}{0.000181}\right)^{.67}$$

$$k_g = 0.00482\ \left(\frac{447}{100}\right)^{.78}\ \left(\frac{505}{100}\right)^{-.11}\ \left(\frac{(0.0012)\quad(0.088)}{0.000181}\right)^{.67}$$

$$k_g = 9.04\ 10^{-3}\ \frac{m}{\text{sec}}$$

K_l is estimated by:

$$K_l = 2.61\ 10^{-7} \left(\frac{V}{100}\right)^2 \left(\frac{D_l}{0.0000085}\right)^{.67}$$

where,

V = the wind velocity at 10 meters over the surface (447 cm/s);

dia = the width of the region (505 cm);

D_g = the gas phase diuffusivity (0.088 cm^2/s); and

D_l = the liquid phase diffusivity (0.98 10^{-5} cm^2/s).

$$k_l = 2.61\ 10^{-7} \left(\frac{447}{100}\right)^2 \left(\frac{0.0000098}{0.0000085}\right)^{.67}$$

$$k_l = 5.73\ 10^{-6}\ \frac{m}{sec}$$

The overall mass transfer can then be written as follows:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\ K_g\ K\ f_p}\right)^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (5.736 10^{-6} m/s);

K_g = the gas phase mass transfer coefficient (9.04 10^{-3} m/s);

f_p = the fraction of the compound in the water phase, 0.4121; and

K = the partition coefficient (0.0055 atm-m^3/mol).

$$K_o = \left(\frac{1}{(5.736)\ (10^{-6})} + \frac{1}{(40.9)\ \ (9.04)\ (10^{-3})\ (0.00555)\ (0.412)}\right)^{-1}$$

$$K_o = 5.697 \cdot 10^{-6} \frac{m}{\text{sec}}$$

The air losses, f_{air1}, from the two-resistance model are as follows, using Equation 6-14:

$$f_{air1} = 1 - EXP\left(-\frac{K_o\ A}{q}\right)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (5.697 10^{-6} m/s);

q = the liquid flow rate (0.10 m^3/s);

A = the surface area of the region (20 m^2); and

f_{air1} = the fraction emitted to the air in the entrance region.

$$f_{air1} = 1 - EXP\left(-\frac{(5.697)\ (10^{-6})\ (20)}{0.10}\right)$$

$$f_{air1} = 0.001139$$

6.4.2.3 Region 2 calculations. Oil floats to the surface of region 2, where it is removed. Since the refinery is assumed to be operating without abnormal problems, the oil is a relatively small fraction of the wastewater and the concentration in the oil is assumed to be in equilibrium with the water. The partition between the gas phase and the oil phase is estimated as follows, using Equation 6-16:

where,

V_p = the vapor pressure of the pure component at the surface temperature (95.2 mm Hg);

mwt = the molecular weight of the oil (180 g/g-mol); and

D = the oil density (0.7 g/cm^3).

$$K_{eq} = \frac{0.0012 \quad V_p \quad mwt}{\rho \quad 28.8 \quad 760}$$

$$K_{eq} = \frac{(0.0012) \quad (95.2) \quad (180)}{(0.7) \quad (28.8) \quad (760)}$$

$$K_{eq} = 0.00134$$

The mass transfer from the thin floating oil layer on the wastewater surface is characterized a resistance of only one phase, the gas phase resistance. The overall mass transfer from this one resistance model, K, is estimated as follows:

$$K_o = K_g \; K_{eq} \qquad (6\text{-}27)$$

$$K_o = (0.00904) \; (0.00134)$$

$$K_o = 1.19 \cdot 10^{-5} \; \frac{m}{sec}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_g = the gas phase mass transfer coefficient (identical to region 1, m/s); and

K_{eq} = the partition between the gas phase and the oil phase, 0.001342.

The fraction of the compound in the water phase is used to correct the partitioning in the gas phase. The fraction of the compound in the water phase is estimated from the octanol-water partition coefficient as described above.

The air losses, f_{air2}, from the one-resistance model are as follows:

$$f_{air2} = 1 - \mathrm{EXP}\left(- \frac{K_o \; A \; \mathrm{owpc}}{q} \right) \qquad (6-27)$$

$$f_{air2} = 1 - \mathrm{EXP}\left(- \frac{1.19 \cdot 10^{-5} \; (50) \; (144.2)}{0.10} \right)$$

$$f_{air2} = 0.576$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (1.19 10^{-5} m/s);

q = the liquid flow rate (0.10 m^3/s);

A = the surface area of the region (50 m^2); and

f_{air2} = the fraction emitted to the air in region 2.

The concentration in the oil phase on the surface is assumed to be in equilibrium with the concentration in the aqueous phase. The exponential form of the estimation of f_{air} prevents the possibility of estimating air emissions that are in excess of the total amount present.

Some of the component will be removed with the oil that is removed from the surface. The fraction in the oil is estimated with the following equation. Components removed with the oil are not available for contributing to air emissions in region 3.

$$f_{roil} = \left(1 - f_{air1}\right) \left(1 - f_{air2}\right) \; f_o \qquad (6-29)$$

$$f_{roil} = \left(1 - 0.001139\right) \left(1 - 0.576\right) \; 0.588$$

$$f_{roil} = 0.25$$

6.4.2.4 Weir calculations. In the case of benzene, the deficit ratio is calculated using the following factors:

$$\ln (r) = 0.0785\ Z^{1.31}\ q^{0.428}\ h^{0.310} \qquad (6\text{-}30)$$

$$\ln (r) = 0.0785\ (0.2)^{1.31}\ (90)^{0.428}\ (0.3)^{0.310}$$

$$\ln (r) = 0.04503$$

where the above constants are for the situation where $Z < 1.2$ m and $q < 235$,

r = Cs/(Cs-Co) deficit ratio, assumes that there is no oxygen before the weir,

Cs = saturated oxygen concentration,

Co = outlet oxygen concentration,

Z = distance of fall (0.2 m), includes 1.5 times the distance from the weir top to the critical depth above the weir,

q = flow rate per length of weir (90 m3/h-m), and

h = the tailwater depth (.3 m).

The natural log of the deficit ratio, ln(r), is calculated as 0.20363. Next, the liquid phase mass transfer coefficient is estimated:

$$K_l \left(\frac{m}{s}\right) = \frac{q}{Z} \left(\frac{D_{lv}}{D_{lo}}\right)^{0.67} \ln(r) \left(\frac{hr}{3600\ s}\right) \qquad (6\text{-}31)$$

$$0.003 \left(\frac{m}{s}\right) = \frac{90}{0.2} \left(\frac{0.98}{2.4}\right)^{0.66} 0.04503 \left(\frac{hr}{3600\ s}\right)$$

Next, the gas phase mass transfer coefficient of toluene is estimated, based upon the reference mass transfer coefficient of benzene.

$$k_g \left(\frac{m}{s} \right) = 0.05 \left(\frac{D_{gv}}{D_{go}} \right)^{0.66} \qquad (6\text{-}32)$$

where,

Kg = the mass transfer coefficient of the volatile organic in air (m/s);

Dgv = the diffusion coefficient of the volatile organic in air (0.088 cm2/s);

Dgo = the diffusion coefficient of the reference material in air (0.088 cm2/s); and

0.05 = the assumed mass transfer coefficient of a turbulent surface.

$$0.05 \left(\frac{m}{s} \right) = 0.05 \left(\frac{0.088}{0.088} \right)^{0.66}$$

The estimated gas phase mass transfer coefficient is 0.05 m/s. Next, the overall mass transfer coefficient is calculated.

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9 \ K_g \ K} \right)^{-1}$$

$$0.00241 = \left(\frac{1}{0.003} + \frac{1}{40.9 \ 0.05 \ 0.00555} \right)^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (0.00305 m/s);

K_g = the gas phase mass transfer coefficient (0.05 m/s); and

K = the partition coefficient (0.00555 atm-m^3/mol).

The overall mass transfer coefficient is 0.00241 m/s. Next, the fraction of air emissions is estimated.

$$f_{air} = 1 - EXP\left(- \frac{K_o\ Z}{q}\ \frac{3600\ sec}{hr}\right)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (0.000868 m/s);

q = the liquid flow rate per length of the weir (90 m^3/h-m);

Z = the distance of fall (0.2 m); and

f_{air} = the fraction of the volatile component emitted to the air.

$$0.019 = 1 - EXP\left(- \frac{0.00241\ (0.2)}{90}\ \frac{3600\ sec}{hr}\right)$$

The fraction of benzene that is emitted to the air due to the weir drop is 0.019.

$$f_{air1} = f_{rEnt} + (1 - f_{rEnt})\ f_{roil} + (1 - f_{rEnt})\ (1 - f_{roil})\ (1 - f_{rinoil})\ f_{rwf}$$

$$f_{air1} = 0.0012+(1-0.0012)\,.576+(1-0.0012)(1-0.576)(1-.25)\ 0.019$$

$$f_{air1} = 0.584$$

The overall fraction of benzene that is emitted from the API separator is as follows:

f_{rEnt} = the fraction lost from the entrance region, 0.001139;

f_{roil} = the fraction lost from the separator region, 0.576;

f_{rinoil} = the fraction removed by the recovered oil, 0.25; and

f_{rwf} = the fraction lost from the waterfall; 0.019.

The overall loss of benzene from the API separator as air emissions is estimated as 0.584. This does not include the fraction recovered in the oil. Estimates of air emissions from the recovered oil are not included in this unit.

6.5 MODEL FOR PRETREATMENT UNITS

In the entrance to a wastewater treatment plant, a pretreatment unit can be used to remove solid objects, grit, or other items that can be separated from the wastewater. The following model is recommended for the estimation of air emissions from a pretreatment unit.

This section provides the following:

- the equations used for the estimation, and
- an example calculation.

6.5.1 Pretreatment Equations

This section presents the model for the pretreatment unit and illustrates the use of the model with a sample calculation. The pretreatment unit has an agitated surface, and can contain agitation by forced submerged air. The total air emissions are the sum of the air emissions from the surface volatilization and the submerged air flow.

If oil is present in the unit, some of the volatile materials will partition into the oil and reduce the concentrations in the water phase.

The mass transfer from the surface of the wastewater in the pretreatment unit is characterized by the resistance of two phases, the liquid phase resistance and the gas phase resistance. The overall mass transfer from this two-resistance model, K, is a combination of the gas and the liquid mass transfer coefficients in Equation 6-10:

$$K_o = \left(\frac{1}{K_l} + \frac{1}{40.9\ K_g\ K\ f_p} \right)^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (m/s);

K_g = the gas phase mass transfer coefficient (m/s);

f_p = the fraction of the compound in the water phase; and

K = the partition coefficient (atm-m^3/mol).

K_g is estimated by

$$K_g = \frac{100}{24300}\left(0.001 + \frac{0.000462\ US}{NSCH^{0.67}}\right)$$

$$US = (6.1 + 0.0063\ v)^{0.5}\ \frac{v}{100}$$

$$K_1 = 0.001$$

$$NSCH = \frac{0.5}{D}$$

where,

V = the wind velocity at 10 meters over the surface (cm/s); and

D_g = the gas phase diffusivity (cm^2/s).

The fraction of the compound in the water phase is used to correct the partitioning in the gas phase. The fraction of the compound in the water phase is estimated from the octanol-water partition coefficient.

$$OWR = \frac{OWPC \quad oilfract}{1 - oilfract}$$

$$f_p = 1 - f_o$$

$$f_o = \frac{OWR}{1 + OWR}$$

where:

OWPC = the octanol water partition coefficient,

oilfract = the fraction of the waste that is oil and insoluble in water,

OWR = the ratio of the amount in oil to the amount in the water,

f_o = the fraction of the component in the oil phase, and

f_p = the fraction of the component in the water phase.

The air losses, f_{air}, from the two-resistance model are as follows, from Equation 6-14:

$$f_{air1} = 1 - EXP\left(-\frac{K_o\ A}{q}\right)$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

q = the liquid flow rate (m^3/s);

A = the surface area of the region (m^2); and

f_{air1} = the liquid flow rate (m^3/s).

6.5.2 Pretreatment Examples

It is assumed that an aqueous stream with no dispersed oil is pretreated in a bar screen unit. The open-bar screen unit used for the example calculations was characterized as having a turbulent region of 20 m^2. Since the concentration of benzene in the wastewater is one part per million by weight. Properties of benzene as well as the constants needed for the sample calculations are presented in Tables 6-6 and 6-7.

The fraction of the compound in the water phase is used to correct the partitioning in the gas phase. The fraction of the compound in the water phase is estimated from the octanol-water partition coefficient.

$$\mathrm{OWR} = \frac{\mathrm{OWPC} \quad \mathrm{oilfract}}{1 - \mathrm{oilfract}}$$

$$f_o = 0$$

$$f_o = \frac{\mathrm{OWR}}{1 + \mathrm{OWR}}$$

$$F_o = 0$$

$$f_p = 1 - f_o$$

$$f_p = 1$$

where,

OWPC = the octanol water partition coefficient;

oilfract = the fraction of the waste that is oil and insoluble in water;

OWR = the ratio of the amount in oil to the amount in the water;

f_o = the fraction of the component in the oil phase; and

f_p = the fraction of the component in the water phase.

The effective diameter of the region 1 surface is 20 m^2. The mass transfer from the wastewater in the flow distribution region is characterized by two phases, the liquid phase resistance and the gas phase resistance. The overall mass transfer from this two-resistance model, K, is a combination of the gas K_g and the liquid mass transfer coefficients K_l. K_g is estimated by the following calculations. (See TABLE 4-1) The Schmidt number, N_{SCH}, and the friction velocity U* are needed for the calculation of K_g.

$$N_{SCH} = \frac{0.5}{0.088}$$

TABLE 6.6 PROPERTIES OF BENZENE USED FOR SAMPLE CALCULATIONS

Variable	Symbol	Number and units
Diffusivity in water	Dl	0.98×10^{-5} cm^2/s
Diffusivity in air	Dv	.088 cm/s2
Molecular weight	Mwt	78 g/g-mol
Henry's law constant	H	0.00555 atm-m3/mol
Diffusivity O2 in water	Do	2.5×10^{-5} cm^2/s
Vapor pressure benzene	vp	95.2 mm Hg
Octanol water partition coefficient	owpc	141.25

TABLE 6-7. UNIT PARAMETER NAMES AND SPECIFICATIONS FOR EXAMPLE CALCULATIONS.

Unit Specification	Symbol	Variable Name	Value
Wastewater flow rate	q	q	0.10 m^3/s
Wind speed	v	v	447 cm/s
Number of units	n	n%	1
Temperature	T	T	25 deg. C
Region 1 area		area.enter	20 m^2
Oil in waste	fo	oilfract	0.00
Density of oil	do	densoil	0.7 g/cm^3
Oil molecular weight	mwt	mwtoil	180

$$U^{*} = \left(6.1 + 0.0063 \ 447 \right)^{0.5} \ \frac{447}{100}$$

$$U^{*} = 13.35$$

$$K_g = \frac{100}{24300} \left(0.001 + \frac{0.000462 \ 13.35}{1.7^{0.67}} \right)$$

upon evaluation, the liquid mass transfer coefficient is specified:

$$K_l = 0.001 \quad (\mathrm{m/s})$$

$$K_g = 2.178 \ 10^{5} \quad (\mathrm{g \ mol/cm2{-}s})$$

The overall mass transfer can then be written as follows, from Equation 6-10:

$$K_o = (\frac{1}{K_l} + \frac{1}{40.9 \ K_a \ K \ f_p})^{-1}$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations (m/s);

K_l = the liquid phase mass transfer coefficient (0.001 m/s);

K_g = the gas phase mass transfer coefficient (2.187 10^{-3} m/s);

f_p = the fraction of the compound in the water phase, 1; and

K = the partition coefficient (0.0055 atm-m^3/mol).

$$5.48 \ 10^{-4} \ \frac{m}{\mathrm{sec}} = (\frac{1}{0.001} + \frac{1}{(40.9) \ (2.187) \ (10^{-5}) \ (0.00555) \ (1)})^{-1}$$

The air losses, fair, from the two-resistance model are as follows from Equation 6-14:

$$f_{air1} = 1 - EXP\,(- \frac{K_o\ A}{q})$$

where,

K_o = the overall mass transfer coefficient based upon the liquid concentrations ($5.48\ 10^{-4}$ m/s);

q = the liquid flow rate (0.10 m^3/s);

A = the surface area of the region (20 m^2); and

f_{air1} = the fraction emitted to the air in the entrance region.

$$f_{air1} = 1 - EXP\,(- \frac{(5.48)\ (10^{-4})\ (20)}{0.10})$$

$$f_{air1} = 0.104$$

6.6 REFERENCES

1. GCA Corporation, Hazardous Waste TSDF Process Sampling. EMB Report 85-HWS-3. October, 1985.

2. U.S. Environmental Protection Agency. Municipal Operations Branch. Process Control Manual for Aerobic Biological Wastewater Treatment Facilities. Publication No. EPA-430/9-77-006. March 1977.

3. Treatment of Selected Internal Kraft Mill Wastes in a Cooling Tower. Georgia Kraft Co. Rome Georgia. August 1971. NTIS 208 217.

4. Nakasone, H. Study of Aeration at Weirs and Cascades. *Journal of Environmental Engineering, ASCE.* 113:64. 1987.

7.0 LAND TREATMENT

This chapter presents the approach used to estimate air emissions from land treatment operations. A mathematical model for diffusion in porous media with simultaneous sorption and biodegradation is presented for estimating emissions from land treatment operations. This model is also applicable to spills, excavations of contaminated soils, solid waste transfer operations, and other situations involving the diffusion of volatile organics in porous media. Analytical models to estimate the air emissions, representative values of land treatment model input parameters, and example calculations are included.

7.1 NARRATIVE DESCRIPTION OF LAND TREATMENT AIR EMISSIONS

Land treatment is one of several land disposal methods used for final disposition of hazardous wastes. At land treatment facilities, wastes are either spread onto or injected into the soil, after which they are normally tilled into the soil. Other activities likely to occur at land treatment facilities include storage of wastes in tanks or surface impoundments, loading and unloading of wastes in vacuum trucks or dump trucks, and dewatering of wastes using filtration devices. All of these activities have emission points associated with them. The following paragraphs describe analytical models used to estimate emissions from the application, tilling, and final disposition of hazardous waste at a land treatment disposal site. Emissions from other land treatment activities, such as truck loading, storage tanks, and fugitive emissions from transfer and handling operations, are estimated using procedures described in Chapter 9 of this report.

Estimating emissions from land treatment may involve one to three independent steps depending on operating practices at a land treatment site. If waste is applied from a vacuum truck to the soil surface, allowed to remain on the surface for a period of time, and then tilled into the soil, emissions are estimated in three steps: (1) during application of waste onto the soil from a vacuum truck, (2) after waste application and before tilling, and (3) after tilling the waste into the soil. If waste is applied to the soil surface and immediately tilled into the soil, emissions are estimated in only two steps: (1) during waste application, and (2) after tilling. If waste is applied by subsurface injection and immediately tilled, only one step is required to estimate emissions.

This section presents three separate analytical models that can be used to estimate air emissions from separate land treatment activities. Primary emphasis is given to the RTI land treatment model that is used to calculate emissions from waste that is mixed with the soil. This condition may exist when waste has been applied to the soil surface and has seeped into the soil or when waste has been injected beneath the soil surface or has been tilled into the soil. The RTI land treatment model is described below in Subsection 7.2.1, which includes separate discussions of the following topics:

Subsection	Topic
7.2.1.2	Biodegradation
7.2.1.4	Effective diffusivity
7.2.1.5	Waste partitioning
7.2.1.10	Model selection rationale

After waste is applied to the surface of the soil by spray application, it seeps into the soil. While the waste is on the surface, the concentrations at the surface can be approximated by the concentration in the waste. During this short period that the waste covers the surface of the soil, the maximum short-term emission rate is expected. For this special case, emissions are estimated as the product of an overall mass transfer coefficient, constituent concentration, and surface area of the land treatment site. The model for estimating the mass transfer coefficient from the surface to the wind was developed by McKay and Matsuga and is briefly discussed in Subsection 7.2.3.

Emissions from a waste stream as it is applied onto the soil surface from a vacuum truck, regardless of waste type, are also calculated as the product of an overall mass transfer coefficient, the surface area of the waste stream, and the concentration of a specific constituent. Preliminary calculations indicate that emissions from the spraying waste application are relatively small and can be ignored in most situations. Even so, a brief discussion of a model for estimating these emissions is presented in Subsection 7.2.2, and the model can be used if desired. Also included in this section are Subsection 7.2.4, which discusses representative values of input parameters for the analytical models, and Subsection 7.2.6, which presents example calculations using each of the three models presented.

At many existing land treatment sites, waste is applied onto the soil from a vacuum truck and is allowed to remain for about 24 hours before being tilled into the soil. Under these conditions, three separate calculations may be needed to estimate air emissions. Emissions during waste application could be estimated using the waste application model described in Subsection 7.2.2; emissions after application but before tilling would be estimated using the RTI land treatment model as described in Subsection 7.2.1 (or, if a visible oil film exists on the soil surface, the oil film surface model as presented in Subsection 7.2.3); and emissions after tilling would be estimated using the RTI land treatment model. At other existing sites, waste is injected into the soil using subsurface injection and is immediately tilled. At these sites, only one calculation is needed to estimate emissions. In this situation, the RTI land treatment model would be used.

7.2 LAND TREATMENT

7.2.1 Land Treatment Emission Model Descriptions

7.2.1.1 Analytical Correlations. Emissions from land treatment after waste is applied to the soil are estimated using a model developed by Clark Allen of Research Triangle Institute (the RTI model). This model assumes that emissions from the surface of the soil/waste mixture are limited by the diffusion of vapors through the pore spaces in the soil/waste mixture and further assumes that an equilibrium concentration of organic vapors exists at all times within the pore spaces. The model is based on Fick's second law of diffusion applied to a flat slab as described by Crank[1] and includes a term to estimate biological decay assuming a decay rate that is first order with respect to waste loading in the soil.

The solution to the diffusion equation developed by Crank is for diffusion out of a slab that initially has a uniform concentration of diffusing material throughout and that has equal concentrations of diffusing material at each surface.

The general solution to the diffusion equation for those conditions, as presented by Crank, is:

$$F = \frac{M_t}{M_o} = 1 - \sum_{n=o}^{\infty} \frac{8}{(2n+1)^2 B^2} \exp * \frac{-D\ (2n+1)^2 B^2 t}{4\ l^2} * , \qquad (7\text{-}1)$$

where,

F = fraction of initially applied material that has diffused out of the slab at time t;

M_t = mass of material that has diffused out of the slab at time t;

M_o = initial mass of material present;

D = diffusion coefficient;

l = distance from center to surface of slab; and

t = time after initial distribution of diffusing material into the slab.

This series solution converges very slowly for small values of time (i.e., Dt/l^2 immediately after waste application or tilling), Crank presented an alternative solution that is valid during this short time. The following equation is obtained from the alternative solution for Dt/l <.213:

$$F = \frac{M_t}{M_o} = \frac{2}{\sqrt{\pi}} \left(\frac{Dt}{l^2} \right)^{1/2} \qquad (7\text{-}2)$$

Equation (7-2) approximates the Crank solution but excludes a small error function correction used by Crank.

To verify the validity of Crank's solution for short times and to test the accuracy of an approximation for use over longer times, the values predicted by the solution for short times and the values obtained using the first term of the series solution [Equation (7-3)] are compared to the values obtained using the first three terms of the series solution. Table 7-1 presents the results for a range of values of the dimensionless parameter, Dt/l^2:

$$F = \frac{M_t}{M_o} = 1 - \frac{8}{\pi^2} \exp\left(- \frac{Dt\pi^2}{4l^2} \right) \qquad (7\text{-}3)$$

Table 7-1 shows that, for values of the dimensionless parameter greater than 0.213, the first term of the series solution, Equation (7-3), can be used to estimate total emissions. The table also shows that the solution for short

TABLE 7-1. COMPARISON OF THE ESTIMATED FRACTION EMITTED USING THREE DIFFERENT EQUATIONS (INTEGRATED FLUX FROM SOIL)

Time parameter (Dt/l^2)	Short-term solution $2*\frac{Dt}{Bl^2}*^{1/2}$	First term of series solution $1 - \frac{8}{B^2} \exp*-\frac{DtB^2}{4l^2}*$	First three terms of series solution
0.000	0.000	0.189	0.067
0.025	0.178	0.238	0.179
0.050	0.252	0.284	0.252
0.075	0.309	0.326	0.309
0.100	0.357	0.367	0.357
0.125	0.399	0.405	0.399
0.150	0.437	0.440	0.437
0.175	0.472	0.474	0.472
0.200	0.505	0.505	0.504
0.213	0.521	0.521	0.520
0.250	0.564	0.562	0.562
0.275	0.592	0.589	0.589
0.300	0.618	0.613	0.613
0.325	0.643	0.636	0.636
0.350	0.668	0.658	0.658
0.375	0.691	0.679	0.679
0.400	0.714	0.698	0.698
0.425	0.736	0.716	0.716
0.450	0.757	0.733	0.733
0.475	0.778	0.749	0.749
0.500	0.798	0.764	0.764
0.525	0.818	0.778	0.778
0.550	0.837	0.791	0.791
0.575	0.856	0.804	0.803
0.600	0.874	0.816	0.816
0.625	0.892	0.827	0.827
0.650	0.910	0.837	0.837
0.675	0.927	0.847	0.847
0.700	0.944	0.856	0.856
0.725	0.961	0.864	0.865
0.750	0.977	0.873	0.873
0.775	0.993	0.880	0.880
0.800	1.009	0.887	0.887
0.825	1.025	0.894	0.894
0.850	1.040	0.900	0.900
0.875	1.056	0.906	0.906
0.900	1.070	0.912	0.912
0.925	1.085	0.917	0.917
0.950	1.100	0.922	0.922
0.975	1.114	0.927	0.927

times, Equation (7-2), is valid for values of the dimensionless parameter below 0.213. Equations (7-2) and (7-3) give identical results for a parameter value of 0.213. This comparison indicates that sufficient accuracy can be attained under all conditions if the equation for short times is used for values of the dimensionless parameter below 0.213 and the first term of the general solution is used for values above 0.213. It is observed that the fraction of material that diffuses out of the slab is linear with respect to the square root of time up to the point where approximately 50 percent of the diffusing material is lost.[2]

The conditions defined for the above solutions by Crank are analogous to diffusion of volatile organics out of a surface layer of a soil/waste mixture as happens in land treatment operations. Because of the symmetry of conditions on which the above solutions are based, an impenetrable plane could, in theory, be inserted at the midpoint of the slab without changing the solution. One-half of the slab with an impenetrable boundary layer on the bottom would represent the surface layer of soil into which waste is mixed during land treatment.

In a land treatment operation, the applied material partitions into several phases including evaporation into a vapor phase, adsorption onto soil particles, and absorption into oil and water in the soil/waste mixture. Only the vapor phase is available for diffusion out of the soil/ waste mixture. Therefore, to apply the above equations to land treatment, the amount of material in the vapor phase must be known. The amount of material that partitions into the vapor phase can be estimated by calculating equilibrium conditions within the soil/waste mixture. This equilibrium is estimated by defining Keq, the ratio of the amount of organics in the vapor phase to the total amount of organics in the soil/waste mixture. The instantaneous emission rate, E, at any time, t, can be estimated by the following Equations (7-4) and (7-5), which are obtained by differentiating Equations (7-2) and (7-3) and adding the equilibrium constant, Keq, and a term to account for wastebiodegradation, $(-t/t_b)$:

$$\text{(short times)} \quad E = \frac{M_o}{l} \left[\frac{KeqD}{Bt}\right]^{1/2} e^{-t/t_b} \text{ , and} \qquad (7\text{-}4)$$

$$\text{(longer times)} \quad E = M_o \left[\frac{2KeqD}{l^2}\right] \exp\left[\frac{-Keq\ D\ B^2\ t}{4l^2}\right] e^{-t/t_b}. \qquad (7\text{-}5)$$

where t_b = the biological degradation time constant.

The above equations account for the removal of organic material from the soil/waste mixture both biological degradation and air emissions. In a land treatment operation, the primary objective is to dispose of organic materials by biodegradation; thus, significant quantities of waste would be expected to be depleted from the soil by biological degradation. Other mechanisms of removal such as leaching and photolysis also are possible but are not accounted for in this model because of the estimated small amount of materials lost by these processes.

7.2.1.2 Biodegradation. Biodegradation at land treatment sites is generally considered to be a first-order process with respect to waste concentration in the soil up to the point where saturation is achieved.[3] In addition to literature sources that make such statements, comments on a draft of this document provided by Chevron Research Company offer further evidence of the first-order nature of biodegradation at land treatment sites.[4] A first-order decay process is defined in the literature as having the following form:[5]

$$\frac{dM}{dt} = - K_b M \ ,$$

where,

M = mass of organic material in the soil; and

K_b = biological decay constant.

Integrating and using the boundary conditions $M = M_o$ at $t = O$ results in:

$$\frac{dM}{M} = -K_b dt \quad ,$$

$$\log M = -K_b t + C_1 \quad ,$$

or

$$M = C_2 e^{-K_b t} \quad ,$$

where C_1 and C_2 are constants of integration. Substituting the boundary conditions gives:

$$M = M_o e^{-K_b t} \quad .$$

K_b has units of s^{-1} and can be expressed as the reciprocal of the biological decay time constant, $1/t_b$. The exponential was introduced directly into the rate relationship, Equations (7-4) and (7-5), to reduce the amount of material available for air emissions by the fraction of material removed by biooxidation.

7.2.1.3 Estimation of equilibrium coefficient, Keq. Partitioning of volatile constituents in the waste is assumed to occur between the vapor space in the soil/waste mixture, adsorbent solids in the soil, and absorbent liquids in the soil and waste. Using 1 cm^3 of the soil/waste mixture as a basis for calculation, the total volume of gas (i.e., void space) in the cubic centimeter is described by the air porosity, $,_a$. Using the ideal gas law, the number of moles of gas in 1 cm^3 of the soil/waste mixture is $P,_a/(RT)$, where P is the pressure of a constituent in the gas phase and is usually equal to XP^* (X is the mole fraction of the constituent in the liquid phase and P^* is the pure component vapor pressure). The moles of constituent in the gas phase in 1 cm^3 of the soil/waste mixture is thus $XP^*,_a/(RT)$. Oil loading in the soil/waste mixture in units of grams of oil per cubic centimeter of mixture is L (g_{oil}/cm^3 mixture), and the total moles of constituent per cubic centimeter of the mixture is XL/MW_{oil}. The equilibrium coefficient, Keq, is defined as the moles of constituent in the gas phase per unit volume of the soil/waste mixture divided by the total moles of constituent per unit volume of the soil/waste mixture. Therefore, the following equation can be written:

$$Keq = \frac{XP^{*}{,}_{a}/(RT)}{X\ L/MW_{oil}} = \frac{P^{*}MW_{oil}{'}_{a}}{RTL} \quad .$$

This equation differs from the usual equation for equilibrium coefficient by the factor $,_a$, which is included to account for the limited air space available within the soil/waste mixture. The ratio of moles per mole and grams per gram can be used interchangeably in this equation. The value of Keq can be calculated from measurements, if available, of constituent concentrations in the pore space and in the soil/waste mixture.

In a similar manner, it can be shown that Keq can be estimated for aqueous wastes with an assumed value of the Henry's law constant, H_c:

$$Keq = \frac{H_c\ 10^6\ {'}_a}{RT{,}_{waste}} \quad .$$

where

$'_{waste}$ = the volume fraction of the soil/waste mixture that is occupied by waste.

In the above equations, it is assumed that equilibrium is controlled by Raoult's law for oily wastes and by Henry's law for aqueous wastes. An aqueous waste is assumed to contain water and organic constituents that are dissolved in water. An example of an aqueous waste is a sludge containing 10 percent solids, 5 percent acetone, 1 percent methanol, 500 ppmw benzene, and the remainder water. If the waste contains oil mixed with the water, or the waste contains volatile constituents at concentrations greater than the solubility in water, it is modeled as an oily waste. It is important to specify the molecular weight of this separate organic phase for this Raoult's law calculation of Keq.

7.2.1.4 Estimation of effective diffusivity. The diffusivity of specific compounds, as reported in the literature, assumes that the diffusion occurs in free air. In a land treatment operation, diffusion of vapors out of the soil must take place within the confines of the air-filled voids within the soil. This characteristic of soil is referred to as the air porosity. The ratio of effective diffusivity of a constituent in the soil to its diffusivity in air can be described by the following equation:[6]

$$\frac{D_e}{D_a} = \frac{’_a^{10/3}}{’_T^{2}} ,$$

where,

D_e = effective diffusivity of constituent in soil;

D_a = diffusivity of constituent in air;

$’_a$ = air porosity of soil; and

$’_T$ = total porosity of soil.

When air porosity and total porosity are the same (i.e., for dry soil), this equation reduces to:

$$\frac{D_e}{D_a} = ’_a^{4/3} .$$

Total porosity refers to the fraction of the land treatment medium that is made up of nonsoil (or nonsolid) materials, i.e., the sum of the void space, water-filled space, and space occupied by the oil in the applied waste.

Soil air porosity undergoes substantial changes over time as soil dries out and when moisture is added by rainfall or by watering. As a result, accurately accounting for soil porosity in an analytical model is difficult. The use of average or typical values of soil porosity may be the most practical approach.

7.2.1.5 Waste partitioning. A large percentage of wastes that are disposed of by land treatment are refinery sludges. These wastes are mostly sludge emulsions and consist of varying fractions of water, oil, and inorganic solids, where oil represents the total organic portion of the waste including volatile compounds. A much smaller amount of land-treated wastes are dilute aqueous solutions of water and organic compounds. When wastes are applied to a land treatment area, volatile materials in the soil have the potential for partitioning into four different phases--a vapor phase, an oil phase where volatile material is dissolved in the oil, a water phase where volatile material is absorbed in the soil moisture, and a soil phase where volatile material is adsorbed by organic carbon within the soil. For oily wastes, VO compounds will preferentially dissolve in oil rather than water so that the fraction of volatile materials in the water phase is estimated to be very small. Partitioning of volatile materials into the soil phase by adsorption is a function of the amount of organic carbon in the soil. It is also estimated to account for only a small fraction of the applied organics because the surfaces in the soil are expected to contain oil from the application and tilling of waste materials that contain oil. This oil in the soil is expected to both absorb the volatile constituents and to interfere with the relatively lower adsorption rates on soil surfaces. For high molecular weight constituents present in aqueous wastes, adsorption may be more important. An equilibrium equation can be written that takes all four phases into account in the estimation of equilibrium vapor concentration in the soil. However, as presented here, the equilibrium equation in the RTI model includes only two phases. Calculations by one researcher looked at the difference in estimated emissions using two-phase partitioning of waste into an oil phase and vapor phase and using four-phase partitioning. The results of these comparisons are given in Table 7-2 and show for the conditions considered that, for soils having an organic carbon content of up to 10 percent, the estimated fraction of applied organics emitted using four-phase partitioning is only about 10 percent less than the estimated fraction emitted using two-phase partitioning. In a given situation, the amount of material adsorbed by organic carbon in the soil is relatively constant; thus, in soils with high organic carbon content, adsorption of materials in the soil may become more significant if low loading rates of oil or aqueous wastes are used. One of the products of biodegradation is organic carbon; thus, land treatment sites that have been active for an extended time may have elevated concentrations of organic carbon. Even so, with the normal oil loading used in land treatment, it is likely that a large fraction of the available adsorption sites would be occupied by the oil itself, thus limiting the effects of adsorption on emissions of the lighter constituents.

For oily sludges, Keq is calculated using vapor pressure and waste loading is calculated exclusive of water content. For dilute aqueous waste, partitioning is estimated to be in a water phase and a vapor phase, and the parameter Keq is calculated using Henry's law constant; waste loading is calculated using the total waste applied. Keq may be calculated from site-specific land treatment soil, vapor, and solids analyses if available. Table 7-3 summarizes the equations that make up the RTI land treatment model.

7.2.1.6 Emissions at Short Times.

When a sludge containing volatile organics is applied onto or tilled into the soil at a land treatment site, the maximum rate of air emissions will occur immediately after application or tilling. Volatile organics will leave the surface and enter the environment through wind currents. Although the RTI model is based on the premise that emissions from land treatment are limited by vapor diffusion through the soil, the maximum rate of air emissions immediately

TABLE 7-2. EMISSION ESTIMATES USING TWO DIFFERENT EQUATIONS FOR THE VAPOR-SOIL PARTITION COEFFICIENT[7]

Organic carbon content of soil (fraction)	Estimated emission fraction--two-phase partitioning	Estimated emission fraction--four-phase partitioning
0	0.622	0.622
0.001	0.622	0.621
0.010	0.622	0.614
0.100	0.622	0.559

TABLE 7-3. RTI MODEL FOR LAND TREATMENT EMISSIONS

Emission rate equations

Short-term solution (K_v t <.22)

$$E = \frac{M_o}{l} \left(\frac{1}{\frac{\epsilon_a}{K_{ea}\ k_G} + \left(\frac{\pi t}{D_e\ K_{ea}} \right)^{.5}} \right) e^{-\frac{t}{t_b}}$$

Long-term solution (K_v t $\geq$ 0.22)

$$E = M_o \left(\frac{2\ K_{eq}\ D_e}{l^2} \right) \exp \left(-\frac{K_{eq}\ D_e\ \pi^2\ t}{4\ l^2} - \frac{t}{t_b} \right)$$

Fraction air emissions

Short-term solution (K_v t <0.22)

$$F_{at} = \left(\frac{K_{eq}\ D_e\ t}{\pi\ l^2} \right) 2 \left(1 - \frac{1}{3}\ \frac{t}{t_b} \right)$$

Long-term solution (K_v t $\geq$ 0.22)

$$F_{at} = \frac{8}{\pi^2} \left(1 + \frac{1}{K_d\ t_b} \right)^{-1} \left(1 - \exp \left(-K_d\ t - \frac{t}{t_b} \right) \right) + .1878$$

Long-term solution (Fa <0.33 and $K_v t_b$ <0.22)

$$F_{at} = F_a \left(1 - \exp \left(-K_d\ t - \frac{t}{t_b} \right) \right)$$

Very long-term solution (t → ∞) ($K_d t_b$ ≥ 0.62)

$$F_a = \frac{0.811_d K\ _b t}{(K_d\ t_b + 1)} + 0.1878$$

Very long-term solution (t → ∞) ($K_d t_b$< 0.62)

$$F_a = \left(\frac{K_{eq}\ D_e\ t_b}{l^2} \right)^{.5}$$

(continued)

TABLE 7-3 (continued)

$$Keq = \frac{P^{*}MW_{oil}}{RT} \frac{’a}{L}$$ (used for oily sludges)[a]

$$Keq = \frac{H_c}{RT} (10^{6}) \frac{’a}{’waste}$$ (used for dilute aqueous waste)

$$k_G = 4.82 (10^{-3}) U^{0.78} Sc_G^{-0.67} de^{-0.11}$$

$$Sc_G = \frac{\mu a}{D_a D_a}$$

$$M_o = LlC$$

$$K_v = \frac{KeqD_e}{l^2}$$ (volatilization constant)

$$K_d = \frac{B^2}{4} K_v$$

If both air porosity and total porosity are known:

$$D_e = D_a \left(\frac{\epsilon_a^{\frac{10}{3}}}{\epsilon_T^{2}} \right)$$

$$D_e = (4A/B)^{0.5}$$

$$D_e = D_a \, ’a^{4/3}$$ (if only air porosity is known)

$$t_b = \frac{4.83 (10^{7})}{B}$$

$L = \frac{W f_{oil}}{Al}$ (for oily sludges); $L = \frac{W}{Al}$ (for dilute aqueous waste)

---

[a] Equilibrium equations are adjusted to account for volume fractions of air and waste within the soil. (continued)

TABLE 7-3 (continued)

Variable	Definition	Data source
Keq	Equilibrium coefficient of constituent in the soil (dimensionless)	Calculated
k_G	Gas-phase mass transfer coefficient(cm/sec)	Calculated
C	Concentration (weight fraction) of constituent in the oil phase or (for dilute aqueous waste)in water	Definition
D_a	Diffusion coefficient of constituent in air,cm^2/s	Data base
D_e	Effective diffusion coefficient of constituent in the soil, cm^2/s	Calculated
E	Emission rate of constituent, $g/cm^2/s$	Calculated
H_c	Henry's law constant for constituent, $atm \cdot cm^3/g$ mol	Data base
l	Depth to which waste is mixed in the soil, cm	Facility operation
L	Oil or aqueous waste loading in the soil,g/cm^3	Calculated from annual throughput
M_t	Air emissions of constituent from the soil, g/cm^2	Calculated
M_o	Initial loading of constituent on the land treatment site, g/cm^2	Calculated
MW_o	Average molecular weight of the oil, g/g mol oil	Estimated
MW	Molecular weight of constituent, g/g mol	Data base
P^*	Pure component vapor pressure of constituent, atm	Data base
R	Ideal gas constant, 82.1 $atm \cdot cm^3/g$ $mol \cdot K$	Literature

(continued)

TABLE 7-3 (continued)

Variable	Definition	Data source
t_b	Time constant for biological decay of constituent, s[b]	Literature, or site specific
t	Time after waste application to the land treatment site, s	Facility operation
T	Temperature of vapor in soil, K	Assumed
$,_a$	Volume fraction of air-filled voids in the soil (soil air-filled porosity) (dimensionless)	Estimated from literature data
$,_T$	Total porosity of the soil (equivalent to dry basis bulk density divided by soil particle density) (dimensionless)	Estimated
,	Volume fraction of waste in the soil waste (dimensionless)	Calculated
B	Biorate of constituent, mg VO/g•h	Data base
K_v	Volatilization constant for constituent, s^{-1}	Calculated
K_d	Modified volatilization constant, s^{-1}	Calculated
K_b	Biodegradation constant for constituent, s^{-1}	Calculated
F_a	Fraction of constituent emitted to the air after a long time	Calculated
F_{at}	Fraction of constituent emitted to the air at time t	Calculated
f_{oil}	Fraction by weight of applied waste that is oil (organic)	Definition
U	Windspeed, m/s	Estimated

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[b] Time constant is the time required for biodegradation of 63.2 percent of a pollutant.

(continued)

TABLE 7-3 (continued)

Variable	Definition	Data source
W	Total waste applied to land treatment site, g	Definition
A	Area of land treatment site to which waste is applied, cm^2 (m^2 in calculation of de)	Definition
Sc_G	Schmidt number (gas phase)	Calculated
de	Effective diameter of land treatment area,m	Calculated
μa	Viscosity of air, g/cm•s	Literature
Da	Density of air, g/cm^3	Literature

after application or tilling will be limited by the gas-phase mass transfer coefficient, k_G. Within a few hours after application or tilling, the rate of air emissions from the volatile components will be substantially less than the maximum rate because the volatiles at the surface have been removed by the wind and the remaining volatiles must diffuse up through a layer of porous solids, a relatively slow process.

The land treatment model can be used for short-term emissions. The emissions from the short-term use of the land treatment model will be somewhat less than the oil-film model, although the initial rate from both of these models is equivalent. The oil film model is used to estimate maximum emission rates and the land treatment model is used to account for surface drying during short-term emission estimations. The equation for the emission rate immediately after application or tilling is:

$$E = \frac{M_o}{l} \left(\frac{1}{\frac{\epsilon_a}{k_G \; K_{eq}} + \sqrt{\frac{\pi \; t}{D_e \; K_{eq}}}} \right) \exp\left(- \frac{t}{T_b} \right) \qquad (7\text{-}6)$$

The basis of the above equation is a resistance in series model where the resistance (inverse of the mass transfer coefficient) is the sum of the resistance of the soil and the resistance at the wind-porous solid interface. The mass transfer coefficient of the soil is defined in

Equation (7-4) in the term: $\left(\frac{\text{Keq D}}{\text{Bt}}\right)^{1/2}$.

The resistance of the soil to mass transfer is the inverse of the above or (Keq D / Bt $)^{-1/2}$. The resistance at the air-soil interface is defined by 1/ Keq k_G. Because Keq has previously been defined as containing a factor to account for soil porosity, this factor (soil porosity) must be included in the above equation to maintain a consistent definition of Keq throughout this discussion. The revised resistance is represented by $,_a$/Keq k_G. Summing the two resistances and substituting into

Equation (7-4) gives Equation (7-6). The gas-phase mass transfer coefficient, k_G, is calculated as described in Table 4-1 for a surface impoundment.

7.2.1.7 Estimating the fraction emitted at short times. The fraction of a constituent emitted to the air after some time, t, can be estimated by integrating the equation for air emissions from time 0 to time t:

$$F_{at} = \left(\frac{Keq\ D_e}{B\ l^2} \right)^{1/2} \int_o^t t^{-1/2}\, e^{-t/t_b} dt \quad .$$

The exponential term can be replaced by a series,

$$e^{-t/t_b} = 1 - \frac{t}{t_b} + \frac{1}{2}\left(\frac{t^2}{t_b} \right) - \frac{1}{6}\left(\frac{t^3}{t_b} \right) + \frac{1}{24}\left(\frac{t^4}{t_b} \right) - \ . \ . \ . \ . \ ,$$

which can be substituted into the above integral, and each of the individual terms integrated. The results of these integrations are:

$$F_{at} = \left(\frac{K_{eq}\ D_e}{\pi\ l^2} \right)^{1/2} 2\ t^{1/2} \left(1 - \frac{1}{3}\left(\frac{t}{t_b} \right) + \frac{1}{10}\left(\frac{t}{t_b} \right)^2 - \frac{1}{42}\left(\frac{t}{t_b} \right)^3 + \ . \ . \ . \right)$$

This series solution converges with only a few terms for values of t/t_b less than 1. Therefore, the following simplification can be used to estimate the fraction emitted (i.e., integrated emissions) at short times:

$$F_{at} = \left(\frac{Keq\ D_e}{B\ l^2} \right)^{1/2} 2t^{1/2} \left(1 - \frac{1}{3}\frac{t}{t_b} \right) . \qquad (7\text{-}7)$$

The resistance to emissions presented by gas-phase mass transfer at the soil surface is only considered important for the estimation of the emission rates immediately after application or tilling. This resistance is omitted in the above equation with little loss in accuracy.

The above equation is used to predict the fraction of a constituent emitted to the air when $K_v t$ is less than 0.22.

7.2.1.8 Estimating the fraction emitted for longer times. For longer times, when most of the constituent is not present in the soil, the short-term solution (Equations (7-4) and (7-7)) will overestimate air emissions. Under these conditions, Equation (7-5) can be integrated to estimate the fraction removed by volatilization. Equation (7-5) can be simplified by defining the constant, K_d, as $\frac{Keq\ D_e\ B2}{4\ l^2}$:

$$E = \frac{M_o 8 K_d}{B^2} \exp * - K_d t - t/t_b * \quad . \qquad (7\text{-}8)$$

Integrating from time 0 to t gives:

$$F_{at} = \frac{8}{B^2} \left(1 + \frac{1}{K_d t_b}\right)^{-1} * 1 - \exp\left(- K_d t - t/t_b\right) * + 0.1878. \qquad (7\text{-}9)$$

In the above equation, terms after the first ($n > 0$) in the series solution are replaced by the constant 0.1878. This equation is used for estimating air emissions when $K_v t$ is greater than or equal to 0.22.

When $K_v t$ is less than 0.22, the following simplification can be used to estimate air emissions at longer times. An exponential decay factor is established to relate the fraction emitted at any time, t, to the fraction emitted at very long times (i.e., $t \to \infty$) as estimated using Equation (7-12), which follows. The resulting equation is:

$$F_{at} = F_a \left[1 - \exp\left(-K_d t - t/t_b\right)\right] \qquad (7\text{-}10)$$

where

F_a = fraction of constituent emitted at very long times ($t \to \infty$).

For very long times (i.e., $t \to \infty$), the fraction emitted can be estimated using the following procedure. The integrated form of the general solution without dropping terms is:

$$F_{at} = \frac{8}{B^2} \sum_{n=0}^{\infty} \frac{1 - \exp\{-(2n+1)^2\ K_d t - t/t_b\}}{(2n+1)^2 + \frac{1}{t_b K_d}} \quad .$$

This equation can be simplified using the following rationale: For large values of t, the exponential terms are negligibly small, and for large values of n, $1/(t_b K_d)$ becomes negligibly small compared to $(2n+1)^2$. If these conditions are true for all terms where n > 0, the simplified equation is:

$$F_a = \frac{8}{B^2} \ast \frac{K_d t_b}{K_d t_b + 1} + 0.2317 \ast \quad .$$

The value of 0.2317 was obtained by evaluating the first 125 terms of the series for n > 0 with negligibly small values of $1/(t_b K_d)$:

$$\sum_{n=1}^{125} \frac{1}{(2n+1)^2} = 0.2317 \quad .$$

Combining terms and simplifying, the equation becomes:

$$F_a = \frac{0.81057 K_d t_b}{K_d t_b + 1} + 0.1878. \qquad (7\text{-}11)$$

The assumptions used in developing Equation (7-11) are not valid for small values of $K_d t_b$ ($K_d t_b$ approximated by the following relationship:

$$F_a = \sqrt{\frac{K_{eq}\ D_e}{l^2}\ t_b} \qquad (7\text{-}12)$$

This relationship was established by using multiple terms of the general solution to calculate values of F_a for a series of input values for the parameters $KeqD_e/l^2$, which is identified as the volatilization constant, K_v, and t_b and then using a curve-fitting routine to derive the relationship in Equation (7-12) for $K_d t_b$.

Table 7-4 presents the results of calculations of the long-term fraction emitted (i.e., t → ∞) using 100 terms of the general solution and inputting several values of the dimensionless ratio, $K_v t_b$, designated as T. This ratio is an indicator of the relative rates of volatilization and degradation. Table 7-4 also shows the results if the above approximating equations are used to calculate the long-term fraction emitted, and it shows good agreement between these results and the results obtained by the general solution.

Table 7-5 shows a comparison of the estimated emission fractions for a range of values of $K_v t$ and t/t_b using the first 100 terms of the general solution and using the approximations given in Equations (7-7) and (7-9). This table shows good agreement between the approximating equations and the rigorous solution.

To calculate the amount of waste remaining in the soil at any time, it is necessary to know both the amount emitted to the air and the amount biodegraded. At very long times (i.e., $t \to \infty$), all waste is assumed to disappear from the soil. Thus, the fraction of waste emitted plus the fraction biodegraded must be equal to 1 if other mechanisms of removal are ignored. Therefore, at very long times:

$$F_b = 1 - F_a \quad , \tag{7-13}$$

where

F_b = fraction of constituent that is biodegraded after a long time (i.e., $t \to \infty$).

7.2.1.9 Tilling. To apply the model to a situation where the land treatment plot is retilled after the initial waste application and tilling, estimates of the amount of waste emitted

TABLE 7-4. ESTIMATED AIR EMISSION FRACTION AT LONG TIMES

Value of T *T = $K_v t_b$*	Estimated fraction (rigorous equation)	Estimated fraction[a]	Estimated fraction[b]
0.050	0.222	0.224	0.277
0.100	0.313	0.316	0.348
0.150	0.381	0.387	0.407
0.200	0.435	0.447	0.456
0.250	0.480	0.500	0.497
0.300	0.518	0.548	0.533
0.350	0.551	0.592	0.563
0.400	0.579	0.632	0.590
0.450	0.604	0.671	0.614
0.500	0.626	0.707	0.635
0.550	0.646	0.742	0.654
0.600	0.664	0.775	0.672
0.650	0.680	0.806	0.687
0.700	0.694	0.837	0.701
0.750	0.708	0.866	0.714
0.800	0.720	0.894	0.725
0.850	0.731	0.922	0.737
0.900	0.741	0.949	0.747
0.950	0.751	0.975	0.750
1.000	0.760	1.000	0.765
1.050	0.768	1.025	0.773
1.100	0.776	1.049	0.780
1.150	0.783	1.072	0.787
1.200	0.789	1.095	0.794
1.250	0.796	1.118	0.800
1.300	0.802	1.140	0.805
1.350	0.807	1.162	0.811
1.400	0.813	1.183	0.816
1.450	0.818	1.204	0.821
1.500	0.822	1.225	0.826
1.550	0.827	1.245	0.830
1.600	0.831	1.265	0.834
1.650	0.835	1.285	0.839
1.700	0.839	1.304	0.842
1.750	0.843	1.323	0.846
1.800	0.846	1.342	0.849
1.850	0.850	1.360	0.853
1.900	0.853	1.378	0.856
1.950	0.856	1.396	0.859
2.000	0.859	1.414	0.862

[a] $F_a = T^{0.5}$.

[b] $F_a = \dfrac{0.81057\ K_d\ t_b}{K_d t_b + 1} + 0.1878$.

TABLE 7-5. RIGOROUS VS. APPROXIMATE ESTIMATES OF EMISSION FRACTIONS

t/t_b	$K_v t$	$K_v t_b$	Estimated fraction (rigorous)	Estimated fraction (approximated by)[a]	Estimated fraction (approximated by)[b]
0.01	0.05	5.00	0.25	0.25	0.28
0.01	0.10	10.00	0.35	0.36	0.36
0.01	0.15	15.00	0.43	0.44	0.44
0.01	0.20	20.00	0.50	0.50	0.50
0.01	0.25	25.00	0.56	0.56	0.56
0.01	0.30	30.00	0.61	0.62	0.61
0.01	0.35	35.00	0.65	0.67	0.65
0.01	0.40	40.00	0.69	0.71	0.69
0.01	0.45	45.00	0.73	0.75	0.73
0.01	0.50	50.00	0.76	0.79	0.76
0.01	0.55	55.00	0.79		0.79
0.01	0.60	60.00	0.81		0.81
0.01	0.65	65.00	0.83		0.83
0.01	0.70	70.00	0.85		0.85
0.01	0.75	75.00	0.87		0.87
0.01	0.80	80.00	0.88		0.88
0.01	0.85	85.00	0.90		0.90
0.01	0.90	90.00	0.91		0.91
0.01	0.95	95.00	0.92		0.92
0.01	1.00	100.00	0.93		0.93
0.10	0.05	0.50	0.24	0.24	0.28
0.10	0.10	1.00	0.34	0.34	0.36
0.10	0.15	1.50	0.42	0.42	0.43
0.10	0.20	2.00	0.49	0.49	0.49
0.10	0.25	2.50	0.54	0.55	0.54
0.10	0.30	3.00	0.59	0.60	0.59
0.10	0.35	3.50	0.64	0.65	0.64
0.10	0.40	4.00	0.67	0.69	0.68
0.10	0.45	4.50	0.71	0.73	0.71
0.10	0.50	5.00	0.74	0.77	0.74
0.10	0.55	5.50	0.77		0.77
0.10	0.60	6.00	0.79		0.79
0.10	0.65	6.50	0.81		0.81
0.10	0.70	7.00	0.83		0.83
0.10	0.75	7.50	0.85		0.85
0.10	0.80	8.00	0.86		0.86
0.10	0.85	8.50	0.87		0.88
0.10	0.90	9.00	0.89		0.89
0.10	0.95	9.50	0.90		0.90
0.10	1.00	10.00	0.91		0.91
0.30	0.05	0.17	0.23	0.23	0.27
0.30	0.10	0.33	0.32	0.32	0.34
0.30	0.15	0.50	0.39	0.39	0.41
0.30	0.20	0.67	0.46	0.45	0.46
0.30	0.25	0.83	0.51	0.51	0.52

See notes at end of table.

(continued)

TABLE 7-5 (continued)

t/t_b	$K_v t$	$K_v t_b$	Estimated fraction (rigorous)	Estimated fraction (approximated by)[a]	Estimated fraction (approximated by)[b]
0.30	0.30	1.00	0.56	0.56	0.56
0.30	0.35	1.17	0.60	0.60	0.60
0.30	0.40	1.33	0.63	0.64	0.64
0.30	0.45	1.50	0.67	0.68	0.67
0.30	0.50	1.67	0.70	0.72	0.70
0.30	0.55	1.83	0.72		0.73
0.30	0.60	2.00	0.75		0.75
0.30	0.65	2.17	0.77		0.77
0.30	0.70	2.33	0.79		0.79
0.30	0.75	2.50	0.80		0.80
0.30	0.80	2.67	0.82		0.82
0.30	0.85	2.83	0.83		0.83
0.30	0.90	3.00	0.84		0.84
0.30	0.95	3.17	0.85		0.86
0.30	1.00	3.33	0.86		0.87
1.00	0.05	0.05	0.19	0.17	0.25
1.00	0.10	0.10	0.26	0.24	0.30
1.00	0.15	0.15	0.32	0.29	0.35
1.00	0.20	0.20	0.37	0.34	0.40
1.00	0.25	0.25	0.42	0.38	0.44
1.00	0.30	0.30	0.46	0.41	0.47
1.00	0.35	0.35	0.49	0.44	0.51
1.00	0.40	0.40	0.52	0.48	0.54
1.00	0.45	0.45	0.55	0.50	0.56
1.00	0.50	0.50	0.58	0.53	0.59
1.00	0.55	0.55	0.60		0.61
1.00	0.60	0.60	0.62		0.63
1.00	0.65	0.65	0.64		0.65
1.00	0.70	0.70	0.66		0.67
1.00	0.75	0.75	0.68		0.68
1.00	0.80	0.80	0.69		0.70
1.00	0.85	0.85	0.71		0.71
1.00	0.90	0.90	0.72		0.72
1.00	0.95	0.95	0.73		0.74
1.00	1.00	1.00	0.74		0.75

[a] Approximated by: $F_{at} = 1.128 \sqrt{K_v t}\,(1-1/3\ t/t_b)$.

[b] Approximated by: $F_{at} = \frac{8}{\pi^2}\left[1 + \frac{1}{K_d t_b}\right]^{-1}\left[1 - \exp\left(-K_d t - t/t_b\right)\right] + 0.1878.$

to the air and the amount biodegraded are required. When retilling occurs, the amount of material remaining in the soil at the time of retilling is estimated using the following equation:

$$F_S = (1 - F'_{at})\, e^{-t/t_b} \quad , \tag{7-14}$$

where,

F_S = fraction of constituent remaining in the soil; and

F'_{at} = fraction of material emitted to the air at time t assuming no biodegradation (F'_{at} can be estimated by setting t/t_b = 0 in Equation (7-7) or (7-9), whichever is appropriate).

To continue modeling emissions after retilling occurs, M_o is set equal to $F_s\, M_o$ and t is reset to zero. If a reapplication of waste occurs, the total waste loading is the sum of the waste remaining in the soil and the newly applied waste:

$$M_o = F_S M_o + M_n \quad , \tag{7-15}$$

where M_n = amount of constituent newly applied to the land treatment site. To continue the modeling after waste reapplication and tilling, t is reset to zero.

7.2.1.10 Model selection.

The RTI model was selected for use in this regulatory effort after a review of three models of land treatment emissions. The models reviewed were the RTI model, the Thibodeaux-Hwang model, and a model developed by EPA's Office of Research and Development located in Ada, Oklahoma (the Ada model). The review considered three selection criteria: technical basis, representativeness, and availability of inputs. The Ada model is the most ambitious of the three in attempting to account for mechanisms of pollutant removal other than air emissions and biodegradation. However, that model requires detailed site-specific model inputs that may not be available or reasonably estimated. Because of these characteristics of the Ada model, it was not considered appropriate for use in the current effort. Both the Thibodeaux-Hwang and the RTI models have input requirements that are reasonably available, both have been compared with available measured data, and both have shown reasonable agreement with the measurements.[8] Apparently, either of these two models is satisfactory as a means of estimating emission rates at specific times for some organic compounds. However, if the Thibodeaux-Hwang model is used to estimate long-term, steady-state emissions, it would predict that all of the applied volatile organics are emitted because it does not account for biodegradation. Such a prediction would contradict data obtained from laboratory and field studies that indicate biodegradation of some organic compounds in land treatment applications.[9] The RTI model, in contrast, estimates biodegradation of individual compounds based on constituent-specific biodegradation rates. The RTI and the Thibodeaux Hwang models predict similar emission rates for initial volatile losses in the absence of biodegradation. Thus, the results of the RTI model show varying levels of biodegradation when used to evaluate the fate of different organic compounds.

In summary, the Ada model has had limited public review, accounts for multiple waste removal mechanisms, requires numerous detailed model inputs, and has no published comparisons of estimated and measured emissions. The Thibodeaux-Hwang model has been publicly reviewed, accounts for one major waste removal mechanism (volatilization), requires reasonably available model inputs, and there are published comparisons of measured and estimated emissions. The RTI model has had limited public review, accounts for the two major waste removal mechanisms (volatilization and biodegradation), requires reasonably available model inputs, and there are published comparisons of measured and estimated emissions. The peer review, emission comparisons, and data availability are compelling reasons for using the Thibodeaux-Hwang model. However, the absence of biodegradation in that model is considered a major shortcoming because of the importance attached to this removal mechanism by industry personnel and many independent researchers. Emission comparisons and data availability for the RTI model are roughly equivalent to those of the Thibodeaux-Hwang model, and the RTI model includes terms that account for biodegradation. The RTI and the Thibodeaux models predict similar emission rates for initial volatile losses in the absence of biodegradation. Thus, the RTI model was selected for use in the standards development process.

7.2.2 Waste Application Model

At land treatment facilities that do not use subsurface injection with immediate tilling, emissions may occur during the time that waste is being applied to the soil surface and while the waste lies on the soil before it is tilled into the soil. No existing models were identified that predict emissions during application of an oily sludge to the soil surface. The approach selected for this case was to calculate an overall mass transfer coefficient of volatile material from the surface of the stream of sludge as it falls from the end of a hose to the soil surface. The mass transfer coefficients were calculated using an equation presented in Section 5.0 (Table 5-1). The constant in the equation for gas-phase resistance was increased by a factor of two in an attempt to account for an increase in mass transfer caused by the motion of the waste stream through the air. The equations for making this calculation are presented in Table 7-6 along with the definitions of the variables used and the sources of input data.

7.2.3 Oil Film Model

Emissions from waste lying on the soil surface are estimated in either of two ways depending on the form of the waste as it lays on the soil surface. In typical situations where the applied waste is spread over the surface of soil, the RTI land treatment model can be used to estimate emissions. The equation for short-term emissions given above as Equations (7-4) and (7-7)

TABLE 7-6. WASTE APPLICATION EMISSION MODEL

Emission equations

$$E = KCA$$

$$A = 2Brl$$

$$K = Keq\ k_G \text{ (used for oily sludges); } \frac{1}{K} = \frac{1}{k_L} + \frac{1}{Keqk_G}$$

(used for dilute aqueous waste);

$$k_G = 9.64(10^{-3})U^{0.78}Sc_G^{-0.67}de^{-0.11};$$

$$Keq = \frac{H}{RT} \text{ (used for dilute aqueous waste)}$$

$$Keq = \frac{P^* D_a MW_{oil}}{P_o D_L MW_{air}} \text{ (used for oily sludges)}$$

$$k_L = 1\ (10^{-6}) + 144\ (10^{-4})\ U^{*2.2}\ Sc_L^{-0.5};\ Sc_L = \frac{\mu_L}{D_w D_w}$$

$$de = *\frac{4A}{B}*^{0.5};\ Sc_G = \frac{\mu_a}{D_a Da}$$

$$U^* = 0.01U(6.1 + 0.63U)^{0.5}$$

Variable	Definition	Data source
E	Emission rate for constituent, g/s	Calculated
K	Overall mass transfer coefficient,m/s	Calculated
Keq	Equilibrium coefficient, dimensionless	Calculated
H	Henry's law constant for constituent, atm cm^3/g mol	Literature
R	Universal gas constant, atm cm^3/ g mol K	Literature
T	Temperature, K	Measured
k_G	Gas-phase mass transfer coefficient,m/s	Calculated
P^*	Vapor pressure of constituent, mm Hg	Literature

(continued)

TABLE 7-6 (continued)

Variable	Definition	Data source
P_o	System pressure (atmospheric pressure), mm Hg	Definition
U	Windspeed, m/s	Definition
Sc_G	Schmidt number on gas side	Calculated
Sc_L	Schmidt number on liquid side	Calculated
μ_a	Viscosity of air, g/cm•s	Literature
D_w	Density of water, g/cm^3	Literature
D_a	Density of air, g/cm^3	Literature
D_L	Density of oil, g/cm^3	Estimated
D_a	Diffusivity of constituent in air, cm^2/s	Literature
A	Surface area of cylindrical waste stream, m^2	Calculated
r	Radius of cylindrical waste stream, m	Measured
l	Length of cylindrical waste stream, m	Measured
C	Concentration of constituent in the waste, g/cm^3	Measured
de	Effective diameter of waste stream surface area, m	Calculated
MW_a	Molecular weight of air, g/g mol	Literature
MW_{oil}	Molecular weight of oil, g/g mol	Estimated
μ_L	Viscosity of water, g/cm•s	Literature
D_w	Diffusivity of component in water, cm^2/s	Data base
U^*	Friction velocity, m/s	Calculated
k_L	Liquid-phase mass transfer coefficient, m/s	Calculated

would be used for this situation. If the applied waste has a visible oil film on top, emissions immediately after spreading are estimated by calculating an overall mass transfer coefficient as described in Chapter 5.0 for an oil film on a surface impoundment. The mass transfer equation was developed by McKay and Matsuga and is based on data obtained from liquid hydrocarbon spills on land and water.[10] The equations used to calculate emissions under this situation are given in Table 7-7 along with definitions of the variables used.

7.2.4 Model Inputs

Typical values of input parameters for the RTI model are based primarily on a data base developed by EPA[11] from site visits and contacts with State, regional, and industry sources supplemented by information from recent literature. These values were chosen as reasonably representative of average or typical practices currently used at land treatment operations. Oil loading in the soil is a model input that is calculated from several other parameters that might change independently. Varying the value of the oil loading rate, thus, has the same effect as varying any one or any combination of the other parameters. Oil loading is defined by waste throughput, the percent oil in the waste, area of the land treatment site, and the depth to which the waste is mixed in the soil (tilling depth). Typical values of oil loading are defined from median values for those parameters by which it is defined. The data base shows annual throughput varying from about 2 Mg/yr to about 400,000 Mg/yr with a median value of about 1,800 Mg/yr. The area of land treatment sites ranges from less than 1 hectare (ha) to about 250 ha with a median value of 5 ha. The data base shows tilling depth varying from 15 cm to one case of 65 cm, with most being in the range of 15 to 30 cm. The single most frequently reported tilling depth is 20 cm, which is selected as a typical value. This value is in line with values of 15 to 30 cm reported

TABLE 7-7. OIL FILM SURFACE EMISSION MODEL

Emission rate equation

$$E = KC_tA$$

$$C_t = C_o \text{ [exp (-Kt/D)]}$$

$$K = k_G \text{ Keq (used for oily sludges)}$$

$$k_G = 4.82 \ (10^{-3}) \ U^{0.78} Sc_G^{-0.67} de^{-0.11}$$

$$Sc_G = \frac{\mu_a}{D_a D_a}$$

$$Keq = \frac{P^* \quad D_a MW_{oil}}{P_o \quad D_L MW_{air}} \text{ (used for oily sludges);}$$

$$de = *\frac{4A}{B}*^{0.5}$$

Variable	Definition	Data source
E	Emission rate for constituent, g/s	Calculated
K	Overall mass transfer coefficient, m/s	Calculated
C_t	Concentration of constituent in the oil phase at time t	Calculated
C_o	Initial concentration of constituent in the waste	Definition
D	Oil film thickness, m	Measured
A	Area of land treatment, m^2	Measured
k_G	Gas-phase mass transfer coefficient, m/s	Calculated

(continued)

TABLE 7-7 (continued)

Variable	Definition	Data source
U	Windspeed, m/s	Definition
Sc_G	Schmidt number--gas phase	Calculated
μ_a	Viscosity of air, g/cm•s	Literature
D_a	Density of air, g/cm^3	Literature
D_a	Diffusion coefficient of constituent in air, cm^2/s	Literature
de	Effective diameter of land treatment area, m	Calculated
Keq	Equilibrium coefficient of constituent	Calculated
P^*	Vapor pressure of constituent, mm Hg	Literature
P_o	Atmospheric pressure, mm Hg	Definition
MW_{oil}	Molecular weight of the oil, g/g mol	Definition
MW_a	Molecular weight of air, g/g mol	Literature
D_L	Density of oil, g/cm^3	Estimated
R	Universal gas constant, atm cm^3/g mol K	Literature
T	Temperature, K	Measured

in another study.[12] The data base shows oil content of the waste streams varying from about 2 to 50 percent, with a median value of about 12 percent and a mode value of 10 percent. The 10-percent figure is selected as typical.

Average molecular weight of the oil from which a particular constituent evaporates is one of the determining factors in the rate of evaporation and thus must be specified. Little data are available as guidance for selecting a value for this parameter. The distribution of constituents by molecular weight in land-treated wastes is not well known. In one field measurement study of land treatment emissions,[13] a value of 282 g/g mol was used as the average molecular weight of the oil. This value was based on distillation of oil from a refinery sludge and identification of the constituent corresponding to the midpoint distillation temperature (i.e., the temperature at which 50 percent of the oil was distilled). The value 282 g/g mol is selected for use. A sensitivity analysis using the RTI model shows that emissions are not highly sensitive to this parameter.

Soil air porosity and total porosity impact the effective diffusivity of a constituent in the soil. Very little soil porosity information has been identified. One study reported measured values of soil porosity in a land treatment plot as ranging from 43.3 to 65.1 percent,[14] with an average value of about 50 percent. The literature values are assumed to represent air porosity. Total soil porosity would include the air porosity and the space occupied by oil and water within the soil. One field study reported measured values of both total porosity and air-filled porosity.[15] Measured values of total porosity ranged from 54.7 to 64.8 percent, with an average value of 60.7 percent. Measured values of air-filled porosity ranged from 27.4 to 46.9 percent, with an average of 37.2 percent. The value of 61 percent for total porosity is assumed to be a representative value. A value of 0.5 is used in the model as a default for air porosity.

Biorate data used in the RTI model data base (CHEMDAT8) represent measured rates in aqueous systems. In order to use the aqueous biorate data in a land treatment process, a factor was established for converting aqueous data to land treatment values using measured data for benzene. A recent publication by the American Petroleum Institute (API) reported experimentally determined values of biological decay constants for land treatment studies using two different soil types.[16] Decay constants were measured for six compounds including two compounds, benzene and toluene, that have aqueous biorates in the land treatment model data base (CHEMDAT8). For benzene, the ratio of the API data, measured in units of day^{-1}, and the aqueous data, measured in units of mg VO/$g_{biomass} \cdot hr$, was calculated as 0.00179. This value is also a close approximation of the ratio of the two data points for toluene, the other compound for which data from both sources were available. The other compounds for which data were reported by API did not have referenced aqueous data in the data base. The above calculated relationship was used to calculate equivalent aqueous data values for those compounds. Reported and calculated values of aqueous biorates and land treatment biological decay constants are presented in Table 7-8. The ratio of 0.00179 is used for all compounds to convert from aqueous biorates to decay constants that can be used in the land treatment model. The input parameter for the land treatment model is a biological decay time constant, t_b, in units of seconds. The equation for calculating t_b from the aqueous biorate is derived as follows.

The biological decay time constant is, by definition, equal to the reciprocol of the biological decay constant, or

$$t_b = \frac{1}{K_b} \quad , \qquad (7\text{-}16)$$

TABLE 7-8. MEASURED AND ESTIMATED BIORATES AND DECAY CONSTANTS FOR SELECTED ORGANIC CONSTITUENTS

Organic constituent	Aqueous biorate, mg VO/g biomass•h	Calculated decay constant, day^{-1}	Measured decay constant, day^{-1}[a]	
			Nunn[b]	Kidman[c]
Benzene	19.0	0.034	0.034	0.013
Ethylbenzene	46.4[d]	0.083	0.083	0.076
Xylene(-o)	40.8[d]	0.073	0.073	0.026
Naphthalene	42.5[d]	0.076	0.076	0.050
Toluene	73.5	0.132	0.106	0.119
Methyl naphthalene	24.0[d]	0.043	0.043	0.059

[a] Reference 17.

[b] Data obtained using a clay loam soil (Nunn soil).

[c] Data obtained using a sandy loam soil (Kidman soil).

[d] Values calculated from API experimental data.

where K_b = biological decay constant. The ratio, r, of decay constant to aqueous biorate is:

$$r = \frac{K_b}{B} \frac{g_{bio}\ h}{mg\ VO\ day} \text{ or } K_b = rB\ day^{-1} \quad .$$

Substituting into Equation (7-16) gives:

$$t_b = \frac{1}{rB}\ day \quad .$$

To obtain a result in seconds, this equation must be multiplied by 86,400 s/day. Making this conversion and inserting the value of r (i.e., 0.00179) gives:

$$t_b = \frac{86,400}{0.00179\ B} = \frac{4.83\ (10^7)}{B} \quad .$$

For situations in which petroleum wastes are landfarmed and no information is known about the nature of the volatile materials, it is possible to estimate a default biorate from the average decay constant values reported in the API investigation, 0.07 day^{-1}, which corresponds to a biorate, B, of 40 mg/g-h. This value is between the values for benzene and toluene in the data base. The average value of the biological rate constant in the two soils investigated by API was not significantly different.

In summary, parameters and selected typical values for use in the RTI model are as follows:

Annual waste throughput = 1,800 Mg
Area of land treatment = 5 ha
Oil content of waste = 10 percent
Average molecular weight of the oil = 282 g/g mol
Soil air porosity = 0.5
Soil total porosity = 0.61
Tilling depth = 20 cm
Temperature = 25 °C.

7.2.5 Estimation of Total VO Emissions

The preceding discussion has been limited to estimating emissions of a single constituent in a hazardous waste. Using the models presented here to estimate total VO emissions can be accomplished using any of several approaches. The most obvious approach, and the one that should give the most accurate results, would be to obtain a detailed analysis of the constituents in the waste being land treated. The emission equations could be used to calculate emissions of each constituent, and total emissions could be calculated by summing the emissions of individual constituents. In many cases, a detailed analysis of the applied waste may not be available, and other, less accurate methods may be needed to estimate total VO emissions. An alternative to the constituent approach could make use of a boiling curve or steam stripping test of a sample of the waste. Experimental data developed by Chevron Research Company[18] indicate that a large fraction of the constituents that boil at temperatures of 400 °F or lower will be emitted to the atmosphere and that those constituents with higher boiling points will tend to remain in the soil for a sufficient time to undergo biodegradation.

Similar results are obtained by applying the RTI land treatment model to the constituents in the CHEMDAT8 data base. If a sample of waste were subjected to a laboratory boiling test or other equivalent test at a temperature of 400 °F, the fraction of oil evaporated would approximate the fraction that potentially would be emitted to the air in a land treatment operation.

A third approach to estimating total VO emissions would again make use of the experimental results generated by Chevron Research. The test results showed that approximately 25 percent of the applied oil in the land treatment test was emitted to the air. In the absence of a detailed constituent analysis and with no boiling or steam stripping test of the waste, a crude estimate of total VO emissions could be made by assuming that emissions are equal to 25 percent of the applied oil. This approximating alternative would only apply to raw oily refinery wastes that have not undergone any pretreatment to remove VO.

7.2.6 Example Calculations

7.2.6.1 Emissions from land treatment soil. The following calculation demonstrates the use of the RTI model to calculate the long-term fraction of applied material emitted to the atmosphere and to calculate the short-term and long-term emission rates and emission fractions. The calculations are made for benzene at a concentration of 2,000 ppm by weight in a waste stream that is 10 percent oil.

Input values are:

Land area = 2.5 ha (half of total area of 5 ha assumed active)

Annual throughput = 1,800 Mg

Oil content of waste = 10% (by weight)

Benzene concentration in oil = 2,000 ppm (by weight) (2 mg/g oil)

Tilling depth = 20 cm

Soil air porosity = 0.5

Soil total porosity = 0.61

Average molecular weight of oil= 282 g/g mol .

a. Calculate oil loading (Equation from Table 7-3):

$$L = \frac{(1{,}800 \times 10^6\ g_{waste})(0.1\ g_{oil}/g_{waste})}{(2.5 \times 10^8\ cm^2)(20\ cm)} = 0.036\ g_{oil}\ /cm^3\ .$$

b. Identify constituent properties of benzene:

B = 19.00 mg VO/$g_{biomass}$•h

D_a = 0.088 cm^2/s

P^* = 95.2 mm Hg = 0.125 atm.

c. Calculate the equilibrium coefficient (Table 7-3):

$$K_{eq} = \frac{P^* \; MW_{oil} \; {}'_a}{RT \; L} = \frac{(0.125\ \text{atm})(282\ \text{g/g mol})(0.5\ \text{cm}^3/\text{cm}^3)}{(82.05\ \text{atm}\bullet\text{cm}^3/\text{g mol}\bullet\text{K})(298\ \text{K})(0.036\ \text{g/cm}^3)}$$

$$K_{eq} = 0.02002 \quad .$$

d. Calculate the biological degradation time constant (Equation from Table 7-3):

$$t_b = \frac{4.83(10^7)}{B} = \frac{4.83\ (10^7)}{19} = 2.54\ (10^6)\ \text{s} \quad .$$

e. Calculate the effective diffusivity of constituent in the soil (Equation from Table 7-3):

$$D_e = D_a \frac{{}'_a{}^{10/3}}{{}'_T{}^2} = 0.088\ \text{cm}^2/\text{s}\ \frac{(0.5\ )^{10/3}}{0.61^2} = 0.0235\ \text{cm}^2/\text{s} \quad .$$

f. Calculate the value of $K_d = \frac{B^2 KeqD_e}{4\ l^2}$:

$$K_d = \frac{(9.87)\ (0.0235)\ \text{cm}^2/\text{s}\ (0.02002)}{4\ (400)\ \text{cm}^2} = 2.9\ (10^{-6})\ \text{s}^{-1} \quad .$$

g. Calculate the fraction of constituent emitted to the air after a long time (Equation (7-11)):

$$F_a = \frac{0.81\ K_d t_b}{K_d t_b + 1} + 0.1878 = 0.90 \quad .$$

h. Calculate the long-term emission rate after 60 h (216,000 s).

$$Keq\ \frac{D_e t}{l^2} = \frac{0.02002 \times 0.0235 \times 216{,}000}{400} = 0.254 \quad .$$

Use Equation (7-5) (long-term equation):

$$E = M_o \left(\frac{2\ K_{eq}\ D_e}{l^2} \right) \exp \left(-\frac{K_{eq}\ D_e\ \pi^2\ t}{4\ l^2} \right) \exp \left(-\frac{t}{t_b} \right)$$

$$E = \frac{2\ (0.72)(2)(0.02002)(0.0235)}{400} \text{ x e } \left(\frac{-0.02002(0.0235)(9.87)(216,000)}{1,600} \right)$$

$$\text{x e}[-216,000/2.54(10^6)]$$

$$= 3.38(10^{-6})\ e(-0.627)\ e(-0.085) = 3.38(10^{-6})\ e(-0.712)$$

$$E = 3.38(10^{-6})\ (0.491) = 1.7(10^{-6})\ .\quad \frac{mg}{cm^2\ s}$$

c. Calculate the short-term emission rate after 15 min (900 s):

$$Keq\ \frac{D_e t}{l^2} = \frac{0.02002 \text{ x } 0.0235\ (900)}{400} = 0.0010$$

$$k_G = 4.82\ (10^{-3})\ U^{0.78}\ Sc_G^{-0.67}\ de^{-0.11}\ ,$$

where

U = windspeed = 4.47 m/s

de = effective diameter of land treatment area

$$de = *\frac{4A}{B}*^{0.5} = 178 \text{ m}$$

$$Sc_G = \frac{\mu g}{D_a\ D_a}$$

where

μg = viscosity of air = $1.81(10^{-4})$ g/cm•s

D_a = density of air = $1.2\ (10^{-3})$ g/cm^3

D_a = 0.088 cm^2/s

$$Sc_G = \frac{1.81\ (10^{-4})}{1.2\ (10^{-3})(0.088)} = 1.71$$

$$k_G = 4.82(10^{-3})\ (4.47)^{0.78}\ (1.71)^{-0.67}\ (178)^{-0.11}$$

$$= 0.0061\ m/s\ (\ 0.61\ cm/s\ )$$

$$E = \frac{M_o}{l} \left(\frac{1}{\frac{\epsilon_a}{K_{eq}\ k_G} + \left(\frac{\pi t}{D_e\ K_{eq}} \right)^{.5}} \right) e^{-\frac{t}{t_b}}$$

$$E = \frac{0.72\ g\ 2\ mg}{1\ cm^2\ 20\ cm\ g} \left(\frac{1}{\frac{0.5}{0.61 \times 0.02002} + \left(\frac{3.14 \times 900}{0.0235 \times 0.02002} \right)} \right) e^{(-900/2.54(10^6))}$$

$$= 0.072\ (0.0004)\ e(-0.0004) = 2.87\ (10^{-5})\ \frac{mg}{cm^2\ s}\ .$$

Table 7-9 shows estimated emission rates and emission fractions for various times up to 40 days (960 hours).

7.2.6.2 Emissions from Waste Application. The following is an example calculation for the application of an oily waste to a land treatment plot using the equations in Table 7-6. For benzene in waste oil, the calculation is:

Input values:

r = 0.038 m

L = 0.46 m

μ_a = 1.81 (10^{-4}) g/cm•s

D_a = 1.2 (10^{-3}) g/cm^3

U = 4.47 m/s

R = 82.05 atm•cm^3/K•g mol

T = 298 K

C = 200 ppm = 200 µg/g = 0.0002 g/cm^3 = 200 g/m^3
(assuming a density of 1 g/cm^3)

A = 2 BrL = 2(3.14)(0.038 m)(0.457 m) = 0.11 m^2

D_L = 1 g/cm^3

MW_a = 29 g/g mol

MW_{oil} = 282 g/g mol.

a. Calculate the effective diameter of the waste stream surface (Equation from Table 7-6):

$$de = *\frac{4A}{B}*^{0.5} = 0.37 \text{ m} \quad .$$

TABLE 7-9. ESTIMATED EMISSION RATES AND FRACTIONS EMITTED VERSUS TIME FOR EXAMPLE LAND TREATMENT CALCULATION

Time after application /tilling,h	Emission rate, 10^{-6} mg/cm^2•s	Equation used	Fraction emitted, fraction	Equation used
1	14.4	Short term	0.073	Short term
2	10.3	Short term	0.104	Short term
4	7.30	Short term	0.147	Short term
8	5.12	Short term	0.207	Short term
24	2.90	Short term	0.356	Short term
48	1.98	Short term	0.497	Short term
96	1.08	Long term	0.674	Long term
192	0.348	Long term	0.827	Long term
480	0.011	Long term	0.899	Long term
960	0.00004	Long term	0.901	Long term

b. Calculate the Schmidt number (Equation from Table 7-6):

$$Sc_G = \frac{\mu_a}{D_a\ D_a} = \frac{1.81\ (10^{-4})\ g/cm \bullet s}{[1.2\ (10^{-3})\ g/cm^3](0.088\ cm^2/s)} = 1.71\ .$$

c. Calculate the equilibrium coefficient
(Equation from Table 7-6):

$$Keq = \frac{P^*}{P_o} \frac{D_a\ MW_{oil}}{D_L\ MW_a} = \frac{(95.2\ mm\ Hg)[1.2(10^{-3})g/cm^3](282\ g/gmol)}{(760\ mm\ Hg)(1\ g/cm^3)(29\ g/g\ mol)}$$

$Keq = 0.0015.$

d. Calculate the gas-phase mass transfer coefficient
(Equation from Table 7-6):

$$k_G = 9.64(10^{-3})\ U^{0.78}\ Sc_G^{\ -0.67}\ de^{-0.11}$$

$$= 9.64(10^{-3})(4.47)^{0.78}(1.71)^{-0.67}(0.37)^{-0.11}$$

$$= 0.024\ m/s\ .$$

e. Calculate the overall mass transfer coefficient (Equation from Table 7-6):

$$K = k_G\ Keq = (0.0015)(0.024)\ m/s = 0.000036\ m/s\ .$$

f. Calculate emissions from a unit volume of waste
(Equation from Table 7-6):

$$E = KCA = 0.000036\ m/s\ \ (200\ g/m^3)\ (0.11)\ m^2$$

$$= 7.92\ (10^{-4})\ g/s\ .$$

Using a calculated fall time of 0.305 s:

$$E = (7.92 \bullet 10^{-4}\ g/s)(0.30\ s) = 2.38\ (10^{-4})\ g\ .$$

Stream volume = $Br^2L = (3.14)(0.038\ m)^2(0.46\ m) = 0.002\ m^3$

$= 2{,}073\ \text{cm}^3$.

Mass of constituent = $(0.002\ \text{m}^3)\ (200\ \text{g/m}^3) = 0.4\ \text{g}$.

g. Calculate the fraction of constituent emitted to the air:

$$\text{Fraction emitted} = \frac{2.38(10^{-4})\text{g}}{0.4\ \text{g}} = 0.00059 = 0.06\ \text{percent.}$$

7.2.6.3 Emissions from an oil layer on soil prior to tilling. An example calculation for butanol-1 in an oil layer on the soil surface of a land treatment site is given below using the equation from Table 7-7.

Input values:

μ_a = $1.81\ (10^{-4})$ g/cm•s
D_a = $1.2\ (10^{-3})\ \text{g/cm}^3$
U = 4.47 m/s
MW_{oil} = 282 g/g mol
D_L = $1\ \text{g/cm}^3$
MW_a = 29 g/g mol
C = $0.0002\ \text{g/cm}^3 = 200\ \text{g/m}^3$
A = $25{,}000\ \text{m}^2$
t = 24 h = 86,400 s
d = 0.072 m .

a. Calculate the effective diameter of the soil surface (Equation from Table 7-7):

$$de = *\frac{4\ A}{B}*^{0.5} = *\frac{4 \times 25{,}000}{B}*^{0.5} = 178\ \text{m} .$$

b. Calculate the Schmidt number (Equation from Table 7-7):

$$Sc_G = \frac{\mu_a}{D_a D_a} = \frac{1.81\ (10^{-4})\ \text{g/cm}\bullet\text{s}}{[1.2\ (10^{-3})\ \text{g/cm}^3](0.080\ \text{cm}^2/\text{s})} = 1.885 .$$

c. Calculate the equilibrium coefficient (Equation from Table 7-7):

$$\text{Keq} = \frac{P^* \; D_g \; MW_{oil}}{P_o \; D_L \; MW_a} = \frac{(6.5 \text{ mm Hg})[1.2(10^{-3})\text{g/cm}^3](282 \text{ g/gmol})}{(760 \text{ mm Hg})\ (1 \text{ g/cm}^3)\ (29 \text{ g/g mol})}$$

$$= 1.0\ (10^{-4}) \quad .$$

d. Calculate the gas-phase mass transfer coefficient (Equation from Table 7-7):

$$k_G = 4.82(10^{-3})U^{0.78}Sc_G^{-0.67}de^{-0.11} = 4.82(10^{-3})\ (4.47)^{0.78}(1.89)^{-0.67}$$

$$\times\ (178)^{-0.11}$$

$$= 5.7\ (10^{-3}) \quad .$$

e. Calculate the overall mass transfer coefficient (Equation from Table 7-7):

$$K = k_G \text{ Keq} = [5.7\ (10^{-3}) \text{ m/s}][1.0\ (10^{-4})] \text{ m/s} \quad .$$

$$K = 5.70\ (10^{-7}) \text{ m/s.}$$

f. Calculate the fraction of constituent emitted to the air at time t (Equation from Table 7-7):

$$f = 1 - \frac{C_t}{C_o} = 1 - e^{-Kt/D}$$

$$f = 1 - \exp\ [-5.70\ (10^{-7})(86{,}400)/0.072]$$

$$= 1 - 0.50 = 0.50 \quad .$$

7.2.6.4 Examples of the Use of the Land Treatment Model for Specific Cases. To illustrate how the land treatment model is used to estimate long-term and short-term emissions from various waste management options, the following case studies are presented. Each of these examples represents the land treatment of API separator sludge/DAF float, with the exception of example 5. The waste contains 10 percent organics and is applied at a rate of 2,500 Mg of waste per year. The loading, benzene concentration, and porosity are identical to the example presented in Section 7.2.6.1. The land area is 35,000 square meters.

Example 1. Waste is applied monthly for 9 months of the year. No waste is applied during December, January, or February because the soil is frozen or saturated with water during those months. The waste is applied from a vacuum truck by spraying onto the soil surface with a nozzle. The soil is tilled 24 hours after application and is tilled again (no waste application) after 2 weeks.

Two calculations of air emissions are required: after application and after tilling. The first time period is 1 day and the second time period is 14 days. The amount of waste applied is 2,520 Mg/9 or 280 Mg/application. It is assumed that the oil content in the soil is 0.036 grams of oil/cm^3. The amount of oil applied each application is 0.036/9 or 0.004 g/cm^3. The concentration of benzene in the waste is 2,000 ppmw and the concentration of benzene added to the oil in the soil is 2,000/9 or 222 ppmw each application. The land area is 3,500 square meters. After application, the liquid is assumed to seep into the soil to a depth of 5 cm, and the oil loading in the waste on the soil surface was assumed to be the same as the oil content of the soil.

To estimate the amount of air emissions between application and tilling, the following parameters are used in CHEMDAT8:

• Concentration of benzene:	2,000 ppmw
• Tilling depth:	5 cm
• Time of calculation:	1 day
• Loading (10 percent oil):	0.036 g/cm^3.

The fraction lost during the first day is 98 percent with 0.007 percent lost to biological decay.

The fraction lost after the first tilling is estimated by the use of the following parameters:

• Concentration of benzene:	222 ppmw
• Tilling depth:	20 cm

- Time of calculation: 14 days
- Loading: 0.036 g oil/cm^3.

The calculated fraction lost during the first tilling period is 0.89 to air emissions and 0.095 to biodegradation. This fraction is independent of the concentration of benzene and is expected to also apply to the second tilling period.

The loss of benzene during the month is 97.8 percent during the spreading period and (1-0.978-0.0067) x 0.89 x 100 or 1.4 percent during the tilling periods, for a total air emission loss of 99.2 percent.

Example 2. Waste is applied weekly except when the ground is saturated with water. Waste is applied from a vacuum truck, and the waste is spread over the surface of the soil. The soil is tilled on the day following the application and weekly between applications. The waste is applied monthly to the land treatment plot throughout the year.

As in example 1, two calculations of emissions are required: after application and after tilling. The first time period is 1 day and the second time period is 7 days. The amount of waste applied is 2,520 Mg/12 or 210 Mg/application. It is assumed that the oil content in the soil is 0.036 grams of oil/cm^3. The amount of oil applied each application is 0.036/12 or 0.003 g/cm^3. The concentration of benzene in the waste is 2,000 ppmw and the concentration of benzene added to the oil in the soil is 2,000/12 or 167 ppmw each application. The land area is 3,500 square meters. After application, the liquid is assumed to seep into the soil to a depth of 5 cm, and the oil loading in the waste on the soil surface was assumed to be the same as the oil content of the soil.

To estimate the amount of air emissions between application and tilling, the following parameters are used in CHEMDAT8:

- Concentration of benzene: 2,000 ppmw
- Tilling depth: 5 cm
- Time of calculation: 1 day
- Loading (10 percent oil): 0.036 g/cm^3.

The fraction lost during the first day is 98 percent with 0.007 percent lost to biological decay.

The fraction lost after the first tilling is estimated by the use of the following parameters:

- Concentration of benzene: 167 ppmw
- Tilling depth: 20 cm
- Time of calculation: 7 days
- Loading: 0.036 g oil/cm^3.

The calculated fraction lost during the first tilling period is 0.80 to air emissions and 0.083 to biodegradation. This fraction is independent of the concentration of benzene and is expected to also apply to the second tilling period.

The fraction loss of benzene during four tilling periods is (0.805) + (0.0995)(0.805) + (0.805)(0.0995)^2 + 0.805 (0.0995)^3 or 0.89.

The loss of benzene during the month is 97.8 percent during the spreading period and (1-0.978-0.0067) x 0.89 x 100 or 1.4 percent during the tilling periods, for a total air emission loss of 99.2 percent.

Example 3. The waste is dewatered prior to land treatment. The parameters are the same as those used in example 1, except the waste is dewatered and the filter cake is land-treated. The oil content of the filter cake is 20 percent. The waste is applied from a dump truck and is spread by a bulldozer. The waste is tilled into the soil on the day following spreading. It is assumed that the dewatering process removes 60 percent of the oil from the waste.

As in the preceeding examples, two calculations of air emissions are required: after spreading and after tilling. The first time period is 1 day and the second time period is 14 days. The amount of waste applied is 2,520 Mg/9 or 280 Mg/application. It is assumed that the oil content in the soil is 0.036 grams of oil/cm^3. The amount of oil applied each application is 0.036/9 or 0.004 g/cm^3. The concentration of benzene in the waste is

2,000 ppmw and the concentration of benzene added to the oil in the soil is 2,000/9 or 222 ppmw each application. The land area is 3,500 square meters. After application, the liquid is assumed to be retained in the waste, and the oil loading in the waste on the soil surface is assumed to be the same as the oil content of the waste.

To estimate the amount of air emissions between application and tilling, the following parameters are used in CHEMDAT8:

• Concentration of benzene:	2,000 ppmw
• Tilling depth:	2 cm
• Time of calculation:	1 day
• Loading (20 percent oil):	0.2 g/cm^3.

The fraction lost during the first day is 98 percent with 0.006 percent lost to biological decay.

The fraction lost after the first tilling is estimated by the use of the following parameters:

• Concentration of benzene:	222 ppmw
• Tilling depth:	20 cm
• Time of calculation:	14 days
• Loading:	0.036 g oil/cm^3.

The calculated fraction lost during the first tilling period is 0.89 to air emissions and 0.095 to biodegradation. This fraction is independent of the concentration of benzene and is expected to also apply to the second tilling period.

The air emission loss of benzene during the application period is 98.3 percent during the spreading period and (1-0.983-0.006) x 0.89 x 100 or 1.2 percent during the tilling periods, for a total air emission loss of 99.5 percent. The air emissions on the basis of the untreated waste would depend on the recovery of oil in the dewatering process and the air emissions from the dewatering process.

Example 4. The waste is tilled as it is applied to the soil. The tilling depth is 20 cm. The period between tillings is 3 days. Waste is applied monthly.

Only one calculation of air emissions is required: after tilling. The amount of waste applied is 2,520 Mg/12 or 210 Mg/application. It is assumed that the oil content in the soil is 0.036 grams of oil/cm^3. The amount of oil applied each application is 0.036/12 or 0.003 g/cm^3. The concentration of benzene in the waste is 2,000 ppmw, and the concentration of benzene added to the oil in the soil is 2,000/12 or 167 ppmw each application. The land area is 3,500 square meters.

The fraction lost after the first tilling is estimated by the use of the following parameters:

• Concentration of benzene:	167 ppmw
• Tilling depth:	20 cm
• Time of calculation:	3 days
• Loading:	0.036 g oil/cm^3.

The calculated fraction lost during the first tilling period is 0.60 to air emissions and 0.055 to biodegradation. This fraction is independent of the concentration of benzene and is expected to also apply to the following tilling periods.

The loss of benzene during the first tilling period is 60 percent with (100-60-5.5) or 34.5 percent remaining. The loss of benzene during the second tilling period is 0.60 (34.5) or 20.7 percent, with a fraction of $(0.345)^2$ or 0.119 of benzene remaining. The total loss of benzene for the month is 92 percent.

Example 5. Waste is applied monthly for 9 months of the year. No waste is applied during December, January, or February because the soil is frozen or saturated with water during those months. The waste is applied from a vacuum truck by spraying onto the soil surface with a nozzle. The soil is tilled 24 hours after application and is tilled again (no waste application) after 2 weeks. The waste is aqueous containing 10 percent organics and 2,000 ppmw benzene. The waste contains 10 percent solids by weight.

Two calculations of air emissions are required: after application and after tilling. The first time period is 1 day and the second time period is 14 days. The amount of waste applied is 2,520 Mg/9 or 280 Mg/application. It is assumed that the water content in the soil is 0.10 grams/cm^3. The concentration of benzene in the waste is 2,000 ppmw and the concentration of benzene added to the water in the soil is 300 ppmw each application. The land area is 3,500 square meters. After application, the liquid is assumed to seep into the soil to a depth of 5 cm, and the water loading in the waste on the soil surface was assumed to be the same as the water content of the soil.

To estimate the amount of air emissions between application and tilling, the following parameters are used in CHEMDAT8:

• Concentration of benzene:	300 ppmw
• Tilling depth:	5 cm
• Time of calculation:	1 day
• Loading (10 percent):	0.10 g/cm^3.

The fraction lost to air emissions during the first day is 99.8 percent with less than 0.01 percent lost to biological decay.

7.2.7 Assumptions and Sensitivity Analyses

The RTI model incorporates the following assumptions to simplify development and use of the model:

- Volatilization and biodegradation are the predominant waste removal mechanisms (i.e., other mechanisms can be ignored).
- Waste is mixed uniformly within a surface layer of the soil.
- Waste does not flow as a liquid within the soil.
- The adsorption isotherm of a constituent is linear within the application surface layer and does not change with time.
- No bulk flow of gas is induced within the soil.
- The rate of biological decay/chemical reaction is a first-order process.
- The diffusion coefficient does not vary with either concentration or time.

- The concentration of a constituent in the gas phase at the surface of the soil is much lower than the concentration of that constituent in the gas phase within the soil.
- There is no diffusion of waste into the soil beneath the zone of incorporation.
- Liquid-vapor equilibrium is established at all times within the soil.

The RTI model was evaluated for sensitivity to each of the input parameters. In the analysis, each input parameter was varied over the entire range of reasonable values. The effect on emissions of parameter variations was noted, and the parameters showing the highest sensitivity were identified.

Individual constituent properties were found to have the most significant impact on land treatment emissions. These properties include vapor pressure, diffusivity in air, and biodegradation rate. The more volatile compounds are mostly emitted to the atmosphere unless a volatile compound also has a high biodegradation rate or low diffusivity. Compounds with low vapor pressures tend also to have lower diffusivities; thus, even if such compounds also have moderate or low biorates, they are mostly biodegraded rather than emitted to the air.

Operating and field parameters also have an impact on emissions but to a lesser extent than compound properties. Tilling depth, soil porosity, and waste loading all have an impact on air emissions, with the largest impact on the more volatile compounds. Tilling depth can have a substantial impact on air emissions of volatile compounds, especially if a compound also has a relatively high biorate. As tilling depth increases, materials remain in the soil for a longer time and thus have a greater chance of being biodegraded.

Waste loading can be varied in two ways: by increasing the concentration of a compound in the waste or by increasing the amount of material applied to the soil per unit area. If the concentration of a compound is changed, air emissions change in direct proportion to the change in concentration (i.e., the fraction of the compound that is emitted to the air remains constant). If total waste loading is changed, air emissions change in the same direction as the change in loading but not in direct proportion (i.e., the fraction emitted is lower for higher loading rates). These results assume that a treatment site is not overloaded to the point where biodegradation ceases to be a first-order process.

Average molecular weight of the oil has an effect on air emissions, but the magnitude of the effect is less than that of the other parameters studied. As average molecular weight goes up, the fraction emitted for a specific constituent increases; the fraction emitted decreases if the average molecular weight is reduced.

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8.0 LANDFILLS AND WASTEPILES

8.1 INTRODUCTION

The main facilities in this category that constitute the model plants are waste fixation units, open landfills, closed landfills, and wastepiles.

All wastes that contain free liquids and that are destined for disposal in a landfill must be treated to eliminate the free liquids. This is often accomplished by adding a "fixative" to the waste, such as portland cement, cement kiln dust, or lime flue dust. These materials react with water in the waste and set up to form a dry material that encapsulates or binds the organic constituents of the waste. This fixation process is most often conducted in lined open pits or open tanks into which the liquid waste is poured. The fixative then is added and the materials are thoroughly mixed, most often with a backhoe. Alternatively, mechanical mixers such as pugmills can be used to blend the waste and fixative. Emissions are generated for as long as the waste remains in the pit. Emissions from this process may be estimated by using the open dump model.

A landfill is a facility, usually an excavated, lined pit, into which wastes are placed for permanent disposal. Emissions from open landfills, those still receiving wastes, can be estimated by applying the Research Triangle Institute (RTI) land treatment model.[1] Emissions from closed landfills, those filled to design capacity and with a cap (final cover) installed, can be estimated with the RTI closed landfill model.

Wastepiles are temporary accumulations of waste. They serve a storage function and have a limited life span. Emissions from wastepiles can be estimated by applying the RTI land treatment model.[2]

8.2 CLOSED LANDFILLS

8.2.1 Emission Model Equations

The RTI closed landfill model is used to estimate the time-dependent behavior of emissions from waste placed in a closed (capped) landfill that is vented to the atmosphere and (as a special case) open-landfill waste covered with daily earth covers. This model accounts for escape of the constituent of interest via two primary, independent mechanisms: diffusion through the cap and convective loss from barometric pumping through the vent(s). It is the purpose of this section to describe the model and its evolution in a general way and to present all model equations and major assumptions.

The model is based primarily upon the work of Farmer et al.,[3] who applied Fick's first law for steady-state diffusion to closed landfills. Farmer's equation utilizes an effective diffusion coefficient for the soil cap based on the work of Millington and Quirk.[4] A previous EPA study[5] was dedicated to the evaluation of available models for estimating emissions from hazardous waste treatment, storage, and disposal facilities (TSDF), including closed landfills. This study endorsed the models of Farmer et al.[6] and Thibodeaux[7] for closed landfills, apparently because of their treatment of soil-pore diffusion. Of the two, the Farmer et al.[8] model alone has received experimental verification (although to a limited degree) via a laboratory experiment using hexachlorobenzene-containing waste in a simulated landfill.

The diffusion model of Farmer et al.[9] was subsequently modified by RTI to allow for convective losses of the constituent of interest from the landfill, which can occur from barometric pumping. Furthermore, the decline in the emission rate from closed landfills over the long term was accounted for via the incorporation of a time-dependent decay function.

The barometric pumping emission mechanism results from changes in atmospheric pressure--as the pressure is lowered, gas flows out of the landfill through the vent(s) to equalize internal pressure. The contribution to total emissions resulting from barometric pumping equals the concentration of the constituent of interest in the gas within the landfill multiplied by the total flow of gas from the landfill. It is recognized that under certain conditions (e.g., the presence of significant biomass) biogas could be generated in a landfill. Biogas consists of methane and carbon dioxide, which is produced from the action of bacteria on organic material. Because of the convective or purging action of biogas in removing the constituent of interest in vapor form, biological decay (if it occurs) results in a net increase in the emission rate. However, it should be noted that there is no evidence that there is significant biomass (necessary for biogas generation) in any chemical waste landfill. Therefore, in this analysis it is assumed, as suggested in the literature, that the toxic property of the waste will inhibit biological processes and thus prevent biogas generation.[10] Hence, closed landfill model equations presented in this document account for diffusion through the cap and barometric pumping only.

The equations inherent in the RTI closed landfill model are as follows: Fick's first law for steady-state diffusion, based on the work of Farmer et al.,[11] for a landfill is given as:

$$J_i = -D_{ei} (C_{2i} - C_{si})/l \qquad (8\text{-}1)$$

where,

J_i = vapor flux of the constituent through the soil surface, $g/cm^2 \cdot s$;

D_{ei} = effective diffusion coefficient, cm^2/s;

C_{2i} = concentration of constituent in the air above the cap, g/cm^3 air;

C_{si} = concentration of the constituent in the vapor space beneath the cap, g/cm^3; and

l = cap thickness, cm.

(Because the concentration of the constituent at the surface is negligible, $C_{2i} = 0$.)

Emissions associated with diffusion alone (E_{1i}, g/s) are obtained from the above equation by multiplying by the landfill surface area (A) in cm^2:

$$E_{1i} = J_i \times A. \qquad (8\text{-}2)$$

The effective diffusion coefficient of the constituent in soil, D_{ei}, is computed (using the expression developed by Millington and Quirk[12] and applied by Farmer et al.[13]) from the diffusion coefficient of the constituent in air, D_{ai}, as:

$$D_{ei} = D_{ai}\ (,_{a}^{3.33}\ /,_{T}^{2}\ ) \qquad (8\text{-}3)$$

where,

D_{ai} = vapor diffusion coefficient in air, cm^2/s;

$,_a$ = soil cap air-filled porosity, cm^3/cm^3 (the actual air-filled porosity of the moist soil); and

$,_T$ = total porosity of the soil cap.

The concentration of the constituent of interest in the vapor space beneath the cap is computed using the ideal gas law as follows:

$$C_{si} = P_i MW_i/RT' = P_i MW_i/R(T + 273) \qquad (8\text{-}4)$$

where,

P_i = equilibrium partial pressure of constituent, atm;

MW_i = molecular weight of constituent, g/g mol;

R = gas constant, 82.05 $\frac{cm^3 \cdot atm}{K \cdot g\ mol}$

T' = absolute temperature in the landfill, K; and

T = temperature in the landfill, °C.

Calculation of the equilibrium partial pressure, P_i, depends on the type of waste liquid as follows:

a. For <u>dilute aqueous solutions</u> (where Henry's law applies), the equilibrium partial pressure of constituent within the landfill (P_i, atm) is computed as:

$$P_i = \frac{H_{ci} D_{liquid}\ X_i}{MW_{liquid}} \times 10^6\ \frac{cm^3}{m^3} \qquad (8\text{-}5)$$

where,

H_{ci} = Henry's law constant, $m^3 \cdot atm/mol$;

D = density of waste liquid, g/cm^3 ($1\ g/cm^3$ is generally a good estimate for this parameter);

X_i = mole fraction of constituent i in waste liquid;

where,

$X_i = (C_i/MW_i)/[C_{H_2O}/18 + C_i/MW_i]$;

where,

C_i = weight fraction of constituent i in the original waste liquid;

C_{H_2O} = weight fraction of water in the original waste liquid; and

MW_{liquid} = average molecular weight of waste liquid, g/mol

b. For <u>two-phase (water + organic liquid) or organic liquid waste</u>, the equilibrium partial pressure of the constituent of interest within the landfill (P_i, atm) is computed using Raoult's law:

$$P_i = X_i P_i^* \qquad (8\text{-}6)$$

where,

X_i = mole fraction of constituent in the organic liquid phase;

where,

$X_i = (C_i/MW_i)/[C_i/MW_i + C_{oil}/MW_{oil}]$;

where,

C_i = weight fraction of constituent the original waste liquid;

C_{oil} = weight fraction of oil carrier-liquid in the original waste liquid;

MW_{oil} = molecular weight of oil carrier-liquid, g/g mol; and

P_i^* = pure component vapor pressure of the constituent of interest, atm.

Emissions from barometric pumping are computed as:

$$E_{2i} = Q \times C_{si} \times A \qquad (8\text{-}7)$$

where,

E_{2i} = emissions from barometric pumping, g/s;

Q = flow rate of gas through the vent, expressed as a flux, cm^3/cm^2 landfill area•s;

C_{si} = concentration of constituent in the gas within the landfill, g/cm^3 gas (see Equation 8-4; and

A = surface area of the landfill, cm^2.

The gas flow rate, Q, is estimated using the following procedure.

a. Compute volume of gas available for barometric pumping, assuming the entire void-volume of the waste is available:

$$V_c = D \times A \times ,_{fw} \qquad (8\text{-}8)$$

where,

V_c = volume of void space, cm^3;

D = thickness of waste bed within landfill, cm; and

A = surface area of the landfill, cm^2.

$,_{fw}$ = air porosity fraction of fixed waste (dimensionless).

b. Compute the total volume of gas (cm^3) exiting the vent of the landfill due to changes in barometric pressure and/or temperature within the landfill:

$$V_B = V_C \left[\left(\frac{P_{ref}}{P_1} \right) \left(\frac{T_1 + 273}{T_{ref} + 273} \right) - 1 \right] \qquad (8\text{-}9)$$

where,

V_B = total volume of gas exiting landfill, cm^3;

P_{ref} = initial (reference) barometric pressure, mm Hg;

P_1 = final barometric pressure, mm Hg;

T_1 = final landfill temperature, °C; and

T_{ref} = initial (reference) landfill temperature, °C.

For cases in which $P_1 > P_{ref}$ and/or T_1 V_B may be negative (indicating a condition of gas flow into the landfill and because this condition results in no emissions associated with barometric pumping}, V_B should be set equal to zero to avoid calculational errors in the following steps.

c. Compute the average flow rate of gas from the landfill over the time interval of interest:

$$Q = \frac{V_B}{)t\ A} \qquad (8\text{-}10)$$

where,

Q = average flow rate of gas from the vent due to barometric pumping, cm^3/cm^2 landfill area•s;

)t = time interval over which the change in pressure and/or temperature occurred, s; and

A = landfill area, cm^2.

In an average day, barometric pressure drops 4 mbar from a typical value of 1,013 mbar. Landfill temperature is assumed to remain constant. Hence, under these conditions, P_{ref} = 1,013 mbar, P_1 = 1,009 mbar, $T_{ref} = T_1$ = 15 °C, and)t = 8.64×10^4 s.

Having computed the instantaneous emissions associated with diffusion through the cap and barometric pumping, the total initial emission rate at the time of landfill closure, E_i^* (g/s), is computed as the sum:

$$E_i^* = E_{1i} + E_{2i}. \qquad (8\text{-}11)$$

The total instantaneous emission rate at any time then is computed via an exponential decay function:

$$E_i(t) = \frac{(3{,}600\ \text{s/h})(24\ \text{h/d})(365.25\ \text{d/yr})E_i^*}{10^6}\ \exp\ (-8t)$$

$$E_i(t) = 31.56\ E_i^*\ \exp\ (-8t) \qquad (8\text{-}12)$$

where,

$E_i(t)$ = total time-dependent emission rate, Mg/yr;

E_i^* = initial emission rate, at time of landfill closure, g/s;

t = time since landfill closure, months; and

8 = "decay" constant, months^{-1}.

The "decay" constant, 8, is computed as follows:

$$8 = \frac{(3{,}600\ \text{s/h}) \times (24\ \text{h/d}) \times 365.25\ \text{d/yr}) \times E_i^*}{12\ \text{mo/yr} \times M_{oi}}$$

$$8 = 2.63 \times 10^6\ E_i^*/M_{oi} \qquad (8\text{-}13)$$

where M_{oi} is the total mass of the constituent of interest in the landfill (g). This parameter can be computed from the weight fraction of the constituent in the original waste liquid (C_i), the mass of original waste liquid in a unit volume of fixed waste (W), the landfill surface area (A), and the thickness of the waste layer within the landfill (D):

$$M_{oi} = C_i\ W\ A\ D\ . \qquad (8\text{-}14)$$

The average emission rate from a closed, vented landfill over the time since landfill closure is equal to the integral of the emission rate equation over the time period divided by the time period, which yields the following expression:

$$E_{Ai}(t) = \frac{(3{,}600\ \text{s/h})(24\ \text{h/d})(365.25\ \text{d/yr})\ E_i^*}{(10^6\ \text{g/Mg})8t}\ [1 - e^{-8t}]$$

$$E_{Ai}(t) = \frac{31.56E_i^*}{8t}\ [1 - e^{-8t}] \qquad (8\text{-}15)$$

where

$E_{Ai}(t)$ = average emission rate over the time since landfill closure, Mg/yr

t = time since landfill closure, mo.

Table 8-1 summarizes the equations necessary to apply the RTI closed landfill model.

The model is highly sensitive to the air porosity of the clay cap ($,_a$), which largely determines the diffusion rate through the cap. The model is sensitive to the properties of the constituent of interest, particularly the vapor pressure (P^*_i), Henry's law constant (H_{ci}), and mole fraction in the

TABLE 8-1. RTI CLOSED LANDFILL MODEL

$E_i(t) = 31.56\ E_i^* \exp(-8t)$

$E_{Ai}(t) = \frac{31.56\ E_i^*}{8t} \ast 1 - e^{-8t} \ast$

$8 = 2.63 \times 10^6\ E_i^*/M_{oi}$

$M_{oi} = C_i\ W\ A\ D$

$E_i^* = E_{1i} + E_{2i}$

$E_{1i} = J_i \times A$

$J_i = -D_{ei}\ (C_{2i} - C_{si})/l$

$D_{ei} = D_{ai}\ (,_a^{3.33}/,_T^2)$

$C_{2i} = 0$

$C_{si} = P_i\ MW_i/R\ (T + 273)$

$P_i = \frac{H_{ci}\ D_{liquid}\ X_i}{MW_{liquid}} \times 10^6\ \frac{cm^3}{m^3}$ (dilute aqueous waste liquids)

$X_i = (C_i/MW_i)/(C_{H_2O}/18 + C_i/MW_i)$ (dilute aqueous waste liquids)

$P_i = X_i\ P_i^*$ (two-phase liquid or organic liquid waste)

$X_i = (C_i/MW_i)/(C_i/MW_i + C_{oil}/MW_{oil})$ (two-phase liquid or organic liquid waste)

$E_{2i} = Q\ C_{si}\ A$

$Q = V_B/()t\ A)$

$V_B = V_C \ast \ast \frac{P_{ref}}{p_1} \ast \ast \frac{T_1 + 273}{T_{ref} + 273} \ast - 1 \ast$

$V_C = D\ A\ ,_{fw}$

(continued)

TABLE 8-1 (continued)

Variable	Definition	Data source
A	Landfill surface area, cm^2	Westat survey[a]
C_{si}	Concentration of constituent i in the gas within the landfill, g/cm^3 gas	Calculated
C_{2i}	Concentration of constituent i in air above the cap, g/cm^3	Assumed
C_i	Weight fraction of constituent i in the original waste liquid (dimensionless)	Definition
C_{H_2O}	Weight fraction of water in the original waste liquid (dimensionless)	Definition
C_{oil}	Weight fraction of oil carrier-liquid in the original waste liquid (dimensionless)	Definition
D	Thickness of waste bed within landfill, cm	Westat survey[b]
D_{ai}	Diffusivity of constituent i in air, cm^2/s	Literature
D_{ei}	Effective diffusion coefficient of constituent i in clay cap, cm^2/s	Calculated
$E_{Ai}(t)$	Average emission rate of constituent i over time t since landfill closure, Mg/yr	Calculated
$E_i(t)$	Total instantaneous emission rate of constituent i at time t since landfill closure, Mg/yr	Calculated
E_i^*	Total initial emission rate of constituent i at time of landfill closure, g/s	Calculated
E_{1i}	Initial emission rate of constituent i at landfill closure due to diffusion alone, g/s	Calculated

[a] Reference 14. [b] Reference 15.

(continued)

TABLE 8-1 (continued)

Variable	Definition	Data source
E_{2i}	Initial emission rate of constituent i at landfill closure due to barometric pumping alone, g/s	Calculated
H_{ci}	Henry's law constant for constituent i, m^3•atm/mol	Literature
J_i	Initial diffusion flux of constituent i, g/cm^2•s	Calculated
l	Landfill cap thickness, cm	Literature
M_{oi}	Initial mass of constituent i in the landfill, g	Definition or calculated
MW_i	Molecular weight of constituent i, g/g mol	Literature
MW_{liquid}	Average molecular weight of the dilute aqueous waste liquid, g/g mol (assumed to be 18 g/g mol)	Estimated
MW_{oil}	Molecular weight of the oil carrier-liquid, g/g mol	Definition or estimated
P^*_i	Pure component vapor pressure of constituent i, atm	Literature
P_i	Equilibrium partial pressure of constituent i in the vapor space, atm	Calculated
P_{ref}	Initial (reference) barometric pressure, mm Hg	Meteorological information
P_1	Final barometric pressure after)t, mm Hg	Meteorological information
Q	Average flow rate of gas from landfill vent(s) due to barometric pumping, cm^3/cm^2 landfill area•s	Calculated
R	Ideal gas constant, 82.05 cm^3•atm/g mol•K	Literature
t	Time since landfill closure, mo	Definition

(continued)

TABLE 8-1 (continued)

Variable	Definition	Data source
)t	Time interval used to determine average barometric pumping rate, s	Definition
T	Temperature within landfill, °C	Estimated from literature data
T_{ref}	Initial (reference) landfill temperature, °C	Estimated from literature data
T_1	Final landfill temperature after)t, °C	Estimated
V_B	Total volume of gas exiting landfill in)t, cm^3	Calculated
V_C	Total volume of void space within waste, cm^3	Calculated
W	Mass of original waste liquid in a unit volume of fixed waste, g/cm^3	Definition or estimated
X_i	Mole fraction of constituent i in the aqueous liquid (for dilute aqueous waste) or in the organic phase (for two-phase or organic liquid waste) (dimensionless)	Definition
’a	Air porosity of the clay cap (dimensionless)	Estimated from clay property data
’T	Total porosity of the clay cap (dimensionless)	Estimated from clay property data
’fw	Air porosity of the fixed waste (dimensionless)	Estimated from fixed waste property data
D	Density of dilute aqueous waste liquid (generally equals 1 g/cm^3)	Definition or liquid, g/cm^3
8	Exponential decay constant, mo^{-1}	Calculated

waste liquid (X_i). Because temperature affects volatility, the model is sensitive to temperature. Other parameters to which the model is sensitive include the depth of the fixed waste (D), the air porosity of the fixed waste (,$_{fw}$), the landfill surface area (A), and the barometric pressure change (P_{ref} - P_1). This latter group of parameters is significant in that it impacts the barometric pumping rate or the volume of gas available for pumping. In contrast to these parameters, the model exhibits relatively low sensitivity to the diffusivity of the constituent in air (D_{ai}), the cap thickness (l), and the total mass of the constituent in the landfill (M_{oi}).

The major assumptions associated with the RTI closed landfill model are as follows:

- The liquid waste containing the constituent of interest is assumed to be bound in the fixed waste within the landfill.
- The constituent of interest in the gas within the landfill is assumed to be in equilibrium with the liquid in the waste.
- Adsorption of the constituent of interest onto the soil of the cap is assumed to be negligible.
- The fraction of air-filled space in the landfill cap (air porosity) is assumed to remain relatively constant over the long term.
- The effective diffusion coefficient of the cap is assumed not to vary with either the concentration of the constituent of interest or time.
- The concentration of the constituent of interest in air at the top of the landfill cap is assumed to be effectively 0.
- No biodegradation (with concurrent production of biogas) is assumed to occur due to the suppression of biological processes by the toxic waste.
- The landfill is assumed to be vented to the atmosphere. The volume of gas available for barometric pumping is assumed to consist of the total void-volume of the waste bed.

- No transport of the constituent of interest in moving water is assumed to occur.

8.2.2 Model Plant Parameters for Closed Landfills

The characteristics of a model closed landfill facility are discussed here. This model facility is used as the basis for an example calculation in Section 8.2.3.

The model facility for closed landfills has an area of 1.417×10^8 cm^2 (3.5 acres). This value represents an approximately midrange value from the Westat survey.[16] A reasonable value of landfill depth, also selected from the Westat survey,[17] is 458 cm (15 ft). The landfill cap is assumed to be composed of compacted clay. The cap thickness value of 107 cm (3.5 ft) represents the average of extremes in thickness of clay caps reported in site studies (2 ft to 6 ft).[18] The value used for air porosity of the clay cap is 0.08 (8 percent), while the total porosity is 0.41 (41 percent). These values were computed based on reasonable physical properties and level of compaction for compacted clay.[19] The landfill is assumed to be vented to the atmosphere. The temperature beneath the landfill cap is estimated at 15 °C, which represents the temperature of shallow ground water at a midlatitude U.S. location.[20] This temperature is assumed to remain constant. The landfill is assumed to be exposed to a nominal barometric pressure of 1,013 mbar, which represents an estimate of the annual average atmospheric pressure in the United States.[21] Barometric pumping is estimated for the landfill using a daily pressure drop from the nominal value of 4 mbar. The 4 mbar value represents an estimate of the annual average diurnal pressure drop.[22]

The model closed landfill facility is assumed to contain fixed waste. The waste liquid (before fixation) selected for the facility is assumed to be a two-phase aqueous/organic containing 20 percent chloroform, 20 percent low-volatility organic, {for modeling purposes, this component of the waste liquid represents the oil carrier-liquid} and 60 percent water (by weight). This liquid has an average density of 1.16 g/cm^3. The fixation industry indicates that waste liquid, when combined with fixative, may in actuality increase in volume by as much as 50 percent.[23,24] The volume change, which is a function of the specific waste being fixed and the specific formulation of the fixative, can only be determined experimentally. In view of the inherent variability in the fixation process and the lack of real data, for the purpose of this calculation the assumption is made that the fixation process does not change the waste volume. This assumption is environmentally conservative and may result in an overestimation of the landfill emissions. Actual volume changes that may take place as a result of fixation can easily be accounted for because the change in the calculated emissions is inversely proportional to the change in waste volume. One industry contact indicated that, for the purposes of estimating emissions, the assumption of no volume change during fixation was reasonable.[25] Based on the waste liquid density and the assumption of no volume increase from fixation, the mass of waste liquid in a unit volume of fixed waste is 1.16 g/cm^3. The air porosity of the fixed waste (used to estimate the total volume of gas available for barometric pumping) is taken to be 0.25 (25 percent). This value was inferred from measurements of total porosity and moisture content of various fixed wastes,[26] and, for the purposes of this analysis, is assumed to pertain to waste within the landfill as opposed to waste immediately following fixation. As discussed previously, there is no evidence for significant biomass in any chemical waste landfill. Therefore, in this analysis it is assumed, as suggested in the literature, that the toxic property of the waste will inhibit biological processes and thus prevent biogas generation.[27] Hence, the waste biomass concentration is taken to be 0 g/cm^3.

The properties of chloroform that are pertinent to this analysis include the molecular weight (119.4 g/g mol), pure component vapor pressure at 15 °C (0.162 atm), diffusivity in air at 15 °C (0.10 cm^2/s) and density (1.49 g/cm^3). The low-volatility organic liquid present in the waste has a molecular weight of 147 g/g mol and a density of 1.31 g/cm^3.

Table 8-2 smmarizes the model facility parameters for closed landfills used in the example calculation in Section 8.2.3. For facilities that accept more than one type of waste, the weighted average constituent concentrations may be used.

8.2.3 Example Calculation for Closed Landfill

This section presents a step-by-step calculation of emissions from a closed landfill that is vented to the atmosphere. The equations discussed in Section 8.2.1 and summarized in Table 8-1 are used with the model unit parameters in Section 8.2.2 to estimate emissions from a fixed, two-phase aqueous/organic waste containing chloroform:

- Waste liquid (before fixation): 20 percent chloroform, 20 percent low volatility organic liquid, 60 percent water (by weight)
- Liquid/fixative: 1 unit volume liquid + dry fixative = 1 unit volume fixed waste
- Waste biomass concentration: 0 g/cm^3
- Landfill area: 1.417×10^8 cm^2 (3.5 acres)
- Waste bed thickness: 457 cm (15 ft)
- Cap thickness: 107 cm (3.5 ft)
- Type landfill: vented
- Temperature beneath cap: 15 °C
- Time period for emission calculation: 1 yr.

TABLE 8-2. INPUT PARAMETERS--CLOSED LANDFILL

Parameter	Value
Area	1.417×10^8 cm^2 (3.5 acres)
Waste bed thickness	457 cm (15 ft)
Cap thickness	107 cm (3.5 ft)
Cap air porosity	0.08 (8%)
Cap total porosity	0.41 (41%)
Type landfill	Vented
Temperature beneath cap	15 °C
Typical barometric pressure	1,013 mbar
Daily barometric pressure drop	4 mbar
Waste liquid (before fixation)	Two-phase aqueous/organic
Liquid composition	20% chloroform, 20% low-volatility organic (oil), 60% water (by weight)
Liquid/fixative	1 unit volume liquid + dry fixative = 1 unit volume fixed waste
Liquid in fixed waste	1.16 g/cm^3
Air porosity fixed waste	0.25 (25%)
Biomass concentration	0 g/cm^3
<u>Chloroform properties</u>	
Molecular weight	119.4 g/g mol
Vapor pressure (15 °C)	0.162 atm (123 mm Hg)
Diffusivity in air (15 °C)	0.10 cm^2/s
Density	1.49 g/cm^3
<u>Low-volatility organic[a] properties</u>	
Molecular weight	147 g/g mol
Density	1.31 g/cm^3

---

[a] Also referred to as oil "carrier-liquid."

a. Compute the effective diffusion coefficient, D_{ei} (cm^2/s) (Equation (8-3)):

$$D_{ei} = D_{ai}(\epsilon_a^{3.33}/\epsilon_T^2)$$

$$D_{ei} = (0.10\ cm^2/s)\ (0.08)^{3.33}/(0.41)^2$$

$$D_{ei} = 1.32 \times 10^{-4}\ cm^2/s \quad .$$

b. Compute the equilibrium partial pressure of chloroform in the vapor space, P^i (atm):

The waste before fixation was a two-phase liquid. Hence, Raoult's law applies. The mole fraction for this case is computed as:

$$X_i = (C_i/MW_i)/(C_i/MW_i + C_{oil}/MW_{oil})$$

$$X_i = (0.20/119.4\ g/g\ mol) \div [0.20/119.4\ g/g\ mol + 0.20/147\ g/g\ mol]$$

$$X_i = 0.55 \quad .$$

From Raoult's law (Equation (8-6)):

$$P_i = X_i\ P^*_i$$

$$P_i = (0.55)(0.162\ atm)$$

$$P_i = 8.91 \times 10^{-2}\ atm \quad .$$

c. Compute the concentration of chloroform in the vapor space beneath the cap, C_{si} (g/cm^3 void space) (Equation (8-4)):

$$C_{si} = P_i MW_i/R(T + 273)$$

$$C_{si} = \frac{(8.91 \times 10^{-2}\ atm)(119.4\ g/g\ mol)}{(82.05\ cm^3 \bullet atm/g\ mol \bullet K)\ (15 + 273)}$$

$$C_{si} = 4.50 \times 10^{-4}\ g/cm^3 \ .$$

d. Compute initial chloroform emission flux resulting from diffusion through the cap only, J_i ($g/cm^2 \bullet s$)(Equation 8-1):

$$J_i = -D_{ei}(C_{2i} - C_{si})/l$$

$$J_i = -(1.32 \times 10^{-4}\ cm^2/s)(0\ g/cm^3 - 4.50 \times 10^{-4}\ g/cm^3)$$
$$/107\ cm$$

$$J_i = 5.55 \times 10^{-10}\ g/cm^2{\bullet}s \quad .$$

e. Compute initial chloroform emissions resulting from diffusion through the cap only, E_{1i} (g/s) (Equation (8-2)):

$$E_{1i} = J_i \times A$$

$$E_{1i} = (5.55 \times 10^{-10}\ g/cm^2{\bullet}s)(1.417 \times 10^8\ cm^2)$$

$$E_{1i} = 7.86 \times 10^{-2}\ g/s \quad .$$

f. Estimate the barometric pumping-induced gas flow rate through the vent(s):

1. Compute the volume of gas available for barometric pumping, V_c (cm^3) (Equation (8-8)):

$$V_c = D \times A \times ,_{fw}$$

$$V_c = (457\ cm)(1.417 \times 10^8\ cm^2)(0.25)$$

$$V_c = 1.62 \times 10^{10}\ cm^3 \quad .$$

2. Compute volume of gas exiting the vent due to barometric pressure change, V_B (cm^3) (Equation 8-9):

$$V_B = V_c \left[\left(\frac{P_{ref}}{P_1} \right) \left(\frac{T_1 + 273}{T_{ref} + 273} \right) - 1 \right] \quad .$$

For this case, $T_1 = T_{ref} = 15$ °C, and barometric pressure drops by 4 mbar from the nominal value of 1,013 mbar:

$$V_B = 1.62 \; 10^{10} \mathrm{cm}^3 \left\{ \left(\frac{1{,}013 \text{ mbar}}{1{,}009 \text{ mbar}} \right) \left(\frac{15 \text{ °C} + 273 \text{ K}}{15 \text{ °C} + 273 \text{ K}} \right) - 1 \right\}$$

$$V_B = 6.42 \times 10^7 \text{ cm}^3 \quad .$$

3. Compute the average flow rate of gas over the time interval, Q, ($\mathrm{cm}^3/\mathrm{cm}^2$ landfill area • s) (Equation 8-10):

   The average diurnal pressure drop of 4 mbar occurs within a 24-h period. For convenience, the gas flow from this pressure change is averaged over 24 h (equals 8.64×10^4 s).

   $$Q = \frac{V_B}{\Delta t A}$$

   $$Q = \frac{6.42 \times 10^7 \mathrm{cm}^3}{(8.64 \times 10^4 \text{ s})(1.417 \times 10^8 \text{ cm}^2)}$$

   $$Q = 5.25 \times 10^{-6} \text{ cm}^3/\mathrm{cm}^2 \bullet \mathrm{s} \quad .$$

4. Compute the barometric pumping-induced emission rate,

   E_{2i} (g/s) (Equation (8-7)):

   $$E_{2i} = Q \times C_{si} \times A$$

$$E_{2i} = (5.25 \times 10^{-6} \text{ cm}^3/\mathrm{cm}^2 \bullet \mathrm{s})(4.50 \times 10^{-4} \text{ g/cm}^3)(1.417 \times 10^8 \text{ cm}^2)$$

$E_{2i} = 0.335$ g/s .

g. Compute the total initial emission rate, E_i^* (g/s) (Equation 8-11):

$$E_i^* = E_{1i} + E_{2i}$$

$$E_i^* = 7.86 \times 10^{-2} + 0.335$$

$$E_i^* = 0.413 \text{ g/s} \quad .$$

h. Compute the time-dependent instantaneous emission rate:

1. Compute total mass of constituent i in landfill, M_{oi}:

   First compute W, the mass of original waste liquid in a unit volume of fixed waste. Assuming one unit volume of waste liquid results in one unit volume of fixed waste, this parameter can be computed using the densities of the waste liquid components and their weight fractions as follows:

   $$W = [(1.49 \text{ g/cm}^3)(0.2)+(1.31 \text{ g/cm}^3)(0.2)+(1 \text{ g/cm}^3)(0.6)]$$

   $$\times 1 \text{ cm}^3 \text{ liquid/cm}^3 \text{ fixed waste}$$

   $$= 1.16 \text{ g/cm}^3 \quad .$$

   M_{oi} is then computed as:

   $$M_{oi} = C_i \; W \; A \; D$$

   $$M_{oi} = \frac{20 \text{ g chloroform}}{100 \text{ g liquid}} \times \frac{1.16 \text{ g liquid}}{\text{cm}^3 \text{ fixed waste}} \times 1.417 \times 10^8 \text{ cm}^2$$

   $$\times 457 \text{ cm} = 1.50 \times 10^{10} \text{ g chloroform} \quad .$$

2. Compute the decay constant, 8 (mo^{-1}) (Equation (8-13)):

   $$8 = 2.63 \times 10^6 \; E_i^*/M_{oi}$$

   $$8 = (2.63 \times 10^6)(0.413 \text{ g/s})/1.50 \times 10^{10} \text{ g}$$

$$8 = 7.25 \times 10^{-5}\ \text{mo}^{-1}\ .$$

3. Compute the instantaneous emission rate, E_i, in Mg/yr, after 1 yr (Equation (8-12)):

$$E_i(t) = 31.56\ E_i^* \exp(-8t)$$

$$E_i = (31.56)(0.413\ \text{g/s}) \exp(-7.25 \times 10^{-5}\ \text{mo}^{-1} \times 12\ \text{mo})$$

$$E_i = 13.0\ \text{Mg/yr}\ .$$

i. Compute the average emission rate in the first year, E_{Ai}, in Mg/yr (Equation (8-15)):

$$E_{Ai}(t) = \frac{31.56\ E_i^*}{8t}\ \overset{\ddagger}{\underset{.}{*}}1 - e^{-8t}\underset{-}{*}$$

$$E_{Ai} = \frac{(31.56)(0.413\ \text{g/s})}{(7.25 \times 10^{-5}\ \text{mo}^{-1})\ (12\ \text{mo})}\ \overset{\ddagger}{\underset{.}{*}}1\text{-exp}*\text{-}12\ \text{mo} \times 7.25 \times 10^{-5}\ \text{mo}^{-1}*\underset{-}{*}$$

$$E_{Ai} = 13.0\ \text{Mg/yr}\ .$$

8.3 FIXATION PITS

This section is currently under review. (pages 25-34 not shown)

8.4 OPEN LANDFILLS AND WASTEPILES

8.4.1 Emission Model Equations

The RTI land treatment model[34] (discussed in Section 5.2) is used to estimate the air emission rate of the constituent of interest from open (active) landfills and wastepiles. This model is based on the theory of diffusion out of an infinite flat slab and was intended originally for use in estimating emissions from land treatment operations. The intent of this section is to discuss use of the model with regard to the estimation of emissions from open landfills and wastepiles; a detailed description of the model relevant to land treatment operations and the theoretical basis for the model are presented in Section 5.0 of this report and will not be repeated here.

A land-treatment-type model was selected for estimating emissions from open landfills and wastepiles because (1) no adequate models exist for these sources, and (2) there are a number of similarities in physical characteristics of open landfills, wastepiles, and land treatment operations. A previous EPA study[35] dedicated to the evaluation of models for estimating emissions from hazardous waste TSDF identified only one model for open waste dumps such as landfills and wastepiles--the open dump model. A serious limitation of the model for this application, however, is that it does not account for depletion of the volatilizing chemical from the waste surface. Hence, the open dump model is judged unsuitable for the estimation of emissions from landfills and wastepiles over the time period of interest (months or longer).

The similarity in physical characteristics among open landfills, wastepiles, and land treatment operations is apparent upon close examination--in all three, the waste liquid is ultimately mixed homogeneously with a "carrier" matrix (soil in the case of land treatment; dry fixative in the case of active landfills; and soil, fixative, or some other solid matrix in the case of wastepiles). In all cases, the matrix is porous and permeable, allowing the diffusion of the constituent of interest through the matrix and into the air. Hence, in all cases, diffusion theory can be used to model the emission rate. The notable difference between land treatment operations and open landfills/wastepiles is the presence of an additional mechanism affecting emissions in the case of land treatment--biological decay of the constituent. Because biodegradation is not thought to occur. There is no evidence that there is significant biomass (necessary for biological decay) in any chemical waste landfill. It is assumed that the toxic property of the waste will inhibit biological processes.[36] In open landfills/wastepiles, however, its effect is not accounted for in the modeling of air emissions.

The RTI land treatment model, which was selected for estimating emissions from open landfills and wastepiles, has the following characteristics: a sound basis in scientific theory, limited validation against measured emissions from land treatment operations, and reasonably available input data.[37] The model considers effects such as evaporation of the constituent of interest from interstitial surfaces of the carrier matrix and diffusion of material through air-filled pore spaces.

The equations necessary to apply the land treatment model to open landfills and wastepiles are summarized in Table 7-3. These equations, explained in Chapter 7.0, can be used to estimate the fraction of the constituent emitted (F_t) and the instantaneous emission rate (E). It should be noted that the absence of biodegradation represents a special case that allows some simplification of several of the Chapter 7.0 equations, e.g., Equations (7-4) and (7-5). (The absence of biomass implies that biomass concentration equals 0. Hence, t_b, the time constant for biological decay, equals infinity. Consequently, the exponential term e^{-t/t_b} becomes unity.) Also, the absence of biodegradation implies that the fraction of the constituent emitted after a long time, F_a, would equal unity.

Because the land treatment model was derived originally for land treatment operations, model input parameters are not necessarily in the most convenient units and terminology for open landfills and wastepiles. Hence, several points should be noted:

- Fixed waste is analogous (for modeling purposes) to the waste-laden soil in land treatment.
- M_o, the area-loading of the constituent in g/cm^2, is geared toward land treatment operations. For open landfills and wastepiles, the landfill equivalent should be computed.
- No "tilling" (as discussed in Chapter 7.0) is performed in open landfills or wastepiles.
- Waste liquid is "applied" or mixed with fixative only once. Hence, waste "reapplication" (used in the sense discussed in Chapter 7.0) does not occur in open landfills and wastepiles.
- The waste bed depth in open landfills and wastepiles is analogous to the "depth to which waste is mixed" in land treatment, as discussed in Chapter 7.0.

The approach required to estimate emissions from open landfills or wastepiles is as follows, based on equations in Table 7-3:

1. Compute the loading of waste liquid (L) in the fixative or soil, using the known waste composition. (For two-phase aqueous organics or organic liquid wastes, L should be computed as grams organic phase per cubic centimeter solid material. For dilute aqueous waste liquids, L equals grams aqueous liquid per cubic centimeter solid material.)
2. Compute the effective diffusion coefficient (D_e).
3. Compute the partition coefficient (Keq).
4. Use the appropriate emission equation to compute the fraction of constituent emitted (F_t) and/or the instantaneous emission rate (E). For wastepile calculations, the time input to these equations should be no greater than the life of the wastepile (retention time).

The sensitivity of the land treatment model to some parameters differs in its application to open landfills and wastepiles from that in land treatment operations because of the difference (in some cases) in the expected range of the parameters. In general, it can be stated that, for application to open landfills and wastepiles, the model is sensitive to the air porosity of the solid waste, the liquid loading in the solid waste, the waste depth, the concentration of the constituent in the waste, and the volatility of the constituent under consideration. In contrast, the model exhibits a relatively low sensitivity to the diffusion coefficient of the constituent in air.

The following major assumptions are associated with the RTI land treatment model and its application to open landfills and wastepiles:

- The waste liquid is mixed uniformly with the carrier matrix (either fixative, soil, or some other granular solid material) before placement in an open landfill or wastepile.
- The liquid waste containing the constituent of interest is assumed to be bound in the waste after fixation and placement in the open landfill or wastepile.
- The waste liquid does not flow within the carrier matrix.
- The adsorption isotherm of the constituent of interest is linear within the depth of the waste and does not change with time.
- No bulk flow of gas is induced within the waste matrix.
- The diffusion coefficient does not vary with either concentration or time.
- The concentration of the constituent of interest in the gas phase at the surface of the open landfill/wastepile is much lower than the concentration of the constituent of interest in the gas phase within the waste matrix.

- No diffusion of the waste liquid into depths below the waste layer is assumed.
- Liquid-vapor equilibrium is established at all times within the waste matrix.
- For the case of fixed waste in the landfill or wastepile, the fixed waste mixture behaves as a soil with regard to diffusion of the constituent of interest.
- No biodegradation of the constituent of interest occurs in open landfills or wastepiles.

8.4.2 Model Plant Parameters for Open Landfills and Wastepiles

The characteristics of model facilities for open landfills and wastepiles are discussed here. The model open landfill facility is used as the basis for an example calculation using the model.

8.4.2.1 Parameters for open landfills. The model facility for open landfills has a surface area of 1.42 x 10^8 cm^2 (3.5 acres). This value represents an approximately midrange value from the Westat survey.[38] A reasonable value of landfill depth from the Westat survey[39] was 458 cm (15 ft). The model open landfill is assumed to be half full, and hence has a waste depth of 229 cm (7.5 ft). The landfill is assumed to contain fixed waste. A standard temperature of 25 °C is assumed to apply.

The waste liquid (before fixation) selected for this model facility is assumed to be a two-phase aqueous/organic containing 20 percent chloroform, 20 percent low-volatility organic, and 60 percent water (by weight). This liquid has an average density of 1.16 g/cm^3. The fixation industry indicates that waste liquid, when combined with fixative, may increase in volume by up to 50 percent,[40] depending on the specific combination of waste and fixative. In view of the inherent variability in the fixation process and the lack of real data on volume changes, for purposes of this report, the assumption is made that the waste volume does not change during fixation. Measurements[41] performed on various types of fixed waste yielded a broad range of total porosities.

Fifty percent, as used in this study, is a reasonable estimate of this parameter. These porosity values are assumed to be representative of waste in an open landfill, rather than waste that has recently undergone fixation. A 25-percent air porosity appears to be a reasonable value; this value was inferred from measurements of total porosity and moisture content.[42] As discussed previously, there is no evidence of significant biomass in any chemical waste landfill. Therefore, in this analysis it is assumed, as suggested in the literature, that the toxic property of the waste will inhibit biological processes and thus prevent biogas generation.[43] Hence, the waste biomass concentration is taken to be 0 g/cm^3.

The properties of chloroform that are pertinent to this analysis include the molecular weight (119.4 g/g mol), pure component vapor pressure (208 mm Hg), and diffusivity in air (0.104 cm^2/s). The low-volatility organic liquid present in the waste has a molecular weight of 147 g/g mol.

Table 8-7 summarizes the model facility parameters for open landfills used in the example calculation in Section 8.4.3.

8.4.2.2 Parameters for wastepiles. A review of information in the Westat survey[44] led to the selection of an approximately midrange value for basal area of 4.65×10^6 cm^2. For modeling purposes, the pile is assumed to be flat. A uniform height of 100 cm was inferred, using the Westat information and engineering judgment. All waste ultimately disposed of in the landfill is assumed to be stored initially in the wastepile. The open landfill described previously (Section 8.4.2.1) is assumed to be filled to capacity in 1 yr. Based on the filled landfill volume (1.42×10^8 cm^2 x 458 cm depth = 6.50×10^{10} cm^3), the wastepile volume (4.65×10^6 cm^2 x 100 cm = 4.65×10^8 cm^3), and the filling time of 1 yr, it can be concluded that the wastepile undergoes a turnover rate of 140 turnovers/yr. Hence, the wastepile retention time is 2.6 d/turnover.

TABLE 8-7. INPUT PARAMETERS OPEN LANDFILL

Area	$1.42 \circ 10^{8}$ cm^{2} (3.5 acres)
Waste depth (half full)	229 cm (7.5 ft)
Volume	3.25 10^{10} cm^{3}
Temperature	25 degrees C.
Waste liquid (before fixation)	Two-phase awueous/organic
Liquid composition	20 percent chloroform, twenty percent low-volatility organic, and 60 percent water.
Liquid density (average)	1.16 g/cm^{3}
Liquid/fixative	1 unit volume liquid + dry fixative = 1 unit volume fixed waste.
Air porosity fixed waste	0.25 (25 percent)
Total porosity fixed waste	0.50 (50 percent)
Biomass concentration	0 g/cm^{3}
<u>Chloroform properties</u>	
Molecular weight	119.4 g/g mol
Vapor pressure	208 mm Hg
Diffusivity in air	0.104 cm^{2}/s
<u>Low-volatility organic properties</u>	
Molecular weight	147 g/g mol

The properties of the waste liquid and the resulting fixed waste accommodated by the model wastepile are identical to those for the open landfill (Section 8.4.2.1) and will not be repeated here. Table 8-8 summarizes the model facility parameters used for wastepiles.

8.4.3 Example Calculation for Open Landfill

This section presents a step-by-step calculation of emissions from an open landfill. The equations identified in Table 7-3 are used with the model unit parameters in Section 8.4.2 to estimate emissions from a fixed, two-phase aqueous/organic waste containing chloroform; the same equations would be applied to the estimation of emissions from wastepiles:

- Waste liquid (before fixation): 20 percent chloroform, 20 percent low-volatility organic liquid, 60 percent water
- Liquid/fixative: 1 unit volume liquid + dry fixative = 1 unit volume fixed waste
- Waste biomass concentration: 0 g/cm^3
- Landfill area: 1.42 x 10^8 cm^2 (3.5 acres)
- Landfill depth: 229 cm (7.5 ft)
- Temperature: 25 °C
- Time period for emission calculation: 3.15 x 10^7 s (1 yr).

a. Compute waste loading, L:

Liquid density before fixation = 1.16 g/cm^3

1 cm^3 liquid waste + fixative = 1 cm^3 fixed waste

L = g organic phase/cm^3 fixed waste

$$= (0.20 + 0.20) \times 1.16 \text{ g/cm}^3 = 0.46 \text{ g/cm}^3 \quad .$$

(Note that weight fraction of chloroform in the oil phase [C] = 0.2/(0.2 + 0.2) = 0.50.)

TABLE 8-8. INPUT PARAMETERS WASTEPILES

Surface Area	$4.65 \circ 10^6$ cm^2
Average height	100 cm
Turnover rate	139/yr
Retention time	2.6 days
Temperature	25 degrees C.
Windspeed	4.92 m/s
Waste liquid	Fixed waste
Liquid composition	20 percent chloroform, 20 percent low-volatility organic, and 60 percent water.
Liquid density (average)	1.16 g/cm^3
Liquid/fixative	1 unit volume liquid + dry fixative = 1 unit volume fixed waste.
Air porosity fixed waste	0.25 (25 percent)
Total porosity fixed waste	0.50 (50 percent)
Biomass concentration	0 g/cm^3
Chloroform properties	
Molecular weight	119.4 g/g mol
Vapor pressure	208 mm Hg
Diffusivity in air	0.104 cm^2/s
Low-volatility organic properties	
Molecular weight	147 g/g mol

b. Compute effective diffusion coefficient for fixed waste:

$$D_e = D_a \frac{{’}_a^{3.33}}{{’}_T^{2}}$$

where

$’_a$ = air porosity fixed waste = 0.25

$’_T$ = total porosity fixed waste = 0.50.

Then

D_a = diffusivity of chloroform in air =

$D_a = 0.104\ \text{cm}^2/\text{s}$

$$D_e = (0.104\ \text{cm}^2/\text{s})\ \frac{(0.25)^{3.33}}{(0.50)^2}$$

$D_e = 4.11 \times 10^{-3}\ \text{cm}^2/\text{s}$.

(Note: $D_e/D_a = 3.96 \times 10^{-2}$.)

c. Compute "partition" coefficient, Keq (ratio of gas-phase chloroform to total chloroform in the waste):

For oily waste,

$$Keq = \frac{P^* MW_{oil}}{R\ T}\ \frac{’_a}{L}$$

where,

P^* = pure component vapor pressure of chloroform = (208 mm Hg)/ (760 mm Hg/atm) = 0.274 atm

MW_{oil} = molecular weight low-volatility organic = 147 g/g mol

R = ideal gas constant = 82.05 cm^3•atm/g mol•K

T = temperature within solid waste, K

T = 273 K + 25 °C = 298 K

$$Keq = \frac{(0.274\ \text{atm})(147\ \text{g/g mol})(0.25)}{(82.05\ \text{cm}^3 \bullet \text{atm/g mol} \bullet \text{K})(298\ \text{K})(0.46\ \text{g/cm}^3)}$$

$$Keq = 8.95 \times 10^{-4} \quad .$$

d. Compute fraction of total chloroform emitted, F_t, after 1 year: First, determine which solution applies by computing from the equations in Table 7-3.

$$\frac{Keq_i D_e}{l^2} = \frac{8.95 \times 10^{-4} \times 4.11 \times 10^{-3}\ \text{cm}^2/\text{s}}{(229\ \text{cm})^2}$$

$$= 7.01 \times 10^{-11}\ \text{s}^{-1} \quad .$$

Therefore,

$$\frac{Keq\ D_e t}{l^2} = 7.01 \times 10^{-11}\ \text{s}^{-1} \times 3.15 \times 10^7\ \text{s}$$

$$= 2.21 \times 10^{-3} \quad .$$

$$K_d t = \frac{Keq\ D_e t}{l^2} \quad \frac{B^2}{4} \quad = 5.45\ (10^{-3}) \quad .$$

Because $Keq\ D_e t/l^2$ is less than 0.25, the first equation of Table 7-3 applies, and

$$F_t = 0.72\ (K_d t)^{1/2}$$

$$F_t = 0.72\ (5.45 \times 10^{-3})^{1/2}$$

$$F_t = 0.053 \quad .$$

e. Compute instantaneous emission rate, E, after 1 yr:

1. Compute initial mass of chloroform in landfill:

$$M_{oi} = l\ L\ C$$

where

l = waste depth = 229 cm

L = g organic/cm^3 fixed waste = 0.46 g/cm^3

C = weight fraction chloroform in oil = 0.50.

Then

$$M_o = (229 \text{ cm})(0.46 \text{ g/cm}^3)(0.50)$$

$$M_o = 52.7 \text{ g/cm}^2 \quad .$$

3. Compute instantaneous emission rate, E_i. Because Keq $D_e t/l^2$ 0.213, use the following equation to compute the emission rate:

$$E = \frac{Mo}{l}\left[\frac{1}{\frac{'a}{k_G \, Keq} + \sqrt{\frac{Bt}{Keq \, D_e}}}\right]$$

$$k_G = 4.82\,(10^{-3})\, U^{0.78}\, Sc_G^{-0.67}\, de^{-0.11}$$

U = windspeed = 4.92 m/s

de = effective diameter of landfill area = $\left(\frac{4A}{B}\right)^{0.5}$ = 134 m

$$Sc_G = \frac{\mu g}{D_a D_a}$$

where: μg = viscosity of air = 1.8 (10^{-4}) g/cm/s.
D_a = Density of air = 1.2 (10^{-3}) g/cm^3.
D_a = 0.104 cm^2/s.

$$Sc_G = \frac{1.81\,(10^{-4})}{1.2\,(10^{-3})\,(0.104)} = 1.45$$

$$k_G = 4.82\,(10^{-3})\,(4.92)^{0.78}\,(1.45)^{-0.67}\,(134)^{-0.11}$$

$$= 0.0076 \text{ m/s} = 0.76 \text{ cm/s}$$

$$E = \frac{52.7}{229}\left(\frac{1}{\frac{0.25}{0.76\ x\ 8.95\ 10^{-4}} + \sqrt{\frac{3.14\ x\ 3.15\ 10^{7}}{8.95\ 10^{-4}\ x\ 4.11\ 10^{-3}}}}\right)$$

$$E = 0.230\left(\frac{1}{368 + 5.1810^{6}}\right)$$

$E = 4.43\ (10^{-8})\ g/cm^{2}/s.$

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9.0 TRANSFER, STORAGE, AND HANDLING OPERATIONS

9.1 NARRATIVE DESCRIPTION OF MODEL PLANTS AND EMISSIONS

This chapter presents models for estimating VO emissions of hazardous wastes from container loading, storage, and cleaning; stationary tank loading and storage; spills; fugitive sources; and vacuum truck loading.

9.2 CONTAINER LOADING

This section addresses emission-estimating practices for hazardous waste loading into tank trucks, railroad tank cars, marine vessels, and 55-gal (0.208-m^3) drums.

9.2.1 Emission Model for Container Loading

The process of loading containers with volatile hazardous wastes generates emissions. If containers were assumed to be clean when loaded, only those vapors generated by the loaded waste could be emitted. If containers hold residues of previous volatile wastes, additional emissions from the residues will also be generated.

To calculate container loading losses, the AP-42[1] equation for loading petroleum liquids is applied. This equation was derived for tanks, cars, and marine vessels. It is also applied to 55-gal drums in this case because the loading principles are similar and because no equation has been developed exclusively for small containers such as drums. The loading equation is as follows:

$$L_L = \frac{12.46\ SMP^*}{T}, \qquad (9\text{-}1)$$

where,

L_L = loading loss, lb/10^3 gal of liquid loaded;

M = molecular weight of vapors, lb/lb mol;

P^* = true vapor pressure of liquid loaded, psia; and

T = bulk temperature of liquid loaded, °R (°F + 460).

S = saturation factor, dimensionless (see Table 9-1).

Equation (9-1) for estimating emissions from containers is not applicable to open dumpsters because they are designed with no tops, unlike drums that have limited venting through bungs.

9.2.2 <u>Model Parameters</u>

Containers are considered to be splash-loaded (as opposed to submerged-loaded) for emission-estimating purposes. This loading method creates larger quantities of VO vapors and increases the saturation factor, S, of each volatile compound within the container. A saturation factor is a dimensionless quantity that "represents the expelled vapors' fractional approach to saturation and accounts for the variations observed in emission rates from the different unloading and loading methods.[2] A saturation factor of 1.45 was selected for these emission estimates, based on previous documentation of splash-loading petroleum liquids.[3,4]

Typical capacities for containers are assumed to be as follows:

- Drums: 55 gal (0.208 m^3)
- Tank trucks: 7,000 gal (26.5 m^3)
- Railroad tank cars: 30,000 gal (114 m^3)
- Marine vessels: 20,000 tons.

It is assumed that 55-gal drums and tank trucks are the predominant containers used in the waste management industry. Bulk liquid hazardous waste is shipped predominantly by highway; therefore, hazardous waste tank truck models are used for estimating emissions.

TABLE 9-1. FACTORS FOR CALCULATING PETROLEUM LOADING LOSSES

Cargo carrier	Mode of operation	s factor
Tank trucks and tank cars	Submerged loading of a clean cargo tank	0.50
	Splash loading of a clean cargo tank	1.45
	Submerged loading: normal dedicated service	0.60
	Splash loading: normal dedicated service	1.45
	Submerged loading: dedicated vapor balance service	1.00
	Splash loading: dedicated vapor balance service	1.00
Marine vessels[a]	Submerged loading: ships	0.2
	Submerged loading: barges	0.5

[a] To be used for products other than gasoline.

Molecular weight and vapor pressure are functions of the waste loaded, and 25 °C is considered an annual average ambient operating temperature.

9.2.3 Sample Calculation for Tank Loading

The following sample calculation may be used to estimate VO emissions from tank truck loading of an organic liquid. Waste stream compounds and properties for the sample calculation are as follows. The same waste stream is employed in each sample calculation in this section; only the type of emission source is varied.

Constituent	Weight fraction	Molecular weight (lb/mol)	Vapor pressure (psia)	Mole fraction
Benzene	0.3	78	1.84	0.368
Naphthalene	0.3	128	0.0044	0.224
Phenol	0.4	94	0.0066	0.408

The input parameters for the truck loading model are as follows:

- True vapor pressure of loading liquid, psia: 0.68 (calculated in a., below)
- Molecular weight of vapor, lb/mol: 78.23 (calculated in b., below)
- Saturation factor, dimensionless: 1.45 (splash loading)
- Bulk temperature of liquid loaded, °R: 537
- Annual throughput, gal/yr: 28,000

a. Calculate P^*, true vapor pressure of liquid, by Raoult's Law:

$$P^* = (P_1 \bullet X_1) + (P_2 \bullet X_2) + (P_3 \bullet X_3)$$

where,

P^* = true vapor pressure, psia;

P_1, P_2, and P_3 = vapor pressures of pure components;

X_1, X_2, and X_3 = mole fractions of VO components in liquid;

$$P^* = (1.84 \text{ psia} \times 0.368) + (0.0044 \text{ psia} \times 0.224) + (0.0066 \text{ psia} \times 0.408); \text{ and}$$

$$P^* = 0.68 \text{ (psia).}$$

b. Calculate M, molecular weight of vapors:

$$M = \frac{(P_1 \bullet X_1)}{P^*} \bullet M_1 + \frac{(P_2 \bullet X_2)}{P^*} \bullet M_2 + \frac{(P_3 \bullet X_3)}{P^*} \bullet M_3$$

where

M = molecular weight of vapor

M_1, M_2, and M_3 = molecular weight of each component

$$M = *\frac{1.84 \times 0.368}{0.68}* \times 78 + *\frac{0.0044 \times 0.224}{0.68}*$$

$$\times 128 + *\frac{0.0066 \times 0.408}{0.68}* \times 94$$

$$= 78.23 \text{ (lb/mol).}$$

c. Calculate emissions from truck loading:

$$L_L = \frac{12.46 \text{ SMP}^*}{T}$$

$$= \frac{12.46 \times 1.45 \times 78.23 \times 0.68}{537\ {}^\circ R}$$

$$= 1.79 \text{ lb/1,000 gal}$$

$$\text{Annual emissions, } L_L = \frac{1.79 \times 10^{-3} \text{ lb/gal} \times 28{,}000 \text{ gal/yr}}{2{,}205 \text{ lb/Mg}}$$

$$= 0.023 \text{ Mg/yr} \ .$$

9.3 CONTAINER STORAGE

This section addresses storage emissions from tank trucks, railroad tank cars, 55-gal drums, marine vessels, and open dumpsters.

9.3.1 Emission Model for 55-Gal Drums, Tank Trucks, and Railroad Tank Cars

With regard to 55-gal drums, container storage is considered a location where multiple drums are most likely to accumulate and be stored for more than 90 days. Because drums are designed to be stored with a sealed lid and bung, the potential for breathing losses is minimal. Therefore, breathing loss is assumed to be negligible. However, the potential does exist for a drum to rupture or become damaged and leak during storage. Thus, the emissions from drum storage may be estimated using the same spill fraction used for drum handling--10^{-4} (to be discussed in more detail in Section 9.7, Spills). The following equation is used to estimate emissions from drum storage:[5]

$$E = 10^{-4} \times I \times W_i \times V_i \qquad (9\text{-}2)$$

where,

E = emission from drum storage, Mg/yr;

I = throughput, Mg/yr;

W_i = VO weight fraction; and

V_i = volatilization fraction.

Emission-estimating methodologies have not been developed for storage in tank trucks and railroad tank cars. Only loading information was available in the literature for these containers. The assumed same emission estimates principle for drum storage is applied with an emission factor of 10^{-5} (to be discussed in more detail in Section 9.7, Spills).[6]

9.3.2 Model Parameters for Drum Storage

It is assumed that 50 percent of the VO storage loss from drum spill or rupture will be volatilized. The remaining volatiles will be captured with RCRA spill response measures taken at the facility.

9.3.3 Sample Calculations for Drum Storage

Input parameters:

Waste stream: organic liquid
(See Section 9.2.3 for constituents.)
Waste density: 1.04 Mg/m^3
Drum storage capacity: 182 drums (0.208 m^3/drum)
Turnovers per year: 12
Spill fraction: 10^{-4}
Weight fraction: 1
Volatilization fraction: 0.5.

a. Calculate annual throughput, I, Mg/yr:

$$I = 182 \times 0.208 \ m^3 \times 12 \times 1.04 \ Mg/m^3$$
$$= 472 \ Mg/yr \ .$$

b. Calculate air emissions:

$$E = 10^{-4} \times I \times W_i \times V_i$$
$$= 10^{-4} \times 472 \ Mg/yr \times 1 \times 0.5$$
$$= 0.024 \ Mg/yr \ .$$

9.3.4 Emission Model for Open Dumpsters

Open dumpsters are used to contain waste materials. Volatile organics can diffuse from this waste material to the surface of the waste, where they can be emitted to the atmosphere. Wastes held in dumpsters may range from sludges to contaminated filters. Because an open dumpster is similar to open landfills and wastepiles, the land treatment model is used to estimate the air emission rates of the constituent of interest from open landfills, wastepiles, and open dumpsters. Chapter 7.0

describes the use of the land treatment model for open landfills and wastepiles. The theoretical basis for the land treatment model is presented in Chapter 5.0 of this report and will not be repeated here.

A land-treatment-type model was selected for estimating emissions from open dumpsters because (1) no adequate models exist for this source, and (2) there are a number of similarities in physical characteristics of the wastes in open dumpsters and land treatment operations. A previous EPA study[7] dedicated to the evaluation of models for estimating emissions from hazardous waste TSDF identified only one model for open waste dumps such as landfills and wastepiles--the open dump model. A serious limitation of the open dump model for this application, however, is that it does not account for depletion of the volatilizing chemical from the waste surface. Hence, the open dump model is judged unsuitable for the estimation of emissions from open dumpsters over the time period of interest (months or longer).

The similarity in physical characteristics between open dumpsters and land treatment operations is apparent upon close examination--in both the waste liquid is ultimately mixed homogeneously with a "carrier" matrix (soil in the case of land treatment; waste in the case of open dumpsters). In both cases, the matrix is porous and permeable, allowing the diffusion of the constituent of interest through the matrix and into the air. Hence, in both cases, diffusion theory can be used to model the emission rate. The notable difference between land treatment operations and open dumpsters is the presence of an additional mechanism affecting emissions in the case of land treatment--biological decay of the constituent. Because biodegradation is not thought to occur in open dumpsters, however, its effect is not accounted for in the modeling of air emissions.

The RTI land treatment model, which was selected for estimating emissions from open dumpsters, has the following characteristics: a sound basis in scientific theory, limited validation against measured emissions from land treatment operations, and reasonably available input data.[8] The model considers effects such as evaporation of the constituent of interest from interstitial surfaces of the carrier matrix and diffusion of material through air-filled pore spaces.

The equations necessary to apply the land treatment model to open dumpsters are summarized in Table 7-3. The equations, presented in Chapter 7.0, can be used to estimate the fraction of the constituent emitted (F_t) and the instantaneous emission rate (E). It should be noted that the absence of biodegradation represents a special case that allows some simplification of several of the Chapter 7.0 land treatment equations, e.g., Equations (7-4) and (7-5). (The absence of biomass implies that biomass concentration equals 0. Hence, t_b, the time constant for biological decay, equals infinity. Consequently, the exponential term e^{-t/t_b} becomes unity.) Also, the absence of biodegradation implies that the fraction of the constituent emitted after a long time, F_a, would equal unity.

Because the land treatment model was derived originally for land treatment operations, model input parameters are not necessarily in the most convenient units and terminology for open dumpsters. Hence, several points should be noted:

- The dumpster waste is analogous (for modeling purposes) to the waste-laden soil in land treatment.
- M_o, the area-loading of the constituent in g/cm^2, is compatible with land treatment operations. For open dumpsters, it should be computed from the concentration in the waste, $M_o = l\ LC$.
- No "tilling" (as discussed in Chapter 7.0) is performed in open dumpsters, but the initial mixing upon dumpster loading is equivalent to a tilling.
- Waste liquid is generally not "applied" or mixed with the solids in the dumpster. Hence, waste "reapplication" (used in the sense discussed in Chapter 7.0) does not occur in open dumpsters. If liquid wastes are applied to the surface of the waste

in the open dumpster, then the land treatment application model would be used.

- The waste bed depth in open dumpsters is analogous to the "depth to which waste is mixed" in land treatment, as discussed in Chapter 7.0.

The approach required to estimate emissions from open dumpsters is as follows, based on equations in Table 7-3:

1. Compute the loading of waste liquid (L) in waste, using the known waste composition. (For two-phase aqueous organics or organic liquid wastes, L should be computed as grams organic phase per cubic centimeter solid material. For dilute aqueous waste liquids, L equals grams aqueous liquid per cubic centimeter waste.)
2. Compute the effective diffusion coefficient (D_e). If the sludge is not porous, the effective diffusion coefficient (D_e) equals the product of the total porosity (or volume fraction liquid) and the liquid diffusion coefficient (D_L).
3. Compute the partition coefficient (Keq).
4. Use the appropriate emission equation to compute the fraction of constituent emitted (F_t) and/or the instantaneous emission rate (E). For dumpster calculations, the time input to these equations should be no greater than the holding time of the waste in the dumpster.

The sensitivity of the land treatment model to some parameters differs in its application to open dumpsters from that in land treatment operations because of the difference (in some cases) in the expected range of the parameters. In general, it can be stated that, for application to open dumpsters, the model is sensitive to the air porosity of the solid waste, the liquid loading in the solid waste, the waste depth, the concentration of the constituent in the waste, and the volatility of the constituent under consideration. In contrast, the model exhibits a relatively low sensitivity to the diffusion coefficient of the constituent in air.

The following major assumptions are associated with the RTI land treatment model and its application to open dumpsters:

- The waste liquid is mixed uniformly in the waste solids in an open dumpster and does not drain to the bottom of the dumpster.

- The absorption of the volatile constituent into the waste liquids is linear within the depth of the waste and does not change with time.

- No bulk flow of gas is induced within the waste matrix.

- The diffusion coefficient does not vary with either concentration or time.

- The concentration of the constituent of interest in the gas phase at the surface of the open dumpster is much lower than the concentration of the constituent of interest in the gas phase within the waste matrix.

- The waste liquid does not migrate.

- Liquid-vapor equilibrium is established at all times within the waste matrix.

- No biodegradation of the constituent of interest occurs in dumpsters.

9.3.5 Model Parameters for Open Dumster Storage

The input parameters required for the model are divided into three groups:

- Meteorological conditions. An average annual ambient temperature of 25 °C and an average windspeed of 447 cm/s were used.

- Size of the dumpster. A 4-yd^3 uncovered dumpster with the following dimensions was used:

  Length = 1.85 m (73 in)
  Width = 1.45 m (57 in)
  Height = 1.22 m (48 in)

- Properties of waste stored. These properties include molecular weight, vapor pressure, and diffusivity in air. The properties of specific compounds were obtained from literature sources.

9.3.6 Sample Calculation for Open Dumpster Storage

This section presents a step-by-step calculation of emissions from an open dumpster. The equations identified in Table 7-3 are used with the dumpster input parameters to estimate emissions from an organic waste containing benzene, naphthalene, and phenol.

Input parameters:

Waste stream: organic liquid
VO constituents = benzene, naphthalene, and phenol
Concentration of each constituent in oil, ppmw = 50,000
Initial VO amount, kg = 122.7 (total for three components)
U, windspeed, cm/s = 447
l, waste depth in the dumpster, cm = 122
area of the dumpster, m^2 = 2.68
molecular weight of oil = 282
Total porosity of waste = 0.5
Air porosity of waste = 0.25
T, ambient temperature, K = 298
Dumpster turnovers per year = 2

a. Compute waste loading, L:

The waste is 50 percent by volume solids, 25 percent by volume air, and 25 percent by volume organic oil. At an estimated density of 1 g/cm^3 of oil, the waste loading is 0.25 g oil/cm^3.

b. Compute effective diffusion coefficient for fixed waste:

$$D_e = D_a \frac{\epsilon_a^{3.33}}{\epsilon_T^2} ,$$

where

ϵ_a = air porosity fixed waste = 0.25

ϵ_T = total porosity fixed waste = 0.50.

Then

D_a = diffusivity of benzene in air = 0.088 cm^2/s

$$D_e = (0.088\ cm^2/s)\ \frac{(0.25)^{3.33}}{(0.50)^2}$$

$D_e = 3.48 \times 10^{-3}\ cm^2/s$. (Note: $D_e/D_a = 3.96 \times 10^{-2}$.)

c. Compute "partition" coefficient, Keq (ratio of gas-phase benzene to total benzene in the waste):

For oily waste,

$$Keq = \frac{P^{*}\,MW_{oil}\ ’\ _{a}}{R\ T\ \ _{L}}$$

where

P^{*} = pure component vapor pressure of chloroform
= (95.2 mm Hg)/ (760 mm Hg/atm) = 0.125 atm

MW_{oil} = molecular weight low-volatility organic
= 282 g/g mol

R = ideal gas constant = 82.05 cm^3•atm/gmol•K

T = temperature within solid waste, K

T = 273 K + 25 °C = 298 K

$$Keq = \frac{(0.125\ atm)(282\ g/g\ mol)(0.25)}{(82.05\ cm^3 \bullet atm/g\ mol \bullet K)(298\ K)(0.25\ g/cm^3)}$$

Keq = 0.00144 .

d. Compute fraction of benzene emitted, F_t, after 1/2 year:

Determine which solution applies by computing $\frac{Keq\ D_e\ t}{l^2}$

(Table 7-3):

$$\frac{Keq_i D_e}{l^2} = \frac{0.00144 \times 0.00348\ cm^2/s}{(122\ cm)^2}$$

$$= 3.37 \bullet 10^{-10}\ s^{-1}\ .$$

Therefore,

$$\frac{Keq\ D_e t}{l^2} = 3.37 \bullet 10^{-10}\ s^{-1} \times 1.57 \times 10^{7}\ s$$
$$= 0.0053\ .$$

$$K_d t = \frac{Keq\ D_e t}{l^2}\ \frac{B^2}{4} = 0.013\ .$$

Because Keq $D_e t/l^2$ is less than 0.25, the third equation of Table 7-3 applies, and

$$F_t = 0.72\ (K_d t)^{1/2}$$

$$F_t = 0.72\ (0.013)^{1/2}$$

$$F_t = 0.082\ .$$

e. Estimate annual emissions, Mg/yr:

	Init. VO,	Fraction lost	Annual emissions	
	kg	to air	kg/turnover	kg/yr
Benzene	40.9	0.082	3.37	6.74
Naphthalene	40.9	0.003	0.13	0.26
Phenol	40.9	0.005	0.19	0.38
Total	122.7	0.090	3.69	7.38

9.4 CONTAINER CLEANING

9.4.1 Emission Model for Container Cleaning

An AP-42 document[9] on tank truck cleaning is used as the primary source for container-cleaning emission estimates. AP-42 states that tank truck cleaning typically involves washing the truck interior with agents such as water, steam, detergents, or other chemicals. The document also provides emission factors that are a function of vapor pressure and viscosity. These factors have been applied to emission estimates for cleaning all types of containers, as follows:

Tank truck residue to be removed	Emission factor g/truck (lb/truck)
High vapor pressure, low viscosity	215 (0.474)
Medium vapor pressure, medium viscosity	32.4 (0.071)
Low vapor pressure, low viscosity	5.5 (0.012)

The following equation is used to estimate emissions for container cleaning:

$$E = F_c \times N \times W_i \times 10^{-6} \qquad (9\text{-}3)$$

where

E = cleaning loss, Mg/yr

F_c = emission factor for cleaning, g/container

N = number of cleanings per year

W_i = VO weight fraction.

9.4.2 Model Parameters

In all containers, the primary input parameter for estimating cleaning emissions is the cleaning emission factor, which is determined from (1) residue vapor pressure and viscosity (functions of waste handled), and (2) container volume.

Based on AP-42,[10] a typical tank truck volume of 26.5 m^3 (7,000 gal) is assumed.

Because no data are currently available for drum cleaning, the emission factors for tank trucks were used to calculate cleaning emissions from drums by comparing the proportion of drum volume (55 gal) to that of the tank truck (7,000 gal).

55-Gal drum residue to be removed	Emission factor g/drum	 (lb/drum)
High vapor pressure, low viscosity	1.69	(0.0037)
Medium vapor pressure, medium viscosity	0.25	(0.0006)
Low vapor pressure, low viscosity	0.04	(0.00009)

Emissions from marine vessels have not been addressed because of the low usage of such vessels in the waste management industry.

9.4.3 Sample Calculation for Tank Truck Cleaning

The general assumptions for truck cleaning are as follows:

- Residue: pure organic liquid (benzene)
- Number of truck cleanings per year: 4
- Truck capacity: typical truck
- Weight fraction: 1.

a. Determine the cleaning emission factor, F_c:

(215 g/truck was used because of high vapor pressure and low viscosity of pure benzene residue).

b. Calculate cleaning emissions:

$$E = F_c \times N \times W_i \times 10^{-6}$$

$$= 215 \text{ g} \times 4 \times 1 \times 10^{-6} \text{ Mg/g}$$

$$= 8.6 \times 10^{-4} \text{ Mg/yr} \quad .$$

9.5 STATIONARY TANK LOADING

9.5.1 Emission Model for Stationary Tank Model

Stationary tank working losses are those emissions from waste loading and unloading operations. AP-42's "Storage of Organic Liquids"[11] provides an equation to estimate loading and unloading emissions from storage tanks. The equation was developed for handling VO liquid in the following industries:

- Petroleum producing/refining
- Petrochemical and chemical manufacturing
- Bulk storage and transfer operations
- Other industries consuming or producing organic liquids.

Because hazardous wastes have the potential to contain VO compounds, as do organic liquids, and because they are most commonly stored in the same fashion as these liquid products, the following equation was selected from AP-42:

$$L_w = 2.40 \times 10^{-5} M_v \bullet P^* \bullet V \bullet N \bullet K_n \bullet K_c \qquad (9\text{-}4)$$

where

L_w = working losses, lb/yr

M_v = molecular weight of vapor in storage tank, lb/lb mol

P^* = true vapor pressure at bulk liquid conditions, psia

N = number of turnovers per year (dimensionless)

$N = \dfrac{\text{total throughput per year (gal)}}{\text{tank capacity, V (gal)}}$

V = tank capacity, gal

K_n = turnover factor, dimensionless (for turnovers for turnovers > 36, $K_n = \dfrac{180 + N}{6N}$)

K_c = product factor, dimensionless for crude oil, K_c = 0.84; for all other organic liquids, K_c = 1).

9.5.2 Model Parameters

It is assumed that all stationary tanks are fixed-roof. According to responses to the 1982 Westat Mail Survey,[12] which were examined by the GCA Corporation,[13] there are four sizes of tanks that best represent the waste management industry:

- 5.3 m^3 (1,500 gal)
- 30.3 m^3 (8,000 gal)
- 75.0 m^3 (20,000 gal)
- 795 m^3 (210,000 gal).

Table 9-2 lists typical input parameters for these model tanks. Turnovers per year were selected based on volume of waste processed in waste management scenarios recorded in various documents. Molecular weight and vapor pressure are a function of the waste loaded.

9.5.3 Sample Calculation for Tank Loading Emission Model

Input parameters:

Waste stream: organic liquid (see Section 9.2.3 for constituents)

M_v, molecular weight of vapor, lb/lb mol: 78.23
P^*, true vapor pressure of loading liquid, psia: 0.68
K_c, product factor for working loss: 1
V, fixed-roof tank capacity, gal: 20,000
N, turnovers per year: 44
K_n, turnover factor, dimensionless: 0.848.

a. Calculate M_v, molecular weight of vapor:

(see Section 9.2.3 for calculation).

b. Calculate P^*, true vapor pressure of loading liquid:

(see Section 9.2.3 for calculation).

c. Calculate K_n, turnover factor: because N = 44,

$$K_n = \frac{180 + N}{6N} = 0.848$$

TABLE 9-2. PERTINENT FIXED-ROOF TANK SPECIFICATIONS[14,15,16]

Specifications	Model A	Model B	Model C	Model D
Capacity, m3 (gal)	5.3 (1,500)	30.3 (8,000)	75.7 (20,000)	795 (210,000)
Tank height, m	2.4	2.4	2.7	12.2
Tank diameter, m	1.7	4	5.8	9.1
Average vapor space height, m	1.2	1.2	1.4	6.1
Adjustment for small diameter (dimensionless)	0.26	0.65	0.86	1
Average diurnal temp. change, "C ("F)	11 (20)	11 (20)	11 (20)	11 (20)
Paint factor (dimensionless)	1	1	1	1
Relation of tank to ground	Above	Above	Above	Above
Product factor	1	1	1	1

d. Calculate air emissions:

$$L_w = 2.40 \times 10^{-5} \times M_v \bullet P^* \bullet V \bullet N \bullet K_n \bullet K_c$$

$$= 2.40 \times 10^{-5} \times 78.23 \times 0.68 \times 20{,}000 \times 44 \times 0.848 \times 1$$

$$= 953 \text{ lb/yr}$$

$$= 0.43 \text{ Mg/yr.}$$

9.6 STATIONARY TANK STORAGE

9.6.1 Model Description

Fixed-roof tank storage of hazardous wastes results in VO "breathing" emissions through vents as ambient temperature and barometric pressure fluctuate. Emissions occur in the absence of any liquid level change in the tank. An existing AP-42[17] equation was used to estimate VO breathing losses from hazardous waste storage tanks as follows:

$$L_b = 2.26\ 10^{-2} M_v \left|\frac{P^*}{P_A - P^*}\right|^{0.68} \bullet D^{1.73} \bullet H^{0.51} \bullet \Delta T^{0.5} \bullet F_p \bullet C \bullet K_c \qquad (9\text{-}5)$$

where

L_b = fixed-roof breathing loss, lb/yr

M_v = molecular weight of vapor in tank, lb/lb mol

P^* = true vapor pressure at bulk liquid conditions, psia

P_A = average atmospheric pressure at tank location, psia

D = tank diameter, ft

H = average vapor space height, ft (assumed to be one-half of tank height)

ΔT = average ambient diurnal temperature change, °F (20 °F assumed as a typical value)

F_p = paint factor, dimensionless (see Table 9-3)

C = adjustment factor for small diameter tanks, dimensionless (for diameter $\geq$ 30 ft, $C = 1$; for diameter $<$ 30 ft,

$$C = 0.0771\ D - 0.0013\ D^2 - 0.1334)$$

K_C = product factor, dimensionless (for crude oil, K_C=0.65, for all other organic liquids, K_C = 1.0).

The above equation requires an estimation of the true vapor pressure using the liquid concentration. For very volatile constituents, the liquid concentration depends on the amount lost as air emissions. To correct for the loss to the air in estimating the liquid concentration, the following equation may be used:

$$\text{fraction lost to air} = \frac{Lb}{Lb + Lt} ,$$

where Lt is the tank input of the volatile constituent in pounds per year.

9.6.2 Model Parameters

Table 9-3 identifies the model parameters for estimating tank breathing losses. Molecular weight and vapor pressure are functions of the waste stored.

9.6.3 Sample Calculation for Tank Storage Emission

Model Input parameters:

Waste stream, organic liquid (see Section 9.2.3 for constituents)

M_v, molecular weight of vapor, lb/lb mol: 78.23

P^*, true vapor pressure of loading liquid, psia: 0.68

K_C, product factor for breathing loss: 1

v, fixed-roof tank capacity, gal: 20,000

D, tank diameter, ft: 19

H, average vapor space height, ft: 4.5

)T, diurnal temperature change, °F: 20

F_p, paint factor, dimensionless: 1

C, adjustment factor for small tanks: 0.86 (calculate in c., below)

TABLE 7-3. PAINT FACTORS FOR FIXED-ROOF TANKS[18]

Tank color Roof	Shell	Paint factors (F_P) Paint condition Good	Poor
White	White	1.00	1.15
Aluminum (specular)	White	1.04	1.18
White	Aluminum (specular)	1.16	1.24
Aluminum (specular)	Aluminum (specular)	1.20	1.29
White	Aluminum (diffuse)	1.30	1.38
Aluminum (diffuse)	Aluminum (diffuse)	1.39	1.46
White	Gray	1.30	1.38
Light gray	Light gray	1.33	1.44a
Medium gray	Medium gray	1.40	1.58a

[a] Estimated from the ratios of the seven preceding paint factors.

a. Calculate molecular weight of vapor:

(see Section 9.2.3 for calculation).

b. Calculate true vapor pressure of loading liquid:

(see Section 9.2.3 for calculation).

c. Calculate adjustment factor for small tanks:

$$C = 0.0771 \times 19 - 0.0013(19)^2 - 0.1334$$

$$= 0.86 \quad .$$

d. Calculate air emissions:

$$L_b = 2.26 \times 10^{-2} \; M_v \left[\frac{P^*}{P_A - P^*}\right]^{0.68} \bullet D^{1.73} \bullet H^{0.51} \bullet \Delta T^{0.5} \bullet F_p \bullet C \bullet K_c$$

$$= 2.26 \times 10^{-2} \times 78.23 \times \left[\frac{0.68}{14.7-0.68}\right]^{0.68} \times (19)^{1.73} \times (4.5)^{0.51}$$

$$\times (20)^{0.5} \times (0.86)$$

$$= 300 \text{ lb/yr}$$

$$= 0.14 \text{ Mg/yr} \quad .$$

9.7 SPILLS

9.7.1 Model Description

An ICF study[19] of truck transport to and from TSDF and truck emissions at TSDF terminals provided the background information necessary to estimate spillage losses during TSDF and trucking operations. As a result of this study, spill fractions of 10^{-4} and 10^{-5} were assumed for drum movement of wastes and all other remaining waste movement, respectively. Thus, for every 10,000 Mg of drummed hazardous waste moved, 1 Mg is assumed to be spilled. The following equation is used to estimate spill emissions:

$$E = F_s \times I \times W_i \times V_i \qquad (9\text{-}6)$$

where

E = spill emissions, Mg/yr

F_s = emission fraction, 10^{-4} or 10^{-5}

I = annual throughput, Mg/yr

W_i = VO weight fraction

V_i = fraction for volatilization.

9.7.2 Model Parameters

In both cases of spills, it is assumed that 50 percent of the volatiles in the waste are lost. The remaining 50 percent are recovered by RCRA spill plan response. Therefore, most spills would be mitigated before 100 percent of VO is lost to the atmosphere.

It is assumed that spills do not occur during the transfer of waste into a stationary tank if loading is automated through fixed piping.

9.7.3 Sample Calculation for Drum Storage

Model Input parameters:

Waste stream: organic liquid (see Section 9.2.3 for constituents)
Waste density: 1.04 Mg/m^3
Emission fraction: 10^{-4}
Weight fraction: 1
Volatilization fraction: 0.5
Number of drums handled: 2,184 (0.208 m^3/drum).

a. Calculate annual throughput, I, Mg/yr:

$$I = 2{,}184 \times 0.208\ m^3 \times 1.04\ Mg/m^3$$

$$= 472\ Mg/yr\ .$$

b. Calculate air emissions:

$$E = 10^{-4} \times 472\ Mg/yr \times 1 \times 0.5$$

$$= 0.024 \text{ Mg/yr} \quad .$$

9.8 FUGITIVE EMISSIONS

9.8.1 Emission Model for Fugitives

Waste transfer operations often involve pumping wastes through pipelines into a variety of containment units. Such pumping creates the potential for fugitive emission losses from pumps, valves, and flanges. Table 9-4 presents the Synthetic Organic Chemical Manufacturing Industries (SOCMI) emission factors[20] that had been developed to estimate VO that leak from pump seals, valves, and flanges. These factors are independent of the throughput, type, or size of the process unit.

TABLE 9-4. SOCMI EMISSION FACTORS FOR FUGITIVE LOSSES

Equipment	Type of service	Emission factor (kg/h-source)
Pump seals	Light liquid	4.94 E-2
Valves	Light liquid	7.10 E-3
Flanges	--	8.30 E-4

The following equation is used to estimate fugitive emissions:

$$E = E\ (F_f \times N_i) \times h \times 10^{-3} \qquad (9\text{-}7)$$

where,

E = fugitive emissions, Mg/yr;

F_f = emission factor per source-type, kg/h-source (see Table 9-4);

N_i = number of sources per source-type; and

h = residence time in the equipment (assume = 8,760 h/yr).

9.8.2 Model Parameters

The major input parameters required for the emission model are emission factor, number of sources, and residence time. It is assumed that waste remains in the transfer equipment 24 h/d, 365 d/yr; therefore, VO are continuously being leaked to the atmosphere.

Minimal information has been compiled on typical quantities of pumps, valves, and flanges at waste management facilities. Therefore, previous contractors have turned to data collected from the petroleum refining industry and SOCMI. GCA recommended that "for any hazardous waste filling operation, transfer operation, or handling operation involving pumps, the estimate of two pumps, 35 valves, and 80 flanges be used. This includes tank filling, tank truck or car filling, and drum filling."[21] Because the relationship 2:35:80 appears to be too high for pumping waste into a single drum, one pump, three valves, and eight flanges are used for estimating emissions. GCA recommended that smaller quantities of pumps, valves, and flanges identified by SOCMI be applied for transfer operations to injection wells and incinerators, i.e., 1 pump, 18 valves, and 40 flanges.[22]

9.8.3 Sample Calculation for Fugitive Emission Model

Estimate the annual fugitive emissions from a set of piping lines that connect to a storage tank, given the following information.

Input parameters:

Assume 2 pumps, 35 valves, and 80 flanges associated with the piping equipment.

Assume the waste stream is organic liquid.

Assume waste remains in piping line 24 h/d, 365 d/yr.

a. The emission factor for light liquids was used because of the high VO content.

b. Calculate fugitive emissions:

$$E = (0.0494 \text{ kg/h} \times 2 + 0.0071 \text{ kg/h} \times 35 + 8.3 \times 10^{-4} \text{kg/h} \times 8)$$

$$\times 8{,}760 \text{ h/yr} \times 10^{-3} \text{ Mg/kg} = 3.62 \text{ Mg/yr.}$$

9.9 VACUUM TRUCK LOADING

9.9.1 Emission Model for Vacuum Truck Loading

Emissions from vacuum truck loading are estimated by calculating an equilibrium concentration of organic vapors in the vacuum truck at its operating conditions and assuming that a total volume of gas equal to the vacuum truck volume is emitted to the atmosphere for each loading episode. Equations for making the calculations are presented as follows:

$$E_i = N_v \times Y_i \times MW_i$$

$$Y_i = \frac{X_i P^*}{P_t} \quad \text{(for oily waste)}$$

$$N_v = \frac{V}{[P_o V_G (T/273)]/P_t}$$

where,

E_i = air emissions of compound i, g/truckload;

N_v = total moles of vapor discharged, g mol;

Y_i = mole fraction of compound i in vapor phase;

X_i = mole fraction of compound i in liquid phase;

MW_i = molecular weight of compound i, g/g mol;

P^* = vapor pressure of compound i, mm Hg;

P_t = total system operating pressure, mm Hg;

P_o = atmospheric pressure, mm Hg;

V = vacuum truck volume, m^3;

V_G = volume of 1 g mol of gas at STP, 0.0224 m^3/g mol; and

T = operating temperature, K.

9.9.2 Model Parameters

Based on information obtained during site visits to refineries using land treatment, vacuum trucks have a capacity of about 21 m^3 (5,500 gal) and operate at a pressure of approximately 303 mm Hg. These values are used in estimating vacuum truck emissions.

Molecular weight and vapor pressure are functions of waste loaded, and 25 °C is considered a standard operating temperature.

9.9.3 Sample Calculation

The following is a sample calculation of benzene emissions during loading of a vacuum truck with organic liquid.

Input parameters:

Waste stream: organic liquid
(see Section 9.2.3 for constituents)
VO constituent: benzene
MW_i, molecular weight, g/g mol: 78
P^*, pure compound vapor pressure: 95.2
P_t, system operating pressure, mm Hg: 303
P_o, atmospheric pressure, mm Hg: 760
X_i, mole fraction in liquid: 0.368
V, vacuum truck volume, m^3: 21
V_G, volume of 1 g mol of gas at STP, m^3/g mol: 0.0224
T, operating temperature, K: 298
N, turnovers per year, truckload/yr: 10.

a. Calculate total moles of vapor discharged, g mol:

$$N_v = \frac{V}{[P_a\ V_G\ (T/273)]/P_t}$$

$$= \frac{21\ m^3}{(760\ mm\ Hg \times 0.0224\ m^3/g\ mol \times 298\ K/273\ K)/303\ mm\ Hg}$$

$$= 342.41\ g\ mol/truckload \quad .$$

b. Calculate mole fraction of benzene in vapor phase, Y_i:

$$Y_i = \frac{P^*\ X_i}{P_t} = \frac{95.2 \quad 0.368}{303} = 0.1156\ .$$

c. Calculate air emissions per truckload, g/truckload:

$E_i = N_v \times Y_i \times MW_i$

$= (342.41 \text{ g mol/truckload}) (0.1156) (78 \text{ g/g mol})$

$= 3{,}087 \text{ g/truckload}$.

d. Calculate annual emissions for benzene, Mg/yr:

Annual emission $= E_i \times N$
$= 3{,}087 \text{ g/truckload} \times 10 \text{ truckload/yr}$
$= 30{,}870 \text{ g/yr}$
$= 0.031 \text{ Mg/yr}$.

e. Repeat the above procedures, a through d., to compute emissions for each constituent as follows:

Constituent	E_i,g/truckload	Annual emissions, Mg/yr
Benzene	3,087	0.031
Naphthalene	7	0.00007
Phenol	14	0.00014
Total emissions	3,108	0.0312

9.10 REFERENCES

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19. Reference 5.

20. U.S. Environmental Protection Agency. Control of Volatile Organic Compound Leaks from Synthetic Organic Chemical and Polymer Manufacturing Equipment. Research Triangle Park, NC. Publication No. EPA-450/ 3-83-006. March 1984.

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22. Reference 2.

10.0 COMPARISON OF MODEL RESULTS WITH FIELD TEST DATA

10.1 INTRODUCTION

Predictions from TSDF emission models are compared with field test data in this chapter. In general, considering the uncertainty of field emission measurements, agreement between measured and predicted values is considered reasonable. Measured and predicted emissions generally agree within an order of magnitude.

The following caveats must be considered in any evaluation of the comparison results presented in the following sections:

1. The field test data did not always include all of the input parameters required to use the emission models. In such cases, parameter values representative of field operations were used as defaults.
2. The emission models use average influent and effluent concentrations to estimate annual emissions. Variations in concentrations and constituents are not reflected.
3. Field test data provide information on a limited number of hazardous constituents. Extrapolation of comparisons on limited constituents to all constituents of interest may not always be possible.
4. The method of measuring emissions (e.g., flux chambers and other enclosure systems) could alter the real-world system being tested and affect the representativeness of the measured emissions.

10.2 SURFACE IMPOUNDMENTS AND OPEN TANKS

10.2.1 Summary

Emission test data were available from tests of five quiescent surface impoundments. The overall mass transfer coefficients determined in these tests agreed generally within an order of magnitude with the overall coefficient predicted by the mass transfer correlations described in Chapter 5.0. Predicted values were higher than measured values in some cases and lower in others.

The emission models used for impoundments also were applied to open tanks. The comparison of measured and predicted values for the overall mass transfer coefficient for open wastewater treatment tanks yielded mixed results. For tanks with quiescent surfaces (e.g., clarifiers and equalization basins), the model predictions were generally lower than measured values but agreed within an order of magnitude. For the aerated systems, the model predictions agreed well with material balance and ambient air measurements for an open aerated system.

10.2.2 Details of Comparisons

The approach to the comparison of predicted and measured values is to estimate the overall mass transfer coefficient from the correlations given in Chapter 5.0 and to compare this value to the overall mass transfer coefficient from the test data. The overall mass transfer coefficient from the test data is calculated from a measured emission rate and a measured or estimated bulk concentration in the liquid phase. Note that errors in either the measured emission rate or liquid-phase concentration have a direct effect on the errors in the calculated mass transfer coefficient.

Most of the measured emission data were obtained by flux chamber measurements. At a few sources, ambient air monitoring and material balances were used to determine the emission rate for calculation of the overall mass transfer coefficient.

GCA Corporation performed an analysis of data from impoundments. The results are given in Tables 10-1 through 10-4 for four ponds at two different sites. Site 5 is a commercial hazardous waste facility with a wastewater treatment system onsite. The reducing lagoon receives wastes classified as

TABLE 10-1. COMPARISON OF RESULTS FOR REDUCING LAGOON 1 AT SITE 5[1,2]

	Mass transfer coefficient (x 10^{-6} m/s)	
Constituent	Average flux chamber measurement[a]	Model predictions (for 5 to 10 m/s windspeed)[b]
Benzene	4.9	4.2-17
Toluene	5.0	3.9-15
Ethylbenzene	5.5	3.6-14
Naphthalene	2.6	3.5-14
Methylene chloride	12	4.7-19
Chloroform	5.7	4.3-17
1,1,1-Trichloroethane	7.6	3.9-15
Carbon tetrachloride	11	3.9-16
p-Dichlorobenzene	2.6	3.6-14
Styrene	5.7	3.7-15

[a] Calculated from reported emission rate and corresponding liquid-phase concentration.

[b] Windspeed during the test ranged from 5 to 10 m/s.

TABLE 10-2. COMPARISON OF RESULTS FOR HOLDING POND 6 AT SITE 5[3,4]

	Mass transfer coefficient (x 10^{-6} m/s)	
Constituent	Average flux chamber measurement[a]	Model predictions (for 5 to 10 m/s windspeed)[b]
Benzene	2.7	5.3-21
Toluene	2.3	4.9-19
Ethylbenzene	2.6	4.6-18
Naphthalene	1.6	4.4-18
Methylene chloride	3.1	6.0-24
Chloroform	2.2	5.4-21
1,1,1-Trichloroethane	3.9	4.9-19
Chlorobenzene	<.039	4.9-20
p-Dichlorobenzene	4.3	4.6-18
Acetaldehyde	3.4	5.7-19

[a] Calculated from reported emission rate and corresponding liquid-phase concentration.

[b] Windspeed during the test ranged from 5 to 10 m/s.

TABLE 10-3. COMPARISON OF RESULTS FOR OXIDIZING LAGOON 2 AT SITE 5[5,6]

	Mass transfer coefficient (x 10^{-6} m/s)	
Constituent	Average flux chamber measurement[a]	Model predictions (for 5 to 10 m/s windspeed)[b]
Toluene	0.38	3.8-15
Ethylbenzene	0.037	3.6-14
1,1,1-Trichloroethane	35	3.9-15

[a] Calculated from reported emission rate and corresponding liquid-phase concentration.

[b] Windspeed during the test ranged from 5 to 10 m/s.

TABLE 10-4. COMPARISON OF RESULTS FOR SURFACE IMPOUNDMENT AT SITE 4[7,8]

	Mass transfer coefficient (x 10^{6} m/s)		
	Flux chamber measurement[a]		
Constituent	Average	Range	Model predictions (for 5 to 10 m/s windspeed)[b]
Toluene	2.4	1.9-2.7	6.3-25.1
Ethylbenzene	1.0	0.46-1.4	5.9-23.5
Methylene chloride	8.4	5.6-10.0	7.7-30.5
1,1,1-Trichloroethane	2.6	1.1-3.6	6.3-24.7
Chloroform	12.0	5.4-15.0	7.0-27.6
p-Dichlorobenzene	0.44	0.079-0.75	5.9-23.1

[a] Results for June 22, 1984.

[b] Windspeed during the test ranged from 5 to 10 m/s.

reducing agents from tank trucks. The lagoon is operated on a batch basis and was observed to contain a zone of solids and a surface with a floating oil film. The holding pond receives aqueous wastes from the water treatment system and is filled (and discharged) on a monthly basis. The oxidizing lagoon receives oxidizing agents including halogens and other organic compounds. The accumulation of solids and oil film also was observed on this lagoon. Site 4 also is a commercial hazardous waste facility, and its impoundment is used to contain aqueous wastes.

Table 10-5 presents a comparison of results for Site 3, which is a chemical manufacturing plant that produces primarily nitrated aromatics and aromatic amines. This impoundment is a wastewater holding pond for the wastewater treatment system at the plant. Two wastewater streams that enter the treatment system are distillation bottoms from aniline production (K083) and the nitrobenzene production wastewater (K104).

The results in Tables 10-1 through 10-5 show a reasonable agreement between measured and predicted values of the overall mass transfer coefficient. The measured results for the impoundment in Table 10-3 may have been affected by an oil film observed on the surface or from poor mixing in the impoundment, which can complicate representative sampling of the liquid-phase concentration. Table 10-5 shows good agreement of results for toluene and benzene, which were present in the liquid phase at 2.6 and 17 mg/L, respectively. The liquid-phase concentrations of the other four compounds in Table 10-5 ranged from 0.029 to 0.15 mg/L. The differences in measured and predicted values for these four compounds may have been affected by the accuracy of sampling and analysis of the liquid. The compounds listed in Tables 10-1 through 10-5 are controlled by the liquid-phase mass transfer. Consequently, the results are most dependent on Springer's correlation for k_L (the liquid-phase mass transfer coefficient) and suggest that Springer's model is probably accurate within an order of magnitude.

TABLE 10-5. COMPARISON OF RESULTS FOR WASTEWATER HOLDING LAGOON AT SITE 3[9]

Constituent	Mass transfer coefficient (x 10^6 m/s) Flux chamber measurement	Predicted[a]
Cyclohexane	0.39	3.8
Tetrachloroethylene	0.10	3.7
Toluene	9.0	3.8
Benzene	3.7	4.1
n-Undecane	0.21	2.8
Methylchloride	35.0	3.1

[a] Based on an average measured windspeed of 3.7 m/s and an average temperature of 22 °C.

TABLE 10-6. COMPARISON OF RESULTS FOR PRIMARY CLARIFIERS AT SITE 8[11]

Constituent	Mass transfer coefficient (x 10^6 m/s) Material balance	Ambient monitors	Model prediction
Tetralin	--	227.0	--
2-Ethyl hexanol	96.0	42.0	2.0
2-Ethyl hexyl acrylate	--	123.0	2.7
Naphthalene	179.0	92.0	3.4
1,2-Dichloroethane	58.0	2.9	4.0
Benzene	5.4	18.0	4.1
Toluene	35.0	50.0	3.8
Ethyl benzene	156.0	39.0	3.5

TABLE 10-7. COMPARISON OF RESULTS FOR EQUALIZATION BASIN AT SITE 8[12]

Constituent	Mass transfer coefficient (x 10^6 m/s) Material balance	Ambient monitors	Model prediction
1,2-Dichloroethane	20	19.0	5.0
Benzene	20	8.9	5.1
Toluene	25	42.0	4.7
Ethyl benzene	25	5.4	4.4

TABLE 10-8. COMPARISON OF RESULTS FOR AERATED STABILIZATION BASINS AT SITE 8[13]

	Mass transfer coefficient (x 10^4 m/s)		
Constituent	Material balance	Ambient monitors	Model prediction
2-Ethyl hexanol	0.05	0.01	0.17
2-Ethyl hexyl acrylate	4.8	8.3	2.9
1,2-Dichloroethane	2.0	0.52	5.7
Benzene	12.4	1.1	10.6
Toluene	5.0	5.8	10.1
Ethyl benzene	2.9	0.55	9.9

TABLE 10-9. COMPARISON OF RESULTS FOR COVERED AERATED LAGOON AT SITE 7[15,16]

Constituent	Mass transfer coefficient ($\times 10^4$ m/s) Vent rate measurement	Predicted[a]
1,2-Dichloroethane	0.05	7.2
Benzene	0.30	8.9
Toluene	0.95	8.8

[a] Based on an estimated windspeed (not measured) of 5 m/s[17] and an estimated turbulent area of about 50 percent.[18]

GCA, in a separate document, examined measured and predicted mass transfer coefficients for open tanks that are part of wastewater treatment systems.[10] The results for Site 8, which is an industrial wastewater treatment operation, included a primary clarifier, an equalization basin, and aerated stabilization basins. The various influent and effluent liquid streams were analyzed, and air emissions around the unit were monitored. Overall mass transfer coefficients were calculated from material balance data and from ambient air monitoring. These values are listed in Tables 10-6 through 10-8 along with the predicted values from the mass transfer correlations given in Chapter 5.0. The primary clarifier, equalization basin, and the quiescent portion of the stabilization basin were modeled as quiescent surfaces, and the correlations of Springer and MacKay/Matasugu were used. The turbulent portion of the stabilization basins was modeled using the correlations of Thibodeaux and Reinhardt.

Useful conclusions from the comparison of measured and predicted values are difficult because of the lack of consistent results from air monitoring, probably due to very short sampling periods, changes in the windspeed and direction, and the contribution to emissions from sources near the mentioned source. In addition, material balance calculations are subject to error from changes in influent/effluent flow rates and concentrations of specific compounds. In general, the model predictions for the primary clarifier and equalization basin are lower than the measured values. For the aerated stabilization basin, most of the predicted mass transfer coefficients are higher than the measured values; however, the agreement is within an order of magnitude. The measured values for the primary clarifier may have been higher than the predicted values because of the contribution from nearby sources to measured air concentrations or because of the contribution from the falling film at the clarifier.

GCA also performed an analysis on an aerated lagoon at Site 7.[14] This lagoon was covered and was purged with air at a rate of 1.4 m^3/s (3,000 ft^3/min). Predicted and calculated values for the mass transfer coefficients are given in Table 10-9 and show that predicted values are 1 to 2 orders of magnitude higher. The basis of the predicted values includes Thibodeaux and Reinhardt's correlations for aerated systems. No strong conclusions on the model's validity can be drawn from these data because the dome enclosure over the system and its evacuation rate probably have a direct effect on emissions. In addition, difficulties with air measurements and determination of the appropriate driving-force concentration (assumed to be the bulk liquid concentration) can lead to errors in the calculated values of the overall mass transfer coefficient.

The results of the biodegradation model were also compared to available data from biodegradation measurements. The most desirable comparison would be for a system in which the air emission rate and biodegradation rate were measured directly. However, the extent of biodegradation from studies of real systems has usually been determined by difference from a material balance (what enters the system minus what leaves with the effluent and with air emissions).

Petrasek et al. performed such a study on a large pilot-scale activated sludge system with diffused air aeration.[19] The activated sludge unit was enclosed, and the diffused air that was removed was sampled (for flow rate and concentration) to determine air emissions. This system was designed for a flow rate of 2.2 L/s (35 gal/min) with an air purge rate of 57 L/s. A summary of the operating parameters is given in Table 10-10. The study used a synthetic wastewater that contained individual volatile compounds at levels of 32 to 300 ppb. The biomass concentration was 2 g/L, and the resultant food-to-microorganism (F/M) ratio of 0.5 is well within the recommended design range of 0.2 to 0.6.

Petrasek reported the percent of each compound entering the activated sludge unit that was emitted with the diffused air; the fraction biodegraded could be determined by difference-assuming all unrecovered material was biodegraded. The results are summarized in Table 10-11 and show a range of measured values from 5 percent for chlorobenzene to 62 percent for 1,1,1-trichloroethane. The predictions of the biodegradation model discussed in Chapter 5.0 are also presented in Table 10-11 for comparison. The comparison shows that the model predictions agree well with the Petrasek measurements for nearly every compound.

Another type of comparison between measurements and predictions involves effluent concentrations for well-defined wastewater treatment systems. Namkung and Rittman[22] reported influent and effluent concentrations of volatile organics for two Chicago wastewater treatment plants that receive large shares of industrial discharges. The measurements were made for two large activated sludge units aerated by diffused air. In addition, the system's operational parameters were defined (Table 10-12) and provided the necessary inputs for the mathematical model that includes air emissions (diffused air system) and biodegradation.

The results of measured and predicted effluent concentrations are summarized in Table 10-13. The most convincing comparison is the close match for both plants for tetrachloroethylene, which the authors stated was not biodegradable in these systems. Therefore, a biorate equal to zero was used in the model for this compound. The close agreement between measured and predicted effluent concentrations suggests that this compound is almost entirely removed by air stripping, and the quantity predicted to be air stripped by the model is reasonably accurate.

TABLE 10-10. DESCRIPTION OF PETRASEK'S ACTIVATED SLUDGE SYSTEM[20]

Parameter	Value
Flow rate (L/s)	2.2
Volume (m^3)	59.8
Residence time (h)	7.5
Air rate (L/s)	57
Fraction of surface agitated	0
Biomass concentration (g/L)	2.0
Concentration range for organics (ppm)	0.032 - 0.30
F/M[a]	0.5

[a] F/M = Food to microorganism ratio (lb/lb biomass • day) based on chemical oxygen demand.

TABLE 10-11. COMPARISON OF PETRASEK'S MEASUREMENTS AND MODEL PREDICTIONS

Compound	Reported fraction emitted[a]	Predicted fraction emitted[b]	Fraction assumed biodeg.[a]	Predicted fraction biodeg.[b]
Benzene	0.15	0.19	0.80	0.78
Carbon tetrachloride	0.59	0.54	0.41	0.44
Chlorobenzene	0.05	0.02	0.95	0.97
Chloroform	0.34	0.20	0.66	0.75
Dichloropropane (1,2)	0.32	0.09	0.68	0.88
Ethyl benzene	0.21	0.15	0.79	0.82
Tertachloroethane and -ethene	0.27	0.37[c]	0.73	0.58[c]
Toluene	0.20	0.15	0.80	0.84
Trichloroethane(1,1,1)	0.62	0.57	0.38	0.40
Trichloroethane(1,1,2)	0.25	0.06[d]	0.75	0.87[d]
Trichloroethene	0.41	0.37	0.59	0.59

[a] Data from Petrasek et al.;[21] the fraction biodegraded is assumed to be the fraction unaccounted for based on the analyses of the sludge, the air, and the effluent.

[b] Model predictions based on the equations presented in Chapter 5.0 assuming influent VO concentrations of 0.10 mg/L and operating parameters as provided in Table 10-10.

[c] Arithmetic average for the removal fractions calculated for 1,1,2,2-tetrachloroethane and tetrachloroethene.

[d] Employed 1,1,1-trichloroethane's biodegradation rate constants.

TABLE 10-12. DESCRIPTION OF TWO CHICAGO ACTIVATED SLUDGE UNITS[23]

Operating parameters	Calumet	West-southwest
Volume (m^3)	184,500	802,300
Depth (m)	1.8	1.8
Wastewater flow (m^3/s)	10.0	36.6
Air rate (m^3/s)	55	193
Residence time (h)	5.1	6.1
Total organics (mg/L)	115	180
Biomass (g/L)	2.2	2.0
Fraction surface agitated	0	0
Concentrations (ppb)		
Chloroform, in	4.0	4.4
out	7.1	2.4
Ethylbenzene, in	18	10
out	0.5	BDL
Methylene chloride, in	9.8	48
out	11	11
Tetrachloroethylene, in	16	12
out	2.1	1.6
Toluene, in	85	22
out	6.2	BDL
1,1,1-Trichloroethane, in	13	15
out	2.9	2.2
Trichloroethylene, in	9.7	22
out	0.5	2.1

BDL = Below detection limit.

TABLE 10-13. COMPARISON OF MEASURED AND PREDICTED EFFLUENT CONCENTRATIONS FOR CHICAGO WASTEWATER TREATMENT PLANTS[24]

Compound	Calumet effluent concentrations, ppb		West-southwest effluent concentrations, ppb	
	Measured	Predicted[a]	Measured	Predicted[a]
Chloroform	b	b	2.4	2.3
Ethyl benzene	0.5	0.68	c	0.16
Methylene chloride	b	b	11	7.1
Tetrachloroethylene	2.1	1.0	1.6	0.77
Toluene	6.2	2.9	c	0.69
1,1,1-Trichloroethane	2.9	1.0	2.2	1.1
Trichloroethylene	0.5	0.75	2.1	1.6

[a] Based on the equations presented in Chapter 5.0.

[b] No comparison possible because measured concentration in effluent was greater than measured concentration in influent.

[c] Measured effluent concentration was below detection limit.

The results in Table 10-13 also indicate that 1,1,1-trichloroethane and trichloroethylene are biodegraded. The model predictions used a biorate for these two compounds that was derived from Petrasek's data in Table 10-11. Both Petrasek's data and the comparison in Table 10-13 indicate that these compounds are biodegraded to some extent; otherwise, the measured effluent concentrations in Table 10-13 would have been higher than those predicted by the model with biodegradation included.

Tabak et al.[25] conducted an extensive study of the biodegradability of numerous toxic compounds. They found that, when the microbial culture is properly acclimated, almost all nonpesticide compounds could be, at least partially, biodegraded. Although biodegradation rate constants were not determined, the percent of compound biodegraded was shown to be dependent on the acclimation of the culture, and (although to a lesser extent) dependent on the concentration of the compound used. For every compound tested, the percent biodegraded by the third subculture (presumably the most acclimated) always decreased when the concentration was doubled (unless both cultures were either 100 percent or 0 percent biodegraded), and this decrease was rarely a decrease of a factor of two or more.[26] If biodegradation were strictly a first-order process, the percent biodegraded would be independent of the concentration. If biodegradation were strictly a zero-order process, the percent biodegraded would decrease by a factor of two (for those compounds not biodegraded, 100 percent) when the concentration was doubled. Because an intermediate effect was generally realized, Tabak's results suggest Monod-type biodegradation rate kinetics are appropriate.

Another comparison that can be made is based on a series of field studies, as reported by Coburn et al.,[27] in which batch, biodegradation rate studies were performed while controlling air emissions. The experimental first-order biodegradation rate constant and the predicted, apparent first order rate constant based on the Monod model can be compared in the last two columns of Table 10-14. Note for compounds whose log mean concentrations are near or are greater than the appropriate half-saturation constant (e.g., formaldehyde or methanol), the predicted first-order rate constant according to the Monod model provides a better estimate of the observed biodegradation rate than would be provided assuming simple first-order kinetics (i.e., using K_1 straight from the data base as provided, for comparison, in Table 10-14). Additionally, using the recommended biodegradation rate constants and modeling approach, the predicted biodegradation rates presented in Table 10-14 agree well with the reported biodegradation rates for nearly every experimental run.

A separate study was conducted for EPA to evaluate measured and predicted emissions for aerated waste treatment systems.[29] The correlations of Thibodeaux and Reinhardt were used (as recommended in Chapter 5.0) to estimate the mass transfer coefficients of the turbulent zone. The results showed an agreement between measured and predicted values that were within an order of magnitude. The report concluded that, when adequate descriptions of plant operating parameters are available, reliable emission estimates can be obtained from the models (within the accuracy that results from variations in sampling and chemical analysis). When plant operating parameters are known, the major limitations in the models result from a lack of accurate biooxidation rates and vapor/liquid equilibrium data for specific compounds.[30]

10.2.3 Recommendations for Additional Data

The estimate of emissions from open liquid surfaces is provided by the product of the mass transfer coefficient, driving-force concentration, and surface area. Surface area can be determined with reasonable accuracy. The previous comparison of mass transfer coefficients indicated that they can be estimated within an order of magnitude. Probably the greatest source of uncertainty is in the estimate of the appropriate driving force for mass transfer. The concentration is likely to

TABLE 10-14. COMPARISON OF MEASURED AND PREDICTED BIODEGRADATION RATES

	Log mean	Rate constants[a]			First-order rate constant, L/g/h	
Compound	conc.,[b] mg/L	K_{max}, mg/g/h	K_s, mg/L	K_1, L/g/h	Experiment[b]	Predicted[c]
Acetone	1.35	1.3	1.1	1.15	1.15	0.53
	2.56				0.34	0.36
Benzene	0.005	19	13.6	1.4	0.36	1.4
	0.10				2.1	1.4
Chloroform	0.008	2.94	3.7	0.79	0.36	0.79
	0.002				0.29	0.79
Dimethyl-phthalate	4.2	2.2	0.71	3.1	0.36	0.45
Ethanol	4.9	8.8	9.8	0.90	0.70	0.60
Ethylbenzene	0.005	6.8	3.2	2.1	0.36	2.1
Ethylene oxide (oxirane)	1.7	4.2	4.6	0.91	0.81	0.67
	3.2				0.75	0.54
	3.9				0.37	0.49
Formaldehyde	8.0	5.0	20.	0.25	0.13	0.17
	62.				0.077	0.057
Methanol	250.	18.	90.	0.200	.067	0.053
	480.				0.018	0.032
	490.				0.040	0.031
	495.				0.023	0.031
Methyl ethyl ketone	0.10	2.0	10	0.20	0.24	0.20
	0.27				0.18	0.19
	0.37				0.19	0.19
	0.80				0.16	0.18
Methylene chloride	0.028	22	55	0.40	0.11	0.40
	0.031				0.11	0.40
	0.053				0.36	0.40
	0.15				0.20	0.40
	0.23				0.57	0.40

(continued)

TABLE 10-14 (continued)

Compound	Log mean conc.,[b] mg/L	Rate constants[a] K_{max}, mg/g/h	K_s, mg/L	K_1, L/g/h	First-order rate constant, L/g/h Exper.[b]	Predict.[c]
2-Propanol	2.9	15	200	0.75	0.069	0.074
	6.2				0.085	0.073
Thiobismethane	1.07	0.16	0.17	0.93	0.13	0.11
Toluene	0.014	3.5	30.6	2.4	0.28	2.4
	0.016				0.34	2.4
	0.081				0.63	2.4
	0.14				1.9	2.4
1,1,1-Trichloroethane	0.040	3.5	4.73	0.74	0.38	0.73
	0.16				0.88	0.72
Trichloroethene	0.004	3.9	4.43	0.88	0.41	0.88
Total xylenes	0.097	40.8	22.7	1.8	>2.2[d]	1.8

[a] Recommended rate constants from Appendix D, Table D-1.

[b] From data reported by Coburn et al.;[28] the log mean concentration was calculated as follows:

$$C_{LM} = (C_i - C_f)/\ln(C_i/C_f)$$

where,

C_i = initial concentration, mg/L; and

C_f = final concentration, mg/L.

[c] Calculated as the apparent first-order rate constant using the Monod model (Equation 5-13) based upon the log mean concentration as follows:

$$K_1 = K_{max}/(K_s + C_{LM}) .$$

[d] Final concentration was below detection limit. The final concentration was assumed to be at the detection limit to calculate the first-order rate constant. The actual rate constant should be greater than the reported value.

vary with time and location in the impoundment. The type of flow system and extent of mixing in the liquid also will affect this concentration.

For the less volatile compounds that may be controlled by gas-phase mass transfer, the collection of equilibrium data may be useful to compare with the estimated values used in the models. The comparisons presented in this section primarily address compounds with high volatility in water (high Henry's law constant). Because semivolatile compounds also can be emitted to a significant extent, air emission measurements for these less volatile compounds would be useful for comparison with model predictions.

10.3 LAND TREATMENT

Field data from four test sites and one laboratory simulation were used as a basis for comparing measured emissions with estimated emissions using the RTI land treatment model. Table 10-15 summarizes the tests evaluated. Generally, estimated emissions are within an order of magnitude of measured values. Values of estimated emissions varied both above and below measured values.

Comparisons of estimated and measured emission flux rates are presented graphically in this section. Comparisons of estimated and measured emissions by weight percent of applied material are presented in the next section.

Considering the potential for error in measuring or estimating values for parameters that are input to the model and the potential for error in measuring emissions, differences in the range of an order of magnitude are not unexpected. In making the comparisons, values for all model inputs sometimes were not available in the emission test reports. In these cases, values were estimated using averages of field data or values identified previously as typical or representative of actual land treatment practices.

TABLE 10-15. SUMMARY OF LAND TREATMENT TESTING AND TEST RESULTS

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results Waste constituent	Test results Emission, wt. %
12	West Coast corporate research facility	Laboratory simulation	1986 - 1987	Private corporation	Run 1 (raw waste)	2.5 months	Oil	35
					Run 2 (raw waste)	22 days	Oil	11
					Run 2 (treated waste)	22 days	Oil	1
13	Southwest research facility	Laboratory simulation	1986	EPA	Run 1 (API separator sludge)	31 days		
					Box #1		Oil	5.2
					Box #2		Oil	NA
					Box #3		Oil	6.5
					Box #4		Oil	6.7
					Run 2[a] (IAF float)	31 days		
					Box #1		Oil	15
					Box #2		Oil	NA
					Box #3		Oil	18
					Box #4		Oil	19
14	Midwestern refinery	Flux chamber	1985	ORD	Plot A	8 days	Benzene	81
							Toluene	41
							Ethylbenzene	195
							p-Xylene	16
							m-Xylene	39
							o-Xylene	28
							Naphthalene	1
					Plot B	8 days	Benzene	110
							Toluene	66
							Ethylbenzene	402
							p-Xylene	21
							m-Xylene	83

TABLE 10-15 (Continued)

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results Waste constituent	Emission, wt. %
							o-Xylene	38
							Naphthalene	2
					Plot C	8 days	Benzene	39
							Toluene	17
							Ethylbenzene	140
							p-Xylene	25
							m-Xylene	25
							o-Xylene	17
							Naphthalene	
					Plot D	8 days	Benzene	142
							Toluene	86
							Ethylbenzene	353
							p-Xylene	55
							m-Xylene	79
							o-Xylene	52
							Naphthalene	2
					Plot E	8 days	Benzene	107
							Toluene	63
							Ethylbenzene	345
							p-Xylene	43
							m-Xylene	52
							o-Xylene	39
							Naphthalene	1
					Plot F	8 days	Benzene	84
							Toluene	47
							Ethylbenzene	208
							p-Xylene	13
							m-Xylene	28

TABLE 10-15 (Continued)

							Test results	
Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Waste constituent	Emission, wt. %
							o-Xylene	24
							Naphthalene	1
15	West Coast refinery	Flux chamber	1984	ORD	Surface application	5 weeks	n-heptane	60
							Methylcyclohexane	61
							3-Methyl-heptane	52
							n-Nonane	56
							1-Methylcyclohexene	49
							1-Octene	50
							$-Pinene	17
							Limonene	22
							Toluene	37
							p-, m-Xylene	35
							1,3,5-Trimethylbenzene	21
							o-Ethyl-toluene	32
							Total VO	30
							Total oil	1.2
					Subsurface	5 weeks	n-heptane	94
							Methylcyclohexane	88
							3-Methyl-heptane	77
							n-Nonane	80
							1-Methylcyclohexene	76
							1-Octene	74
							$-Pinene	21
							Limonene	26
							Toluene	56
							p-, m-Xylene	48

TABLE 10-15 (Continued)

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results Waste constituent	Emission, wt. %
							1,3,5-Trimethylbenzene	27
							o-Ethyl-toluene	42
							Total VO	36
							Total oil	1.4
16	Southwest research facility	Laboratory simulation	1983	API/EPA	Run no. 18	8 hours[b]	Oil	9.1
					Run no. 21		Oil	4.4
					Run no. 24		Oil	0.02
					Run no. 27		Oil	0.6
					Run no. 28		Oil	0.1
					Run no. 32		Oil	3.0
					Run no. 33		Oil	2.6
					Run no. 34		Oil	0.01
					Run no. 35		Oil	0.9
					Run no. 36		Oil	78.8
					run no. 37		Oil	9.9
					Run no. 40		Oil	0.7
					Run no. 41		Oil	2.8
16 (con.)					Run no. 44		Oil	4.9
					Run no. 45		Oil	49.9
					Run no. 46		Oil	7.7
					Run no. 47		Oil	6.9
					Run no. 48		Oil	5.0
					Run no. 49		Oil	9.7
					Run no. 50		Oil	1.1
					Run no. 51		Oil	0.47

TABLE 10-15 (Continued)

Site No.	Test site location	Test description	Test year	Test sponsor	Test procedures	Test duration	Test results	
							Waste constituent	Emission, wt. %
10	Gulf Coast commercial TSDF	Flux chamber	1983	ORD	Single test[c]	69 hours	Total VO	0.77
						50 hours	Benzene	3.91
17	Midwestern refinery	Flux chamber	1979	API	Centrifuge sludge			
					Test no. 5	19.9 hours	Oil	0.1
					Test no. 6	307 hours	Oil	2.5
					API separator sludge[d]			
					Test no. 7	619 hours	Oil	13.5
					Test no. 8	122 hours	Oil	1.1
					Test no. 9	520 hours	Oil	13.5

API = American Petroleum Institute.
IAF = Inducted air flotation.
ORD = Office of Research and Development.

[a] Sludge applied to Box #1 and Box #3 as duplicate test; sludge treated with mercuric chloride to eliminate (or reduce) bioactivity applied to Box #4 and no sludge applied to Box #2, which served as a control.

[b] Each run for which results are reported was 8 hours.

[c] Test was conducted using aged wastes.

[d] Allowed to weather for 14 days in open 5-gal buckets in an outdoor open shelter prior to application.

In the 1985 test at a Midwest petroleum refinery (Case 1),[31] emission measurements were made at sample locations in six test plots. For each plot, emission measurements were made after waste application but before the plot was tilled, again after the waste was tilled, and for another period after a second tilling. All measurements were made using a flux chamber and tenax traps. Emission rates were measured for six specific organic constituents: benzene, toluene, p-xylene, o-xylene, m-xylene, and naphthalene. Benzene and toluene were selected as a basis for comparing measured and estimated emissions in this test. The comparison was made for test plot A after the waste was tilled for the first time. Estimated emissions for each compound are higher than the measured values but generally are within a factor of 10. Estimated and measured values are shown graphically for benzene and toluene in Figures 10-1 and 10-2, respectively.

At the West Coast refinery (Case 2),[32] emission tests were made using three adjacent plots marked off in the land treatment site. The center plot was used as a control and had no waste applied while waste was applied to the other two plots. One plot had waste applied to the soil surface and the other had waste applied by subsurface injection. Flux chambers were situated on each test plot and emission measurements were made during three different test periods each lasting 4 days. Canister air samples, sludge samples, and liquid samples were analyzed by gas chromatography (GC). Emissions of both total VO and selected specific constituents were measured during the test. For comparing measured and estimated emissions, total VO and toluene emissions from the surface application plot were used. Estimated emission rates for both toluene and total VO agree reasonably well with measured rates but range from higher to lower than measured rates at different times. Estimated cumulative emissions over the entire test period agree reasonably well with the measured values. For both toluene and total VO, estimates covered a 4-day period with a till occurring after 2 days.

Estimated and measured values over the 4-day period for which the comparison is made are generally within an order of magnitude, as can be seen in Figures 10-3 and 10-4. Measured values were reported as half-day average emission rates.

For the test at the commercial hazardous waste site in 1983, (Case 3),[33] waste was applied to a single test plot and tilled into the soil. Air emission measurements were made over a 3-day period using a flux chamber and gas canisters. Sampling locations were selected randomly, with a control point used to provide a common sampling position each day. Sample analyses were made by GC. Emission comparisons of measured and estimated emissions were made for total nonmethane hydrocarbon (NMHC) emissions using data generated by GCA in a separate study of the data from this test.[34] As with previous tests, estimated emission flux rates were greater than measured values but mostly were within a factor of 10 or less of the measurements. Estimated cumulative emissions also were substantially higher than measured values. Estimated and measured values of instantaneous emission flux rates are shown in Figure 10-5.

In the 1979 test at the Midwest petroleum refinery (Case 4),[35] three test plots were laid out. One plot was used as a control and had no waste applied, one plot had an API separator sludge applied, and the other plot had a centrifuge sludge applied. A 1-ft^2 collector box was placed on the test plot and continuously purged with fresh air. The outlet from the box was analyzed for total VO (as methane and NMHC) using a continuous hydrocarbon analyzer. For one test run, total VO emissions were estimated with the land treatment model for comparison with the measured values. Measured and estimated values are shown graphically in Figure 10-6. As can be seen, the estimated and measured values agree quite well for this test. Total cumulative emissions for each test were also estimated using the model and compared with measured values. The estimated values were generally higher than measured values for these emissions.

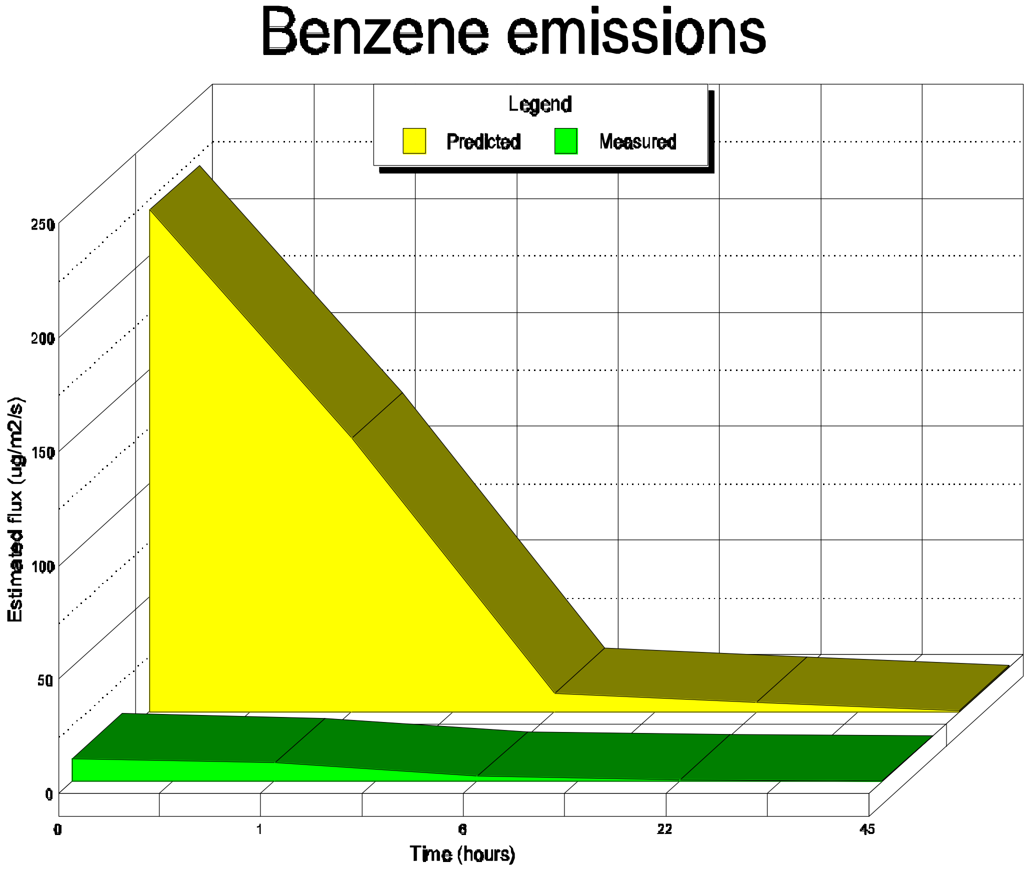

Figure 10-1. Estimated vs. measured benzene emission flux rates-Case 1.

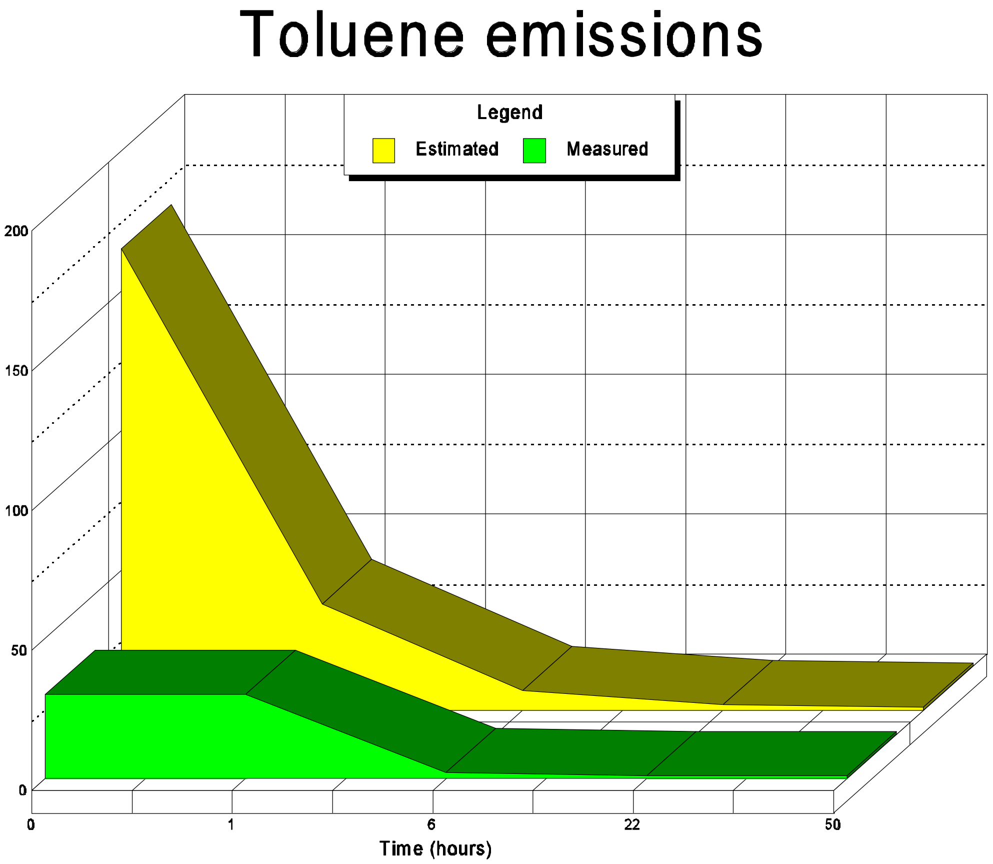

Figure 10-2. Estimated vs. measured toluene emission flux rates-Case 1.

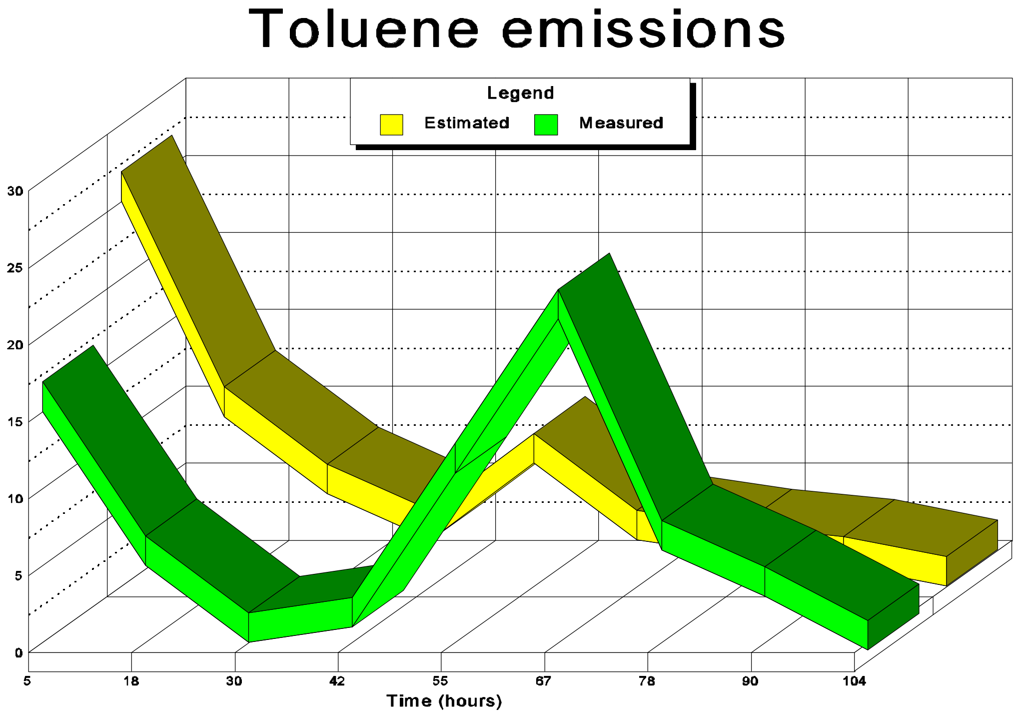

Figure 10-3. Estimated vs. measured toluene emission flux rates-Case 2 (data for 4 days only).

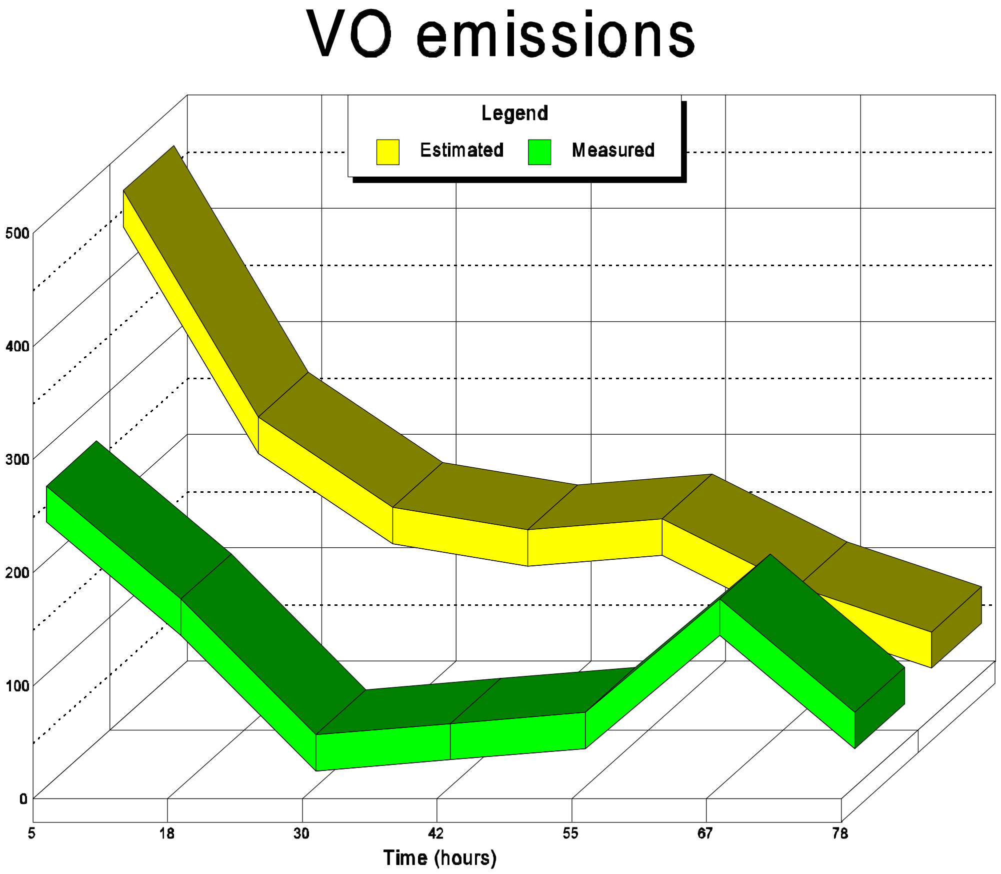

Figure 10-4. Estimated vs. measured VO emission flux rates-Case 2.

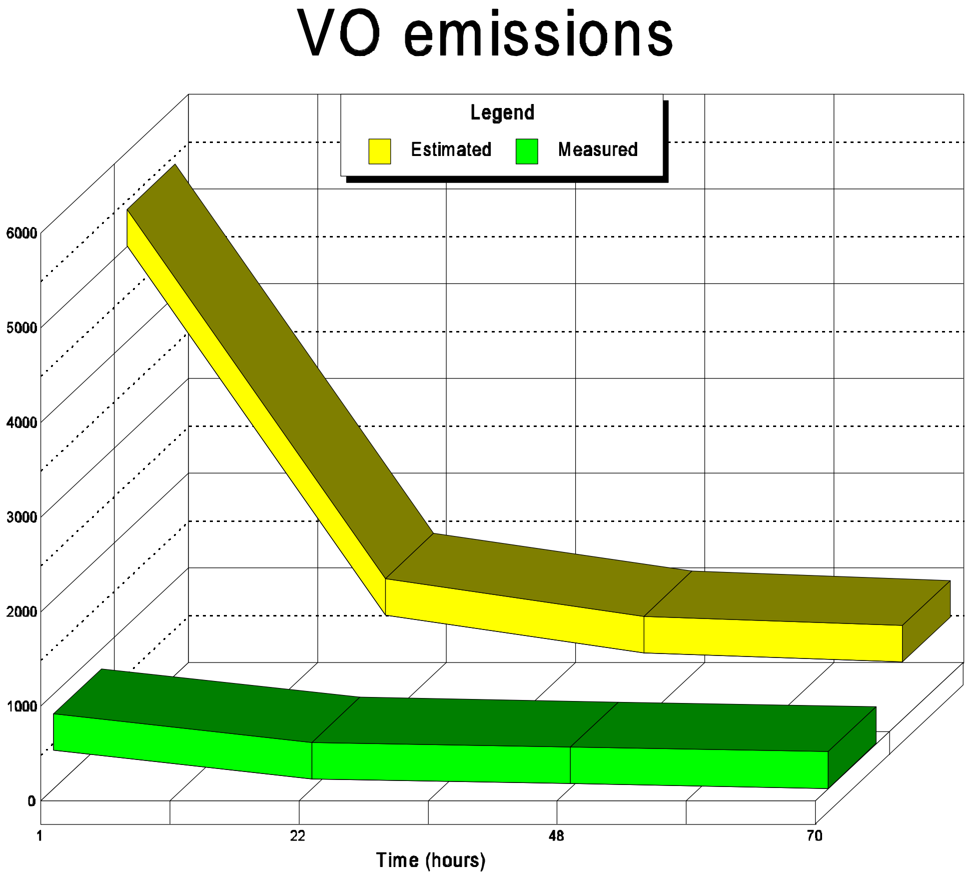

Figure 10-5. Estimated vs. measured VO emission flux rates-Case 3.

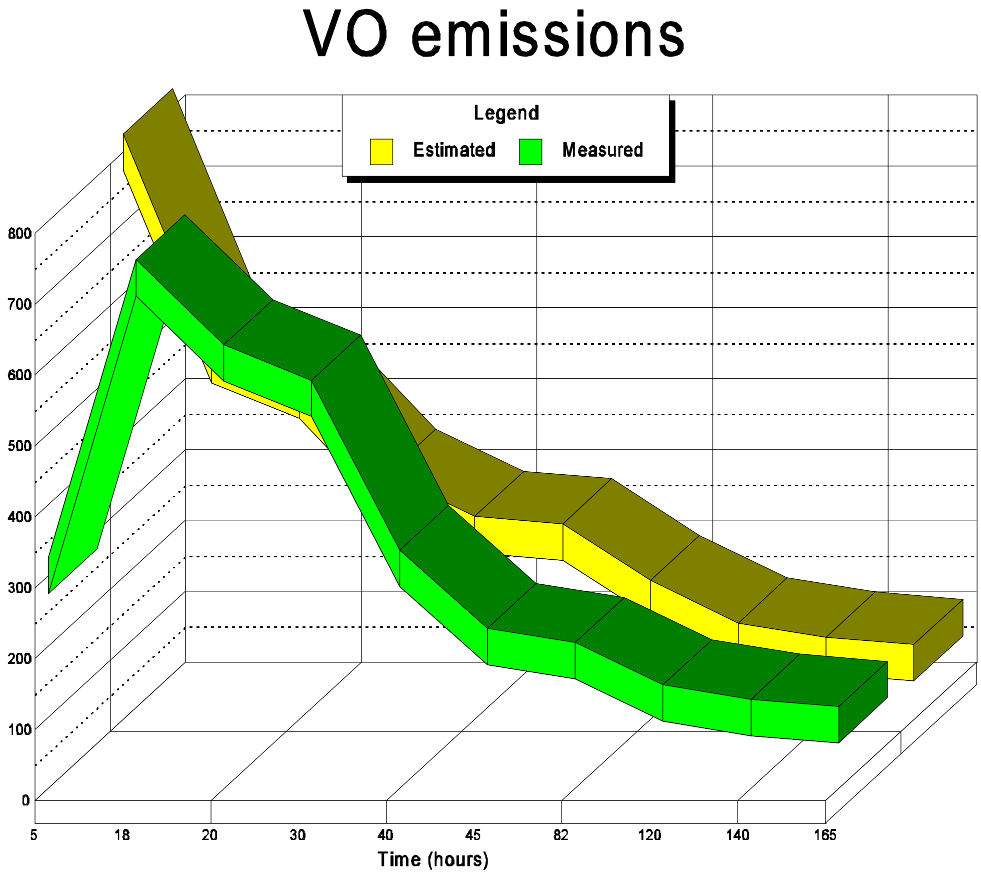

Figure 10-6. Estimated vs. measured VO emission flux rates-
Case 4.

10.3.1 Midwest Refinery--1985 (Case 1)

Table 10-16 presents the model input values used to compare estimated and measured emissions for plot A of the Case 1 test data. The information in Table 10-16 represents data for plot A as reported in the test report. Similar information was reported for plots B through F and those data were used as appropriate for input to the model. Table 10-17 shows measured emissions of six constituents made during the test. In this test, the waste was allowed to stay on top of the soil for 24 hours before it was tilled into the soil. Measured emissions during the first 24 hours were combined with measured emissions after tilling to get total emissions. Table 10-17 shows variations in measured emissions among the different test plots and shows emissions greater than applied material for some plots and some waste constituents. In Table 10-17, weight fraction represents the fraction of applied material that is emitted to the air. For ethylbenzene, all plots have measured emissions in excess of the amount applied. To compare measured and estimated emissions, the RTI land treatment model can be used for estimating emissions both before and after tilling. Estimated cumulative emissions for benzene and toluene for all plots are shown in Table 10-17 and show reasonable agreement with measured values.

10.3.2 West Coast Refinery (Case 2)

The data in Table 10-18 were used to estimate emissions of toluene and total VO from the surface application plot at the Case 2 land treatment facility. Estimated and measured cumulative emissions are compared in Table 10-19. The comparisons were made for total VO (as determined by purge and trap) and for toluene.

TABLE 10-16. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic loading	0.0236 g/cm^3	Calculated from field data
Tilling depth	20 cm	Field data
Soil air porosity	0.40	Field data
Soil total porosity	0.61	Field data
Benzene concentration[b]	0.000249	Calculated from field data
Toluene concentration[b]	0.000632	Calculated from field data
Benzene diffusivity	8.80 E-02 cm^2/s	Data base
Toluene diffusivity	8.70 E-02 cm^2/s	Data base
Benzene vapor pressure	95.2 mm Hg	Data base
Toluene vapor pressure	30.0 mm Hg	Data base
Benzene biorate	19.0 mg VO/g•h	Data base
Toluene biorate	73.0 mg VO/g•h	Data base
Molecular weight of oil	282 g/g mol	Assumed

[a] Source of field data: Reference 36. Data represent conditions in plot A.

[b] Weight fraction of oil.

10.3.3 Commercial Waste Disposal Test (Case 3)

Table 10-20 shows the inputs used to estimate emissions from the Case 3 land treatment operation. No specific constituent data were available so emissions were estimated using average characteristics of the total organic phase. Results are shown in Table 10-21. The comparison is made for the estimated versus measured cumulative weight percent of applied oil that is emitted after 24 hours and after 68 hours, which is the duration of the entire test.

10.3.4 Midwest Refinery--1979 (Case 4)

The information in Table 10-22 was used to estimate emissions from the Case 4 facility test. No specific constituent data were available; emissions were estimated for total organics using average parameter values. Results are presented in Table 10-23. The comparisons are for the cumulative weight percent of applied oil that was emitted over the entire period of each test.

10.4 LANDFILLS AND WASTEPILES

Emission testing has been performed on at least one active (open) landfill at each of five sites. Only three of these sites have closed or inactive landfills at which emission measurements were performed. No emission test data are available for wastepiles.

Meaningful comparisons can be performed of emission test data with mathematical model predictions provided that all key model input parameters are available from the tests. A review of documentation from the emission tests indicates that generally more than half of the needed model input parameters (other than chemical property data) are unknown, despite the fact that several emission tests were performed with the stated intention of validating emission models. Examples of key model input

TABLE 10-17. MEASURED AND ESTIMATED EMISSIONS—CASE 1

Test location	Measured cumulative emissions[a]													
	Benzene		Toluene		Ethylbenzene		p-Xylene		m-Xylene		o-Xylene		Naphthalene	
	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.
A	271.81	0.81	348.71	0.41	57.97	1.95	7.39	0.16	96.40	0.39	21.11	0.28	2.15	0.01
B	299.86	1.10	454.28	0.66	96.46	4.02	7.50	0.21	163.84	0.83	23.18	0.38	2.31	0.02
C	188.35	0.39	209.96	0.17	59.27	1.40	15.83	0.25	87.17	0.25	18.76	0.17	3.08	0.01
D	459.42	1.42	703.08	0.86	101.05	3.53	23.92	0.55	185.32	0.79	38.02	0.52	3.35	0.02
E	382.23	1.07	576.10	0.63	109.31	3.45	20.74	0.43	136.39	0.52	31.56	0.39	2.46	0.01
F	324.88	0.84	464.97	0.47	71.55	2.08	6.87	0.13	78.04	0.28	21.39	0.24	2.44	0.01

Test location	Estimated cumulative emissions			
	Benzene		Toluene	
	µg/cm^2	wt. frac.	µg/cm^2	wt. frac.
All	--	0.83	--	0.53

TABLE 10-18. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic (oil) loading	0.0328 g/cm^3	Estimated from field data
Tilling depth	20 cm	Field data
Soil porosity	0.5	Field data
Molecular weight of oil	282 g/g mol	Field data
Toluene concentration	0.00157 (wt. fraction of oil)	Calculated from field data
Toluene diffusivity	8.70 E-02 cm^2/s	Data base
Toluene vapor pressure	30.0 mm Hg	Data base
Toluene biorate	73.0 mg VO/g•h	Data base
VO concentration	0.04 (wt. fraction of oil)	Calculated from field data
VO diffusivity	6.60E-02 cm^2/s	Average from field data
VO vapor pressure	14.6 mm Hg	Average from field data
VO biorate	23.68 mg VO/g•h	Average from field data

[a] Source of field data: Reference 37.

TABLE 10-19. ESTIMATED VS. MEASURED EMISSIONS--CASE 2

	Time after tilling, day/h	Estimated emissions, wt. %	Measured emissions, wt. %
Toluene	33/793	31	37
Total VO	33/793	32	30
Total oil	33/793	1.3	1.2

TABLE 10-20. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic loading	0.0406 g/cm^3	Calculated from field data
Tilling depth	19.6 cm	Field data
Soil porosity	0.5	Assumed
Oil Molecular weight	282 g/g mol	Assumed
Vapor pressure	0.57 mm Hg	Calculated by GCA[b]
Diffusivity in air	2.70 E-02 cm^2/s	Average from field data
Biorate	23.68 mg VO/g•h	Average from data base

[a] Source of field data: Reference 38.

[b] Reference 39.

TABLE 10-21. ESTIMATED VS. MEASURED TOTAL VO EMISSIONS--CASE 3

Time after tilling, h	Estimated emissions, wt. % total applied oil	Measured emissions, wt. % total applied oil
68.00	4.5	0.77

TABLE 10-22. INPUT PARAMETERS FOR RTI LAND TREATMENT MODEL[a]

Parameter	Value	Source
Organic loading	0.002125 g/cm^3	Estimated from field data
Tilling depth	20 cm	Assumed
Soil porosity	0.5	Assumed
Molecular weight of oil	282 g/g mol	Assumed
Diffusivity in air	9.12 E-02	Average from data base
Vapor pressure	0.76 mm Hg	Calculated by GCA[b]
Biorate	23.68 mg VO/g•h	Average from data base

[a] Source of field data: Reference 40.

[b] Reference 41.

parameters that are generally unknown or poorly defined include waste porosities (air and total), average waste bed temperature (for active and closed landfills), waste composition at depths greater than the surface layer, barometric pressures, clay cap porosities (air and total), clay cap thickness, waste bed depth, and (for active landfills particularly) time between core sampling and air emissions determination. To apply the models, representative default values have been used where necessary. Because of the necessity to estimate key input parameters, the comparisons that follow are of extremely limited value for model validation. To achieve validation of emission models, additional field tests or laboratory experiments are needed for active and closed landfills and wastepiles.

Field data from two sites were used for comparison with the land treatment model as applied to active landfills. These sites (5 and 8) were chosen because of similarity in constituency of selected chemicals and relative availability of model input parameters. However, it should be noted that at each of the sites more than half of the needed model input parameters were not available from the tests and thus required estimation.

Information on the waste composition within closed landfills was insufficient to allow use of the closed landfill model. At two of the three closed/inactive landfill sites (4 and 5), no solid samples of waste were taken; at the remaining site (Site 9), a single soil core was apparently extracted from the 3-ft clay cover, providing no information about the composition of the waste below the cover. However, it should be noted that Farmer et al.[42] (who developed the precursor to the RTI closed land-fill model, it accounts for diffusion through the clay cap only, not barometric pumping) mentioned that their model has received experimental verification via a laboratory experiment using hexachlorobenzene-containing waste in a simulated landfill.

Following are the results of the comparison for active landfills at Sites 5[43,44] and 8[45]. Table 10-24 presents model input parameters used in the application of the RTI land treatment model to an active landfill at Site 5. Table 10-25 presents a comparison of measured and predicted emission rates for the Site 5 landfill.

Model predictions for the chemicals assessed here are higher than field data values by a factor ranging from 13 to 441. This discrepancy may be largely a result of the presence of daily earth covers (6 in. thickness) and layers of drums within the waste bed--neither of which are accounted for by the model. Other contributing factors may include the estimation of key model input parameters (e.g., air porosity of waste, temperature of the constituent within soil) and the nonrepresentative nature of the waste sample (obtained at the surface) for describing the waste composition at depth.

Table 10-26 presents model input parameters used in the application of the RTI land treatment model to an active landfill at Site 8. Table 10-27 presents a comparison of measured and predicted emission rates for the Site 8 landfill.

Model predictions of the emissions at Site 8 are, in general, closer to field data than were the predictions made for Site 5. Better overall agreement may be due to the absence of drums and daily earth covers in this landfill.

10.5 TRANSFER, STORAGE, AND HANDLING OPERATIONS

10.5.1 Models Documented in AP-42

Emission methods for the following models were taken from AP-42; they have been developed from the field data in the petroleum industry and should be applicable to TSDF:

- Container loading (from AP-42, Section 4.4)[52]
- Container cleaning (from AP-42, Section 4.8)[53]
- Stationary tank loading (from AP-42, Section 4.3)[54]
- Stationary tank storage (from AP-42, Section 4.3).[55]

10.5.2 Fugitive Emissions

Fugitive emission sources have been studied extensively for the petroleum and Synthetic Organic Chemical Manufacturing Industries (SOCMI) facilities.[56] These SOCMI emission factors are assumed to be applicable to similar operations at TSDF.

10.5.3 Spillage An ICF[57] study of truck transport to and from TSDF and truck emissions at TSDF terminals provided the information necessary to estimate spillage losses during TSDF and trucking operation. However, no field test data is available for comparison.

10.5.4 Open Dumpster Storage Emissions No field data were available for comparison.

TABLE 10-23. ESTIMATED VS. MEASURED EMISSIONS--CASE 4

Test	Elapsed time, day/h	Estimated emissions, wt. % total applied oil	Measured emissions, wt. % total applied oil
5	1/20	5.0	0.14
6	13/307	14.0	2.5
7	26/619	16.0	13.5
8	5/122	14.0	1.1
9	22/520	28.0	13.4

TABLE 10-24. MODEL INPUT PARAMETERS USED IN APPLICATION OF THE LAND TREATMENT MODEL TO AN ACTIVE LANDFILL AT SITE 5[a]

Parameter	Value	Data source
L, total organic loading in soil	2.65 x 10^{-3} g/cm^3	Inferred from field data (solid sample analysis) assuming soil density = 2.3 g/cm^3
C_i, weight fraction of constituent i in organic phase	Xylene: 0.178 Methylene chloride: 8.48 x 10^{-4} Tetrachloroethylene: 1.37 x 10^{-3}	Field data (solid sample analysis)
T, temperature of constituent vapor in soil	25 °C	Default value
l, depth of waste in landfill	229 cm (7.5 ft)	Default value
’$_T$’, total porosity of waste	0.50 (50%)	Default value
,$_a$, air porosity of waste	0.25 (25%)	Default value
S_b, soil biomass concentration	0 g/cm^3	Default value
MW_{oil}, molecular weight of organic carrier liquid	150 g/g mol	Default value
t, time between soil sampling and air emission measurement	900 s (15 min)	Engineering judgment

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[a] Landfill 10, General Organic Cell.[46,47]

TABLE 10-25. COMPARISON OF MEASURED AND PREDICTED EMISSION RATES SITE 5 ACTIVE LANDFILL[a]

prediction, Chemical	Field data result, $\mu g/m^2 \cdot s$	Model $\mu g/m^2 \cdot s$
Xylene	32.8	440.0
Methylene chloride	0.734	14.0
Tetrachloroethylene	0.0111	4.9

[a] Landfill 10, General Organic Cell.[48,49]

TABLE 10-26 MODEL INPUT PARAMETERS USED IN APPLICATION OF THE RTI LAND TREATMENT MODEL TO AN ACTIVE LANDFILL AT SITE 8[50]

Parameter	Value	Source
L, total organic loading	1.71×10^{-6} g/cm^3	Field data in soil
C_i, weight fraction of VO_i in organic phase	Xylene: 0.012 1,1,1-TCE: 0.19 Tetrachloroethylene: 0.096	Field data (solid sample analysis)
T, temperature of VO vapor in soil	25 °C[a]	Default value
l, depth of waste in landfill	229 cm (7.5 ft)	Default value
$'_T$, total porosity of waste	0.50 (50%)[b]	Default value
$'_a$, air porosity of waste	0.25 (25%)[b]	Default value
S_b, soil biomass concentration	0 g/cm^3	Default value
MW_{oil}, molecular weight of organic carrier liquid	150 g/g mol	Default value
t, time between soil sampling and air emission measurement	900 s (15 min)	Engineering judgment

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[a] Soil surface temperatures at this site were reported at 26 to 36 °C. The model unit default value of 25 °C is applied to the constituent within the soil in this analysis.

[b] A single "porosity" value of 31.7 percent was reported for this site, based on one soil sample. Because this value is not defined explicitly, and may not be representative of typical waste in the landfill, the model unit default values of air porosity and total porosity were applied in this analysis.

TABLE 10-27. COMPARISON OF MEASURED AND PREDICTED EMISSION RATES FOR THE SITE 8 ACTIVE LANDFILL[51]

Chemical	Field data result, $\mu g/m^2 \cdot s$	Model prediction, $\mu g/m^2 \cdot s$
Total xylene	6.21	0.23
1,1,1-Trichloroethane	3.57	3.8
Tetrachloroethylene	6.31	1.9

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11.0 TECHNICAL SUPPORT FOR THE IDENTIFICATION OF COLLECTION SYSTEMS AS MAJOR EMISSION SOURCES

11.1 INTRODUCTION

This chapter provides a summary of information that is currently available relevant to the identification of the potential significance of air emissions from collection systems. Most of the relevant investigations are included, including two recent investigations sponsored by the Chemical Manufacturers Association (CMA). Information obtained from these CMA sponsored investigations were used by OAQPS to revise the air emission models for collection systems. Section 11.1 lists the data sources that are referenced in this chapter, followed by a summary table for each data source. Although the data are variable in the type of source tested, the methods used for of data collection, and types of compounds, the conclusions from the data analysis in the different studies are generally similar. These studies support the potential for release of most of a higher volatility organic material from the wastewater to the atmosphere during the path of the wastewater from the point of origin to the wastewater treatment system.

Predictions from theoretical emission models are compared with field test data in this chapter. In general, considering the uncertainty of field emission measurements, agreement between measured and predicted values is considered reasonable. Those data sets of measured air emissions that were used as the basis of collection system model parameter selection and data correlation generally agreed with the models with less than 20 percent difference.

Several conclusions are apparent and seem to be supported by the data. These conclusions are listed as separate sections in this document, and the data supporting each conclusion is summarized in each section. The sections in this document that present the major conclusions are listed below.

Section number	Conclusion illustrated
Section 11-2. page 11-2	Information is available which supports the identification of collection systems as significant emission sources.
Section 11-3. page 11-15	Organic compounds will volatilize in the headspace of the collection system.
Section 11-4. page 11-19	Uncontrolled wastewater collection systems can have significant discharges of headspace to the atmosphere.
Section 11-5. page 11-25	The fraction of organic compounds that is lost in uncontrolled collection systems can be high, greater than 40 percent.

11.2 SUMMARY OF REFERENCES FOR AIR EMISSIONS FROM COLLECTION SYSTEMS

CMA FIELD TEST: DU PONT OLD HICKORY	24 -48 percent of organic materials were volatilized from one run of a collection main. There were low flow and high ventilation conditions during the field test.

CMA LABORATORY TEST: ENVIROMEGA	The air loss from open uncontrolled drain hubs were tested both with and without waste flow into the drain hub. In the case of the model predictions of drain losses, the data for the open drain without waste flow demonstrated 6.6 percent loss of toluene from a drain (run 7). This agrees favorably with the model predictions of 6.1 percent (BACT\LAER). The fraction lost from the system was even greater when waste was discharged into the drain hub. 50 percent equilibrium was observed for low air flow in sealed junction boxes.
Jensen, ET. AL. Research Journal, WPCF	30+ percent of a volatile material (krypton) was volatilized and lost from one run of a collection main.
SHELL TESTS	Significant concentrations of organic compounds were detected in the headspace of a petrochemical collection system at the Shell facility. The magnitude of the headspace concentrations was greater than the equilibrium values from the liquid concentrations. (see also Fingas)
Fingas, *et al.*	Lab scale collection system. Investigated the effects of gasoline spills on the headspace concentrations in the collection system. Soon after entering the system, the higher volatility constituents in the fuel were lost to the headspace. The headspace after the initial discharge contained the lesser volatility chemicals due to the high loss of the more volatile chemicals.

EPA TRACER INVESTIGATION: ROHM AND HAAS	Greater than 95% loss of a series of organic compounds was observed from discharge into a trench and conventional sewer. Hexane disappeared from both the headspace and the liquid during the flow through the collection system.
EPA TRACER INVESTIGATION: COASTAL EAGLE POINT REFINERY	40 -54% loss of organic compounds was observed from discharge into a series of open junction boxes with water seals.
R. L. Corsi, PH.D. DISSERTATION	Measured concentrations in collection main which were at equilibrium, Run 1. Other runs were not at equilibrium. Review of literature.
R. L. Corsi, ENVIROMEGA, AND WASTEWATER TECHNOLOGY CENTRE	27-40% loss of duterated chloroform and 20-24% loss of ethylene dibromide was reported in a model of a collection system drop structure.
BP OIL TRACER INVESTIGATION: LIMA REFINERY	30-56% loss of chloroform in a collection main. The loss was a function of the sewer temperature.
AMOCO REFINERY	The fraction lost to the atmosphere could not be estimated due to lack of information of organic compound partition into or out of an oil layer. 17 -60% loss of organic compounds from the wastewater in a collection main was estimated from field tests that measured wastewater concentrations and flow rates.

AMOCO REFINERY (continued)	The measured collection system losses were used to estimate the overall losses. Greater than 99% loss of benzene was estimated for the overall collection system by extrapolating the measured rates on the basis of opening areas.

TABLE 11-1. LITERATURE REVIEW, I

TITLE:	Method for measurement of reaeration in gravity sewers using radiotracers
AUTHORS:	Niels Aagaard Jensen, Thorkild Hvitved-Jacobsen
SOURCE:	Research Journal WPCF, Volume 63, Number 5, pages 758-767, July/August 1991.
SUMMARY:	30+ percent of a volatile material (krypton) was volatilized and lost from a reach of a collection main. The article states that tracer gas buildup in the headspace might be significant for sewers.
METHODS:	The water flow was 0.02 M^3/s in a 0.6 m conduit with a 1358 m run. To avoid headspace equilibrium effects, the tracer was injected into the water. The mass transfer was calculated from the changes in the ratio of a volatile tracer (krypton 85) to a non-volatile tracer (tritium).
COMMENTS:	The study appeared to be carefully done, with excellent reproducibility among three runs. This study indicates that significant loss of highly volatile materials may occur even in closed runs of ventilated conduits, even with compounds dissolved in water.

TABLE 11-2. LITERATURE REVIEW, II

TITLE:	Field Evaluation of Wastewater Drain System Emissions: Rohm and Haas Bristol Facility, Bristol, Pa., April 1993.
AUTHORS:	Radian Corporation 155 Corporate Woods, Suite 100, Rochester, N.Y.
SOURCE:	Submerged drain into an open trench. The wastewater fell into a conventional collection system.
SUMMARY:	Compounds were dissolved into water and added to wastewater. The loss of compounds from part of the unit collection system was as follows: hexane, 98%; acenaphthene 71%, chlorobenzene, 96%; and 111 trichloroethane, 87%.
METHODS:	Loss was measured by the ratio of loss of volatile constituent to the loss of non-volatile constituents. The volatilization of organics was confirmed by headspace concentrations (not quantified by headspace).
COMMENTS:	This investigation indicates the potential for significant air emissions. The high losses of the organic compounds that were observed are consistent with the laboratory data of Fingas.

TABLE 11-3. LITERATURE REVIEW, III

TITLE:	Industrial Wastewater Field Evaluation of Wastewater Drain System: Emission Test Report, Coastal Eagle Point Oil Company, Westville, N.J. September 1993.
AUTHORS:	Radian Corporation 155 Corporate Woods, Suite 100, Rochester, N.Y.
SOURCE:	Open drain into water sealed hub. Open junction boxes with submerged entrance.
SUMMARY:	Compounds were dissolved into water and added to wastewater. The loss of compounds from part of the unit collection system was as follows: nitrobenzene, 40%; chlorobenzene, 33%; and 111 trichloroethane, 54%. Covering the sumps reduced the air emissions to 29%, 33%, and 46%.
METHODS:	Loss was measured by the ratio of loss of volatile constituent to the loss of non-volatile constituents. The volatilization of organics was confirmed by headspace concentrations (not quantified by headspace).
COMMENTS:	This investigation indicates the potential for significant air emissions, even for relatively controlled systems.

TABLE 11-4. LITERATURE REVIEW, IV

TITLE:	Estimation of BTEX Emissions from BP Oil Refinery Waste Water Collection System. BP Oil Refining Environmental. Presented at the Air Toxic Workshop, San Diego, CA, March 31, 1993.
AUTHORS:	D. E. Isaacson, BP Oil Refining Environmental.
SOURCE:	Collection main that served multiple refinery units.
SUMMARY:	Compounds were dissolved into water and added to wastewater. The loss of compounds from the collection system was as follows: chloroform in the hot zone of collection system, 56% average; and chloroform in the normal temperature zone, 30%, with an overall loss greater than 80%..
METHODS:	Loss was measured by the ratio of loss of volatile constituent to the loss of non-volatile constituents. Lithium chloride was used to define liquid flow rates.
COMMENTS:	This investigation indicates the potential for significant air emissions from collection mains.

TABLE 11-5. LITERATURE REVIEW, V

TITLE:	Measurement of Hazardous Air Pollutant Emissions from Wastewater Collection System Components.
AUTHORS:	Enviromega Ltd. PO.Box 1249, Burlington, Ont. L7R 4LB, April, 1993. CMA sponsored research.
SOURCE:	Drop structures, process drains, open discharge into a water sealed hub, open discharge into an unsealed drain hub.
SUMMARY:	The air loss from open uncontrolled drain hubs were tested both with and without waste flow into the drain hub. In the case of the model predictions of drain losses, the data for the open drain without waste flow demonstrated 6.6 percent loss of toluene from a drain (run 7). This agrees favorably with the model predictions of 6.1 percent (BACT\LAER). The fraction lost from the system was even greater when waste was discharged into a water sealed drain hub. The air emissions from the open discharge of waste into a water sealed drain ranged from 10% to 60%, depending on the flow rate and compound volatility. Methanol was significantly volatilized under the test conditions.
METHODS:	Toluene, tetrachloroethylene, trichloroethene, and 1,4 dichlorobenzene were added to a sewer reach. The concentrations added to the sewer, the concentrations in the gas, and the ventilation rates were measured.
COMMENTS:	The data from this investigation were used to revise the air emission models for specific collection elements.

TABLE 11-6. LITERATURE REVIEW, VI

TITLE: Volatile and Semi-Volatile Organic Compound Emissions from Sewer Drop Structures.

AUTHORS: R. L. Corsi et al. University of Guelph; H. Monteith, Enviromega Ltd. PO.Box 1249, Burlington, Ont.; and H. Melcer, Wastewater Technology Center, Burlington, Ontario.

SOURCE: Drop structures.

SUMMARY: 27-40% loss of duterated chloroform and 20-24% loss of ethylene dibromide was reported in a model of a collection system drop structure.

Methanol was significantly volatilized under the test conditions.

METHODS: The air loss from a drop structure was tested by measuring the concentrations of ethylene dibromide and duterated chloroform in the inlet and exit of the drop structure. The concentrations added to the sewer, the concentrations in the gas, and the ventilation rates were measured.

COMMENTS: The authors conclude that data from this investigation indicate that sewer drop structures may be significant contributors to overall semi-VOC and VOC emissions from sewers.

TABLE 11-7. LITERATURE REVIEW, VII

TITLE:	Sampling for Fugitive HAP Emissions From A Wastewater Collection Sewer Reach at the DuPont Old Hickory Site.
AUTHORS:	Enviromega Ltd. PO.Box 1249, Burlington, Ont. L7R 4LB, September, 1993. CMA sponsored research.
SOURCE:	165 m (450 ft) reach of a sewer. The wastewater depth was very shallow, 2 to 5 inches.
SUMMARY:	"Using the measured dose solution concentration the percentage VOC emissions ranged from 24% to 48%. Using the target concentration of VOCs in the dose solution, the percentage emissions ranged from 16% to 29%." (p.45)
METHODS:	Toluene, tetrachloroethylene, 1,1,2,2 tetrachloroethane, and 1,4 dichlorobenzene were added to a sewer reach. The concentrations added to the sewer, the concentrations in the sewer, and the mass air emissions were measured.
COMMENTS:	"The consistency and magnitude of the decreases [in wastewater concentration] suggests substantial losses of VOCs to the atmosphere." (p.36)

TABLE 11-8. LITERATURE REVIEW, VIII

TITLE:	Ph.D. Dissertation of R. L. Corsi, University of California, Davis, 1989.
AUTHORS:	R. L. Corsi
SOURCE:	Collection main
SUMMARY:	Compounds were added to wastewater. The concentrations of organic compounds in the headspace of the collection main were approximately the same as equilibrium values for Run 1. The concentrations were less than equilibrium for other runs.
METHODS:	Loss was measured by the concentrations of organic constituents and the flow rate. The volatilization of organics was quantified by headspace concentrations and flow rates.
COMMENTS:	This thesis indicates the potential for significant air emissions. A literature review is included.

TABLE 11-9. LITERATURE REVIEW, IX

TITLE:	Fuels in Sewers: Behavior and countermeasures, Journal of Hazardous Materials 19 (1988) 289-302.
AUTHORS:	M. F. Fingas, K. A. Hughes, and A. M. Bobra
SOURCE:	Laboratory collection system.
SUMMARY:	Vapors in sewers have two distinct origins, entry vaporization and mass transfer during transport. The wastewater loses the more volatile components during entry.
METHODS:	Gasoline was spilled in one end of the collection system. The volatilization of organics was confirmed by headspace concentrations and liquid concentrations.
COMMENTS:	This investigation indicates the potential for significant air emissions, even for relatively controlled systems.

TABLE 11-10. LITERATURE REVIEW, X

TITLE:	Method 25D Development and Testing at the Shell, Deer Park Industrial Wastewater Facilities, June 1991.
AUTHORS:	Radian Corporation 850 Mo-Pac Boulevard, Austin, Texas
SOURCE:	Collection system in a large petrochemical complex. Sources included drains, sumps, and manhole covers.
SUMMARY:	Significant concentrations of organic compounds were detected in the headspace of a petrochemical collection system. The magnitude of the headspace concentrations was as great or greater than the equilibrium values from the liquid concentrations. Screening tests of headspace in equilibrium with the liquid confirmed that the headspace concentrations were greater than equilibrium.
METHODS:	The volatilization of organics was confirmed by headspace concentrations, measured headspace flow rates into the air, and concentrations in the liquid.
COMMENTS:	This investigation indicates the potential for significant air emissions, because of high headspace gas concentrations.

TABLE 11-11. LITERATURE REVIEW, XI

TITLE:	An Air Quality Evaluation of the Amoco Yorktown Refinery as Part of the Amoco-USEPA Pollution Prevention Project., September 13, 1991
AUTHORS:	Amoco Corporation Environmental Affairs and Safety Department.
SOURCE:	Collection system in a large oil refinery petrochemical complex. Sources included drains, sumps, and manhole covers.
SUMMARY:	Three sewer openings were tested, using an enclosure and a vent opening of 0.27 ft^2. An average of 0.2 Mg benzene /yr was reported from the small vent opening, based upon three sets of tests. The refinery collection system openings were estimated as 1200 ft^2, suggesting very large amounts of benzene lost from the collection system if the reported losses of benzene were extrapolated on the basis of area of openings. The vent rate from the small vent opening was 200 ft/min, consistent with vent rates for manhole covers reported in Section 3 of this document. Material balances suggested organic compound loses of up to 60 percent in the collection main. The fraction lost to the atmosphere could not be determined because the concentrations in the oil layer were not determined. Organic compounds could partition into or out of the oil layer.
METHODS:	Existing operation of the refinery was tested with concentrations in the vented gas, concentrations in the water, and gas flowrate measured.
COMMENTS:	This investigation indicates the potential for significant air emissions, because of high headspace gas concentrations. These data seem to be consistent with the data of Fingas and the EPA vent rates.

11.3. ORGANIC COMPOUNDS WILL VOLATILIZE IN THE HEADSPACE OF THE

COLLECTION SYSTEM

11.3.1 Importance of Gas Concentrations.

The gas concentrations in the collection system headspace are important because they determine the air emissions. The rate of air emissions is the product of the concentration in the headspace and the flow rate of the headspace out of the collection system and into the air.

It should be noted that the discharge of volatile material into existing wastewater collection systems can lead to dangerous and explosive conditions in the collection system headspace. None of the comments presented in this section should be interpreted that such a potentially dangerous condition could not exist. The discharge of organics into a collection system is not intrinsically safe, and any explosion potential should be carefully evaluated and properly handled on an individual basis.

11.3.2 Industry Comments

Open wastewater drains at some companies are no longer used when benzene concentrations are 50 ppm or more[1]. The widespread replacement or covering of open drains for environmental reasons would reduce the rates of benzene loss from that section of the collection system. Many other commenters have suggested that open drains are common at other companies.

For safety reasons junction boxes and sumps are sealed and purged with an inert gas atmosphere. This reduces or eliminates air flow through open units[2]. The use of these techniques would eliminate air flow directly to the atmosphere from these units (when the seals work as designed). Opening the sumps to the air would not assure that explosive concentrations would not be present.

11.3.3 Fingas, et al.

Fingas[3] modeled a collection system to investigate the effects of gasoline spills on the headspace concentrations in the collection system. Soon after entering the system, the higher volatility constituents in the fuel were lost to the headspace (explosion hazard). Downstream of the point of introduction of the fuel, the headspace of the collection system contained lower boiling compounds. These data suggest that much of the highly volatile compounds can be lost to the headspace early in the path through the collection system. This also suggests that the concentration of organic compounds in the headspace can be much greater than expected from the liquid composition in the wastewater.

11.3.4 Shell Petrochemical Facility

A comparison of measured and predicted estimates of air flow rates from the wastewater collection system was developed from data collected at that facility[4].

The gas concentrations were measured and calculated by several different methods for a number of different locations in the Shell petrochemical facility wastewater collection system. This paragraph briefly describes the different types of data that were taken for evaluating the fate of organic compounds in the Shell petrochemical facility collection system.

11.3.4.1 TLV sniffer. The TLV sniffer was used to measure concentrations in the gas phase in the collection system headspace and in the "jar test" of equilibrium headspace.

11.3.4.2 HNu. The HNu sniffer was used to measure concentrations in the gas phase in the collection system headspace and in the "jar test" of equilibrium headspace.

11.3.4.3 Canister. A test probe was introduced into the headspace of the collection system conduits and a sample of the headspace gas was withdrawn into an evacuated canister. The concentrations in the canister were analyzed on a compound specific basis, so that total organic values could be estimated by summing the individual compound values.

11.3.4.4 Equilibrium headspace. A sample of the liquid in the wastewater collection system was withdrawn by a bailer and used to fill a jar half full of liquid. The jar was capped and was shook vigorously for a few seconds. The cap was opened enough to briefly measure the headspace concentration in the jar by the TLV sniffer and by the HNu sniffer.

11.3.4.5 Liquid sample analysis. A sample of the liquid in the wastewater collection system was withdrawn by a bailer and used to fill 40 ml VOA vials. The concentration of compounds in the wastewater was measured by Method 8240. The concentration of the compounds that would be in equilibrium with the liquid concentration was calculated by multiplying the liquid concentrations by the Henry's law constants. The Henry's law constants were obtained from the pure component data base of Chemdat8.

11.3.4.6 Results of tests. Ratios of headspace and liquid equilibrium concentrations indicate that in general, the headspace concentration was much greater than the corresponding equilibrium value with the liquid. The following list illustrates that the organic content of the headspace was greater than the equilibrium value with the liquid. The headspace ratios presented in the list are the value of organics measured in the canister to the theoretical values calculated from the measured liquid concentrations.

- location 1b, ratio: 13
- location 5, ratio: 36
- location 5c, ratio: 33
- location 6, ratio: 61
- location 10, VCM plant discharge, ratio: 18
- location 1b, ratio: 13

CMA representatives indicated that the collection system was likely warmer than the 25 C assumed for the Chemdat7 data base. They suggested that the Shell headspace concentrations would be more appropriately represented by equilibrium, or a ratio of 1.

The concentrations in the headspace of the collection main are much greater than expected. This suggests that the wastewater may have lost significant quantities of organics early in the path of the waste through the wastewater collection system. The higher concentrations in the headspace were not removed by the flow of wastewater under the headspace. These data could be interpreted to suggest that there is a limited rate of mass transfer between the headspace and the waste.

The predicted and observed rates of headspace flow in the petrochemical wastewater collection system is presented in Table 12. These data indicate that, although the flow velocity was highly variable, the magnitude of the velocity was comparable to the predicted value.

11.3.5 Ph.D. Dissertation of R. L. Corsi

The data obtained by Corsi in municipal wastewater collection systems clearly demonstrate that equilibrium can be established in collection system mains. The measured concentrations of chloroform in the headspace of Run 1 was almost exactly equal to the theoretical equilibrium value of the headspace concentration. The data also indicated that the assumption of equilibrium may not be true for high waste flow in very large collection mains. Corsi also presents data supporting the importance of equilibrium in determining air emissions from collection systems. In Run 1, the following data were obtained by Corsi:

TABLE 12. COLLECTION SYSTEM EQUILIBRIUM DATA

Measured parameter	units	value
Concentration in gas (outlet, Table 6-13)	mg/m^3	1.3
Concentration in liquid (measured in bag, calculated for inlet, Table 6-9)	mg/m^3	9.6
Calculated parameter	units	value
Henry's law constant (ratio of above concentrations)	mg/m^3 gas per mg/m^3 liquid	0.135
Henry's law constant (theoretical, Table 6-4)	mg/m^3 gas per mg/m^3 liquid	0.12

These data demonstrate that the assumption of equilibrium in Run 1 could be valid. Other runs do not necessarily illustrate equilibrium.

Page 170: Mass transfer models were used to estimate the loss of organic compounds from waste collection system components. Rapid saturation of the wet well atmosphere was observed for a lower volatility organic material. A greater removal of vinyl chloride (18%) was predicted from the same model. This theoretical calculation suggests that equilibrium can be established in collection mains.

Page 176: Both the Henry's law constant and the mass transfer coefficient can increase with temperature. Theoretically, the chloroform standard loss value from residential sewers increased from 28% to 46% at higher temperatures. This theoretical calculation suggests that equilibrium values can be important in determining air emission losses from collection systems.

Page 181: <u>Conclusion 2.</u> Discharge of organic compounds to smaller interceptors located five kilometers or more from a treatment plant can lead to emissions comparable to those at the treatment facility. This is particularly true during periods of low wastewater flow, high ventilation flow rates, or for VOCs with high Henry's law constant. This conclusion states that equilibrium values are important in determining air emission losses from collection mains.

Page 182: <u>Conclusion 3.</u> High gas flows in combined sanitary/storm sewers should approach infinite ventilation conditions, and much higher relative emissions than would be expected in separate sanitary sewers. Under conditions of high ventilation the mass transfer is not restricted by the limitations of equilibrium. The converse is that equilibrium is important at lower ventilation conditions.

Page 182: <u>Conclusion 7.</u> Rapid organic compound accumulation in sewer atmospheres leads to low organic compound losses from drops, unless high ventilation rates are present, e.g. forced ventilation. This statement indicates that equilibrium is rapidly achieved in collection systems, and this equilibrium can be the rate controlling factor for air emissions (equilibrium can limit air emissions).

Page 183: Conclusion 9. Elevated wastewater temperature, e.g. 40°C as opposed to 20°C, significantly increases organic compound emissions by increasing the mass transfer coefficient, Henry's law constant, and buoyancy-driven ventilation. This conclusion indicates that equilibrium partitioning is a significant factor in determining the magnitude of air emissions from collection systems.

Page 184: Conclusion 4. Sensitivity of emissions to organic compound characteristics increases at lower ventilation rates, where Henry's law constant is the dominant physico-chemical property. This conclusion indicates that equilibrium partitioning is a significant factor in determining the magnitude of air emissions from collection systems at lower ventilation rates.

11.4 UNCONTROLLED WASTEWATER COLLECTION SYSTEMS CAN HAVE SIGNIFICANT DISCHARGES OF HEADSPACE.

The rates of loss of organic materials from collection systems depend on both the ventilation rates of the collection system and the concentrations in the headspace of the system. The data presented in this section indicate that the discharge of headspace from collection systems are at least as great as the model predictions.

CMA indicated that a realistic flow of air from an open drain is 1.9 ft/sec (114 ft/min). The current collection system emission model and our field data indicates a slightly lower flow velocity than the CMA value. Other data, including industry reported rates at Amoco, indicate higher air flow rates than this estimate.

11.4.1 Shell facility

This petrochemical facility was not ideally suited for the verification of the velocity predictions because the system generally had sealed manhole covers. The system had elevated vents which were inaccessible for testing. These vents are expected to divert air flow away from surface openings in the collection system. The weather was overcast and raining on one of the sampling days. The wind direction was variable, the wind speeds were low and variable, and the wind direction also depended on the location relative to buildings. The measured ventilation rates at the Shell facility are presented in Tables 11-13, 11-14, 11-15, and 11-16.

11.4.2 Velocity screening at Pulp Mills

A series of 5 pulp mills were vistied and ventilation rates were measured at collection system openings. The data were reported in Table 11-13.

11.4.3 Rohm and Haas Chemical Plant Collection System

There was a strong relationship between the wind speed and the air flow in the waste collection system. The data was taken at random times on the first day of testing to learn about the flow patterns of gasses in the collection system and to identify appropriate sampling conditions. The collection system vent rates were into the system or out of the system, depending on wind speed and direction. The wind speed changes the flow and the flow direction of the air in the waste collection system. At low wind speeds, the flow of the water in the system produces a suction on the surrounding air. At high wind speeds, the pressure of the air causes flow out of the system. When wind flows in the direction of the opening of a conduit, the wind pressure can cause a flow of air out of the collection system, removing organic compounds from the headspace of the collection system. In the system with the absence of wind, the flow of the water induces air to flow along with the waste, carrying air into the system and discharging the air at some point downstream.

The concentrations and velocities were measured in the headspace venting during the tracer tests at Rohm and Haas. This confirmed the potential for air emissions.

11.4.4 Velocity screening at industrial plants

The wastewater collection systems of several industrial plants were inspected. Screening measurements were made at these sites with an Alnor velometer (low velocity probe) to evaluate the magnitude of collection system emissions air flow rates. The primary concern was to determine the magnitude of the measured air flow velocities and to compare these measured velocities with the predicted velocities from the air emission models.

Based upon the results of the velocity screening measurements, the following observations can be stated:

- The velocities from the openings in the wastewater collection systems were variable, but the ranges of velocities from the different sources were not highly variable.
- The preliminary results of using the model for site specific conditions was favorable, with reasonable agreement (factor of 2) between the predicted and measured velocities.
- To improve the agreement between the model results and the observed collection system velocities, model plant parameters that were more representative were used in the theoretical estimations. Examples of sources that were modified include open drains under grates (higher emissions than predicted) and sealed drain system (lower emissions than predicted).

11-5. THE FRACTION OF ORGANIC COMPOUNDS LOST IN UNCONTROLLED COLLECTION SYSTEMS

11-5.1 Shell facility

A formal material balance was not possible in the Shell facility wastewater collection system because the liquid flow rates and

TABLE 11-13. SCREENING VALUES FOR AIR VELOCITIES AT COLLECTION SYSTEM OPENINGS

Location	Velocity at opening [a]	
	ft/min	ft/sec
Chemical collection system, Shell		3
Drain grate, Shell		2
Chemical collection system, Shell	80	1.3
Open drain, Shell	65	1.1
Manhole (1 in dia. opening), Shell	200	3.3
Open drain, Shell	40	0.66
Closed drain, Shell	60	1.0
Opening, Shell	120	2
Sump opening, Shell		0-2
Sample point drain, Shell	150	2.5
Sample point drain, Shell		0 (slow fumes out)
Chemical collection system Sump, Shell	110	1.8
Drain opening, Shell		0-1
Horizontal flow in collection system,		
PULP MILL 2	50	0.83
Manhole cover, Pulp mill 2	300	5.0
Manhole cover, Pulp mill 2	100-150	1.7-2.5
PULP MILL 3		
Grate over collection system	50-100	0.83-1.7
Grate	50	0.83
Lift station opening	40-50	0.67-0.83
Lift station opening	60	1
PULP MILL 4		
Floor drain (2 x 1 ft)	50	0.83
Floor trench, (1-2 ft/s)	50	0.83
Floor trench	0-50	0-1
Main drains between process units	100	1.7
Small vent on main collection conduit	>300	5
Grate on main collection conduit	150	2.5
Grate on main collection conduit	160-170	2.7-2.9
Grate open drain	50	0.83
PULP MILL 5		
Grate at end of trench	100	1.7

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[a] Measured with an Alnor velometer, low velocity probe. Ft/sec reported without corresponding ft/min obtained by visual inspection of plume rise.

TABLE 11-14. A COMPARISON OF PREDICTED AND MEASURED AIR VELOCITIES AT WASTEWATER COLLECTION SYSTEM OPENINGS

Location	Velocity at opening (ft/min)[a]	
	measured	predicted
Drain, Shell	65,40,60,120	122 (A2)[b]
Manhole cover, Pulp mill 2	300	124 (B3)
Manhole cover, Pulp mill 2	100-150	191 (B2)
Average drain velocities	67	84
Average manhole cover opening velocities	198	128
Average junction opening velocities	88	66

[a] Measured with an Alnor Velometer, low velocity probe. Predicted values based upon a wind velocity of 3.5 MPH (300 ft/min).

[b] Wind effect (3.5 MPH) probably overestimates emissions because actual wind velocity was lower (tall process units, wind direction different from stack emissions at high elevation)

TABLE 11-15. SCREENING OF AIR FLOWS AND GAS CONCENTRATIONS FROM SHELL CHEMICAL COLLECTION SYSTEM SOURCES: MAIN PLANT [a]

Location	time	Velocity (ft/min)[b]	Concentration(ppm)		Headspace test(ppm)[c]	
			HNu	TLV	HNu	TLV
6	14:22	150	120	3100	25-30	120
6	14:43	40	130	3000		
7	15:08	-150	1	20	4	60
5	15:12	65 to 75	80	1200	6	0
5A	15:26	low +	60			
10	15:28	230	60	5000	20	0X100
5C		210	130	5900	1	35
11		<0	2	120		
1B		0 to 60	150	6900	20	300

[a] Measurements 2/6/90, main process areas leading to wastewater treatment. Included are tank farms, alcohol distillation, vinyl chloride monomer production, plant E, plant BFA, spillage, and flows from other process areas. Test points are locations at Shell.

[b] Measured with an Alnor velometer, low velocity probe. Positive values indicate flow out of the collection system. Flow rates less than the detection limit of the instrument (20 ft/min) are indicated as low if they could be detected by visual inspection.

[c] A sample of wastewater was taken from the sample point and placed in a glass jar. The jar was capped and shaken vigorously. The sample probe of the test instrument was inserted into the headspace of the partially open jar. The reading was taken when reaching steady state, usually 5-10 seconds.

TABLE 11-16. COMPARISON OF MEASURED AND PREDICTED AIR FLOWS FROM SHELL CHEMICAL COLLECTION SYSTEM SOURCES: PHENOL ACETONE[a]

Velocity Location	Measured Velocity		Predicted
	time	(ft/min)[b]	(ft/min)[c]
sump(water)	9:50		
sump(oil)		50	124 (B3)
A drain		120-150	122 (A2)
D manhole			
B drain		30	122 (A2)
C manhole		150	124 (B3)
sump(water)	17:23		
sump(oil)		30-40	124 (B3)
A (average)	17:37	200	128

[a] Measurements 2/6/90, phenol acetone units. The major area flows were sample point A, dephenolator extraction bottoms 80 gpm, and sample point B, cumene decanting wastewater 20 gpm. Reference Figure 3. The weather was overcast and raining.

[b] Measured with an Alnor velometer, low velocity probe. Positive values indicate flow out of collection system. A range of velocities indicates that the meter reading was rapidly cycling between the limits of the range.

[c] The flow rates of air out of the unit are estimated by the protocol described in this document, with a wind velocity of 3.5 MPH Actual wind velocity at the site were variable and generally less than 5 MPH Weather conditions were overcast with some rain. The case used to represent field conditions is presented in parenthesis.

concentrations of all the branch streams were not characterized. From estimates of liquid flows in the various points in the main collection branch it is possible to establish a mass flow rate of each constituent by multiplying the concentration of the constituent by the liquid flow. This estimate of the material balance is of limited significance for some compounds due to these factors, but a more certain conclusion can be stated for the fate of chloroform.

The simplified material balance is presented for 1,2 dichloroethane and chloroform in Tables 11-4 and 11-5.

1,2 dichloroethane and chloroform were not significantly present in the collection main before the vinylchloride monomer (VCM) plant discharge. After the point of discharge from the VCM plant, the 1, 2 dichloroethane in the liquid was retained at roughly the same mass flow rate down the collection main. Chloroform disappeared from the collection main shortly after discharge from the VCM plant. The total organics in the headspace at the discharge point from the VCM plant contained much higher concentrations of organics than expected from the equilibrium values in the liquid.

These material balances suggest that relatively little of the low volatility materials are removed from the liquid in the main collection system flow:

- acetone (y/x) = 1.4
- 1,2 dichloroethane (y/x) = 66

The addition of unknown side streams containing dichloroethane could possibly interfere with the material balance and cause an underestimate of the losses of dichloroethane.

Table 11-17. A SIMPLIFIED MATERIAL BALANCE FOR 1,2 DICHLOROETHANE IN THE COLLECTION MAIN, SHELL.

Location	Flow (gpm)	Concentration (ppmw)	Flow rate of compound (g/min)
5	534	0	0
10	711	1.84	4.9
5C	962	1.04	3.6
1B	1217	1.14,1.22	5.2,5.6

This table demonstrates that the flow rate of 1,2 dichloroethane did not substantially change in the collection main from location 10 to location 1B.

TABLE 11-18. A SIMPLIFIED MATERIAL BALANCE FOR CHLOROFORM IN THE COLLECTION MAIN, SHELL.

Location	Flow (gpm)	Concentration (ppmw)	Flow rate of compound (g/min)
5	534	not present	0
10	711	.11	0.29
5C	962	not present	0
1B	1217	not present	0

This table demonstrates that the flow rate of chloroform was significantly lowered in the collection main from location 10 to location 1B.

The concentration of chloroform in the gas phase was 73.2 ppmv at location 10. This was among the top 12 gas phase constituents. There was a steam discharge from location 10 and the location received wastes from vinyl chloride manufacturing.

The material balances suggest that higher volatility materials such as chloroform are significantly and possibly entirely lost in the main collection system flow:

- chloroform (y/x) = 188

The addition of side streams to the main collection system flow was not of great enough volumetric flow rate to account for the disappearance of chloroform from the system by dilution; therefore, the loss of chloroform is assumed to be due to volatilization.

11.5.2 Rohm and Haas Tracer Investigation

Tracers are compounds that are introduced into a wastewater stream to measure the rate of release of the organic compounds due to air emissions from the collection system. To measure the losses of organic compounds in wastewater collection systems the concentration of the tracers are measured in the water phase and in the air leaving the system.

Four organic tracers were continuously added to the collection system at one of the points of waste discharge into the collection system. The tracers were selected from a combination of volatile material, semivolatile material, and non-volatile materials. The concentrations of the tracers were measured downstream of the tracer addition point. The ratio of the concentrations of the tracers that were measured were then compared to the initial ratio, so that the loss from the system could be calculated, as well as the relative loss from the system.

The concentration of volatile tracer and the flow rate in the collection system permit a calculation of the flow rate of tracer. A comparison of this flow rate to the rate of addition of tracer permits an independent assessment of the fraction of the volatile constituent that is lost as air emissions.

The tracer was added at location A. Location A was a trench outside a process building. Water flowed in the trench at a fairly high rate. The drain pipes from a process centrifuge discharged into the trench. The plant has reasonably steady flow of water into the collection system at Location A. The flow into the wastewater accumulation tank (Location D) was measured by the height increase in the tanks when there was no wastewater being pumped out of the tanks.

Three separate peristaltic pumps were used to deliver the organic materials to the trench stream. The non-volatile metals were dissolved in water, chlorobenzene and chloroethane were combined in a tank, and hexane and acetonaphthene were combined in a third tank. The solutions were dripping from the exit tubes (subsurface) at a rate of approximately 1.5 drops per second. The hexane drop rose to the surface of the flowing water below the exit tubes, and rapidly flashed from the surface. As the hexane was removed from the surface, the acetonaphthene was deposited on the surface (very thin light refractive layer). By the end of the channel, the circulation patterns in the water had collected the acetonaphthene toward the center of the water's surface.

The four sample points in the wastewater collection system were designated A, B, C, and D. The concentrations in the wastewater were monitored during the test period. A summary of the results of the tracer investigation is presented below. There were greater than expected loss of each volatile material in the collection system. Hexane was lost to a significant extent in the drain channel before it entered the subsurface collection system, as indicated by visual and olfactory observations. Hexane was apparently lost quickly by flashing early in the path through the collection, but the residual hexane also was lost significantly between points B and C and between points C and D.

Compound	Average fraction lost	Henry's Law(y/x)
hexane	0.977	4270
acenaphthene	0.713	6.3
chlorobenzene	0.959	209
111 trichloroethane	0.866	967

The data suggest that acenaphthene may have been significantly removed as air emissions, but there was the potential for sampling and analytical difficulties for this compound. The canister headspace sampling program did not include acenaphthene analysis.

Chlorobenzene was lost significantly as the tracer flowed through the collection system. The concentrations detected at location A were greater than expected from the rate of release of chlorobenzene into the collection system. The reason for the high concentrations measured at location A may be related to the location of the sampling line. The overall loss of chlorobenzene in the collection system was much greater than expected from the air emission models.

As in the case of chlorobenzene, 1,1,1-trichloroethane was lost significantly as the tracer flowed through the collection system. The concentrations detected at location A were greater than expected from the rate of release of trichloroethane into the collection system. The reason for the high concentrations measured at location A may be related to the location of the sampling line. The overall loss of 1,1,1-trichloroethane in the collection system was much greater than expected from the air emission models. Chlorobenzene and 1,1,1-trichloroethane were lost significantly between points B and C and between points C and D.

TABLE 11-19. THE MEASURED RELEASE OF TRACER CONSTITUENTS FROM THE COLLECTION SYSTEM HEADSPACE BY CANISTER MEASUREMENT AND AIR FLOW RATE MEASUREMENT.

Location	1,1,1 trichloroethane (mg/min)	chloro-benzene (mg/min)	hexane (mg/min)
1	689	77.9	31.7
2	265	34.9	12.8
3	25.9	9	1.8
4	70.9	12.8	1.77
5	4.48	4.8	0.096
6	0.28	0.3	0.006
7	28.4	3	0.14
8	0.036	0.028	0.002
9	0.036	0.028	0.002
10	83.9	24	0.41
11	0.062		
12	0.31		
13	102	27.6	0.45
14	2.19	12.4	0.169
15	166	32	0.32
total	1438.5	238.8	49.7
released	1367.3	1118.5	775.2

This table illustrates that significant rates of loss of tracer materials were detected leaving selected collection system openings. This table is not to be interpreted as a material balance, because all sources of air release were not monitored, and because these sources are variable in flow (results based on one point sampling).

The loss of the non-volatile tracers (copper and zinc) through the collection system was much less than the loss of organic compounds. These data confirm that the ratio of the concentrations of the higher volatility organic compounds to non-volatiles decrease during the flow through the collection system, indicating a substantial loss of organic materials. The estimate of zinc loss was 21 % and the copper loss was 38%. The appearance of a loss for the tracer metals was likely due to errors in the wastewater flow measurement.

The results of the canister sampling of the headspace of the collection system, together with the flow rates of the collection system headspace gas leaving the system, indicate that volatilization of the tracer constituents into the headspace is a significant pathway for tracer loss in the collection system. The following table presents a summary of some of the measured releases of tracer constituents into the environment, based on limited sampling at selected openings in the wastewater collection system. It was observed that tracer organic compound loss was observed from openings in the collection system that were distant from the tracer wastewater flow path.

In summary, the tracer testing at the chemical plant indicated high loss of organic compounds. Significant concentrations of organic compounds were detected in the headspace. The magnitude of the measured emission rates in the gas were consistent with the loss from the liquid. No material balance was possible due to variable flow and many vent locations. If the absence of hexane in the liquid was due to hexane floating on the surface, the headspace concentrations would contain hexane. The headspace analysis showed very little hexane, but contained more of the lesser volatile components, indicating almost total loss of hexane.

11.5.3 Amoco refinery material balance

The waste concentrations of benzene, toluene, and several other compounds were measured at various points in the waste collection system of the Amoco refinery between the production units and the wastewater treatment plant. Based on those measurements, a material balance was carried out to identify the potential for the release of air emissions.

The material balance results indicated a disappearance from the wastewater but the high loss of organic compounds could have been only apparent because of sampling problems. Partitioning into an oil phase that was present in the wastewater was not accounted for. The mechanism for a high loss in a collection main could involve the organic compound partitioning into an oil phase, and the oil phase floating to the top of the waste stream.

The air emission models for the waste collection system predict a few percent loss in the part of the system investigated. The CMA estimates with a trench model that approximately 1 percent organics are lost per collection system run (between manholes). With the CMA approach the maximum loss would be expected to be less than 5% between the unit exits and the API separator inlet. The collection system model predicts much higher air emissions near the waste entrance (not measured) than downstream in a collection main (where the data were taken). The loss of organic compounds in the entire system is therefore theoretically expected to be substantially greater than the loss of organic compounds in the section of the collection system investigated by the Amoco refinery.

The data suggests the potential for significant fractions of the organic compounds that may be lost to the air in the collection mains, much greater than the collection system trench models estimate. If the data are correct, they would suggest that the CMA estimates and the collection system model estimates using the limits of mass transfer from the bulk of the liquid waste may omit significant factors that control the release of organic compounds in the collection system. Table 11-20 summarizes the results of the material balances.

11.5.4 Amoco Refinery Vent Measurements

This refinery was tested for ventilation rates by enclosing and placing a vent over selected openings in the collection system. The vent rate was 200 ft/min. This measured vent rate was consistent with the average manhole cover vent rate measured in the EPA screening program. The air models suggest that increasing the area of the opening will increase the total flow of air from the system, and therefore increase the air emissions. The average benzene loss for this vent was 0.2 Mg benzene per year. One way to estimate the overall collection system ventilation rate is to extrapolate on the basis of vent rate and the opening area. If the vent rate were reduced to the average value for large openings in the collection system (88 ft/min)

TABLE 11-20. ESTIMATED DISAPPEARANCE OF VOLATILES FROM THE WASTEWATER OF THE COLLECTION MAIN AT THE AMOCO REFINERY.

Location of loss	benzene	toluene	ethyl benzene	xylene
Unit exit to F04[a]	1.9	0.7	1.9	1.2
F04 to API separator	16	27.4	59.6	32.7
total loss to separator inlet[a]	17.6	27.9	60.3	33.5
API separator inlet to separator outlet	39.3	29.6	0	50
API outlet to activated sludge inlet	13.5	17.5	71.4	6.6

[a] includes contributions estimated from tank farm (not reported). These concentrations estimated from the tank farm are less than the concentrations reported for the Ultraformer (greatest contribution to total flow). The concentrations from the tank farm were selected to produce estimated emissions from the unit exit to F04 that are comparable to the CMA estimate.

and the open area was increased to the reported area of the total collection system (1225 ft^2), the estimated loss from the collection system would equal over 99 percent. The actual percent loss is expected to be somewhat less than this value due to potential under reporting the concentrations leaving the collection system.

11.5.5 Tracer testing at the Coastal Eagle Point Refinery

This tracer test indicated that there were significant losses of organic compounds from a refinery wastewater collection system. The collection system had some air emission controls (water seals at the junction box inlets).

The air emission losses appeared to be significantly less than from previous testing at a more open collection system at Rohm and Haas (all of the higher volatility organic compounds seemed to be lost at the previous test).

The data quality was compromised to some extent by the variable flows in the tracer feeds. Analysis of the concentration ratios of different organic compounds fed simultaneously tended to confirm the calculations based on the ratios of the volatile tracers to the cobalt tracer.

The predicted losses from the simple collection system air emission models (Section 4.2.1) were similar to the results of the tracer testing.

Two non-volatile reference tracers were used, cobalt and copper. These two tracers did not have identical response in the collection system, even though the recovery of the compounds was excellent in the analytical tests. The results of the analysis of the loss of organic compounds with both metal tracers indicated significant loss of higher volatility organic compounds in the collection system. These results are summarized in the Table 11-21.

TABLE 11-21. A COMPARISON OF THE OVERALL LOSS OF VOLATILES BASED UPON TWO DIFFERENT NON-VOLATILE TRACERS.

Compound	Overall fraction lost with cobalt ratios	Overall fraction lost with copper ratios
111 trichlorobenzene	.51	.41
chlorobenzene	.38	.26
nitrobenzene	.60	.27

If the volatile and the non-volatile had identical concentration ratios in all of the collection system, there would be no air emission losses.

If compounds differ in Henry's law, a measure of volatility, the relative amount of the compounds would be expected to change if compounds were removed from the collection system by means of a mass transfer mechanism that depended on volatility. In the case of chlorobenzene and 111 trichloroethane, the ratio of the concentration of the less volatile compound to the more volatile compound increased in each sampling period, with an estimated range of chlorobenzene loss of 2 to 9 percent from the drain. These two compounds were injected as tracers together and were sampled and analyzed together. The use of this concentration ratio results were much less reproducible for the nitrobenzene, perhaps because a different analytical method was used for nitrobenzene and the other organic compounds. Even with the lack of reproducibility the ratios of chlorobenzene to nitrobenzene showed a decrease on average, as expected.

This method of estimating the loss from the drains results in similar results to the predictions of case A3, air flow due to density (Section 4.3.3), even though the model assumptions did not match the physical conditions of the refinery collection system. The results are presented in Table 11-22.

TABLE 11-22. A COMPARISON OF THE MEASURED LOSS OF VOLATILES FROM A DRAIN TO THE PREDICTED LOSS OF VOLATILES FROM THE DRAIN.

Compound	Fraction lost from measured concentration ratios	Fraction lost from case A3 model prediction
111 trichlorobenzene	.053	.032
chlorobenzene	.21	.126
If two compounds with different volatilities had identical concentration ratios in the collection system, there would be no air emission losses.		

11.5.5.1 Comparison of an Estimation of volatilization loss to the measured loss based upon concentrations relative to the metal tracer. It is assumed that the metal tracer will not volatilize or be sorbed in the collection system. The tracer test was carried out over a period of several days and there did not seem to be evidence of sorption in the system, either for the metals or the organics. If the concentration of the organic compounds relative to the metal tracer decreases as the compounds travel through the collection system, the fraction loss can be attributed to volatilization. The following tables present the tracer results and compare the calculated fraction loss due to volatilization to the predicted values.

TABLE 11-23. A COMPARISON OF CHLOROBENZENE TRACER RESULTS AND PREDICTED VALUES.

Location of Emissions	Test results	Cumulative Prediction
drain		.032
Junction box	.09	.12
2 junction boxes	.05	.29
2 junction boxes	.38	.42

This table compares the results of the tracer analysis with cobalt ratios at the Coastal Eagle Point Refinery to the previously predicted air emissions (chlorobenzene case A3 for drain, .098 junction box emission factor, Section 4.3.3).

TABLE 11-24. A COMPARISON OF 111 TRICHLOROETHANE TRACER RESULTS AND PREDICTED VALUES.

Location of Emissions	Test results	Cumulative Prediction
drain		.12
Junction box	.239	.23
2 junction boxes	.285	.40
2 junction boxes	.507	.54

This table compares the results of the tracer analysis with cobalt ratios at the Coastal Eagle Point Refinery to the previously predicted air emissions (case A3 for drain, .12 junction box emission factor, Section 4.3.3).

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Page 11: In the four city study Levins *et al.* (1979) observed the reduction in both occurrence and concentration of trihalomethanes from tap water to wastewater (Corsi suggested loss from activities such as showers). This suggests that organic compounds can be lost before the waste reaches the collection mains.

Page 11: Another observation is the occurrence of highly volatile carbon tetrachloride in industrial sewers, and the absence of this compound in treatment plant influent, suggesting significant volatile emissions from combined sewer systems. This suggests that organic compounds can be lost, even in the collection mains.

Page 17: The U. S. EPA investigated methodologies for estimating the risk of human exposure to toxic contaminants. Computational modeling significantly underestimated measured ambient levels of chloroform and carbon tetrachloride, and it was suggested that the difference might be due to area sources, *e.g.* sewers. Volatilization from sewers was observed to be a major loss mechanism for dichloropropane and dichloroethane. This statement also suggests that organic compounds can be lost, even in the collection mains.

Page 19: The laboratory investigation of Fingas *et al.* (1988) demonstrated that the low boiling point fraction (higher volatility organic compounds) were lost into the headspace during system entry and may be distributed across the gas flow cross-section. The high boiling point fraction (less volatile) were retained in the wastewater and were lost to the headspace during the flow of the waste. This investigation also suggests that high volatility organic compounds can be lost before the waste reaches the collection mains.

Page 182: <u>Conclusion 4.</u> If organic compounds are discharged well upstream of wastewater treatment facilities and traverse building laterals and many smaller reaches with steep channel slopes prior to reaching an interceptor, cumulative emissions of organic compounds are likely to be higher than those which occur at an associated treatment facility.

Page 182: <u>Conclusion 5.</u> Extensive relative removal (greater than 50%) of organic compounds is likely following potable water discharge to building laterals leading to street sewers.

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APPENDIX A

A GUIDE THROUGH THE LITERATURE

APPENDIX A

A GUIDE THROUGH THE LITERATURE

A.1 INTRODUCTION

There is concern that volatilization of organic compounds from hazardous waste treatment, storage, and disposal facilities (TSDF) poses a public health problem. These organic emissions may adversely affect ambient air quality. However, there are other competing mechanisms or pathways through which organic compounds can leave hazardous waste facilities. These include adsorption, migration, runoff, biological or chemical degradation, hydrolysis, oxidation, and hydroxyl radical reaction. Consequently, the potential hazard of volatilization should be assessed in relation to the potential importance of these other pathways.

Sources of potential organic losses include, among others, surface impoundments, landfarms, landfills, and wastewater collection and treatment units. The important competing pathways have been identified in earlier sections of this report. This evaluation has been based on field and laboratory measurements as well as predictive or mathematical models of these pathways. This appendix supplements the body of the report; it serves to direct the reader through the literature concerning organic pathways.

For the convenience of the reader, a comprehensive source list is presented in Appendix B of this report. In addition to the references cited in this appendix and in the individual sections of the report, this bibliography lists other literature of interest for organic pathways and emission models.

A.2 SURFACE IMPOUNDMENTS

A.2.1 Volatilization Direct measurement of volatilization rates from surface impoundments is extremely complicated. Hwang and Thibodeaux[1] reviewed the concentration profile and plume mapping technique and proposed a new method requiring fewer concentration measurements. This latter technique has yet to gain popularity. Thibodeaux et al.[2] used the concentration profile technique to measure the rate at which selected organic compounds were emitted to the air from basins in the pulp and paper industry. The ranges of the average flux for methanol and acetone were 1.4 to 3.8 $ng/cm^2 \bullet s$ and 0.028 to 0.10 $ng/cm^2 \bullet s$, respectively, which were higher than background. Radian[3] obtained emission rates from four different hazardous waste sites containing surface impoundments as well as landfills and landfarms. They used the concentration profile, transect, materials balance, and vent sampling approaches. These methods[4,5] are also applicable to other nonpoint source hazardous waste facilities such as landfills and landfarms.

Volatilization rates from surface impoundments can be estimated via mathematical models. Mackay and Leinonen[6] predicted air emissions from nonaerated surface impoundments receiving influent irregularly (unsteady state). The liquid and gas mass transfer coefficients in this model were modified by Mackay and Yeun.[7] Thibodeaux et al.[8] developed predictive models for both aerated and nonaerated steady-state surface impoundments. DeWolf and Wetherold[9] critiqued these models and presented a protocol for their proper use. Shen[10] modified the nonaerated model of Thibodeaux et al.[11] In an extensive review of these and other predictive models, GCA[12] judged the theoretical work of Thibodeaux et al.[13] and Mackay and Leinonen[14] as most suitable for predicting air emissions from surface impoundments.

The use of these mathematical models for predicting volatile emissions is less expensive and faster than actual field measurements. However, to be cost-effective, these mathematical models must provide accurate estimates of volatilization rates. It is disappointing to note that relatively few validation studies are reported in the literature. A description of these follows.

Hwang[15] compared predicted and measured emission rates of toluene and 1,1,1-trichloroethane from an evaporation pond. The transect method was used for field measurements, and the models summarized in Hwang[16] provided the predicted rates. For each organic compound, the predicted result was within the confidence limits of the average measured result. Balfour et al.[17] used the Thibodeaux et al.[18] model to predict emissions from these surface impoundments. Emission rates were measured via the flux chamber in all three ponds as well as via the concentration profile in the third pond. In this latter pond, the emission rate of most compounds as determined using the flux chamber was statistically greater than that determined using the concentration profile. Furthermore, results of a comparison of measured versus predicted emission rates were inconclusive. Vaught[19] used the Springer et al.[20] and Mackay and Yeun[21] approaches to predict air emissions from quiescent surface impoundments. He concluded that volatilization rates predicted from the Mackay and Yeun model were comparable to rates measured via the flux chamber. In contrast, the predicted rates from Springer et al. exceeded the measured rates.

A.2.2 Other Pathways The role of other pathways in the removal of organic compounds from surface impoundments has not been addressed extensively in the literature. However, biological removal mechanisms associated with stabilization ponds and lagoons[22] will be applicable where conditions of pH, temperature, and nutrient levels are suitable for biological growth.

A.3 LAND TREATMENT

For the past 25 years, the petroleum industry has operated land treatment, sludge farming, and land disposal facilities. The pharmaceutical and organic chemical manufacturers recently have considered this method of hazardous waste disposal because of its comparatively reasonable cost, simplicity, and use of natural processes. How does a land treatment effectively and safely treat and dispose of organic compounds? The purpose of land treatment is to exploit the microbiological actions of the upper soil layer to degrade toxic organic material at a controlled rate. Although photo-degradation takes place in a land treatment facility,[23] the short time that the materials are exposed to direct sunlight and the screening effect of the oil in which hazardous materials are suspended make this pathway negligible. Several other pathways may exist: volatilization, runoff, and leaching.[24,25] However, these latter mechanisms do not occur at a properly sited, operated, and maintained RCRA-permitted land treatment facility.

A.3.1 Degradation The chemical structure of the hazardous waste, application and mixing techniques, and soil characteristics (texture, temperature, moisture content, oxygen level, nutrient level, pH, and the kind and number of microbes) affect biodegradation.[26,27] Although biodegradation is purported to be the principal mechanism for removal of organic compounds by land treatment, only a few experiments have attempted to quantify the resulting removal. A laboratory simulation of land treatment of oily sludge revealed that 85 percent of the polynuclear aromatics degraded.[28] Results from Snyder et al.[29] are comparable: oil removal on fertilized plots approached 80 percent at 1 year postapplication.

Mathematical models for degradation could not be found in the literature.

A.3.2 Volatilization Techniques for direct measurement of volatilization at landfarms[30,31] were discussed previously.

Exogenous factors affecting volatilization in land treatment include properties of the soil, waste application techniques, mixing schedules, and atmospheric conditions.[32,33,34]

Farmer and Letey[35] proposed five gradient models for pesticide volatilization rates from the soil based on diffusion laws. The models accommodate soil-incorporated pesticides with and without significant mobility in flowing water. With nonincorporated pesticides, vapor density relationships and air flow rate rather than movement in the soil control the volatilization rate. These approaches do not, however, accommodate subsurface injection. Thibodeaux and Hwang[36] developed a gradientless model of air emissions from petroluem waste landfarms. Their approach accurately predicted the volatilization of dieldrin reported in Farmer and Letey[37] and is considered most suitable for estimating air emissions from land treatment.

A.3.3 Migration and Runoff Migration and runoff of organic compounds from a landfarm may occur after improper application or treatment of the hazardous waste. A description of factors affecting these two pathways appeared in Reference 38. Results from a laboratory study of refinery and petrochemical sludge[39] suggested that the presence of hazardous waste in runoff decreases with time after application. In addition, leachate water collected 1.5 meters below the subsurface was essentially free of toxic components.

However, as previously mentioned, migration and runoff do not occur at a properly sited, operated, and maintained RCRA-permitted land treatment facility. This paragraph is included for the sake of completeness.

A.4 LANDFILLS

A.4.1 Volatilization Direct measurements of organic compound emissions from landfills are possible. During field tests conducted for EPA's Office of Air Quality Planning and Standards (OAQPS), Radian[40] measured air emissions from landfills at three of the four monitored hazardous waste TSDF. Markle et al.[41] collected air samples from three landfills representative of those used by the polyvinyl chloride industry for health hazard evaluations. To compare the efficiencies of water and soil coverings in reducing volatilization, Farmer et al.[42] measured emission rates from simulated landfills.

Numerous equations also have been developed to model organic compound emissions from hazardous waste landfills. The procedure of Farmer et al.[43] based on Fick's law for steady-state diffusion, estimates emission from covered or buried landfills. This was later modified by Shen.[44] Thibodeaux's[45] emission models differentiate covered landfills by the presence or absence of internal gas generation. Another approach[46] incorporates time-varying atmospheric pressure into the emission model. Volatilization rates from landfills with no covering, i.e., open dumps, were modeled by Shen.[47] DeWolf and Wetherold[48] recommend Shen's[49] emission model for covered landfills. GCA, in their excellent comprehensive review of these and other emission models, prefers the work of Farmer et al.[50] and Thibodeaux.[51]

Field validation of these mathematical models has not been reported in the literature. Despite this, Baker and Mackay[52] employed Shen's[53] model in their protocol to evaluate toxic air pollution <u>downwind</u> of hazardous waste landfills.

A.4.2 <u>Migration</u> Several scientists have investigated the potential problem of migration of toxic contaminants from landfills. Rovers and Farquhar[54] suggested that the production of leachate within a landfill is not uncommon. However, the migration of harmful compounds through adjacent soils is not significant. Shen and Tofflemire[55] reported that annual losses of PCB to migration from uncovered landfills in the Hudson River Basin (New York) were substantially less than losses to volatilization.

A.4.3 <u>Other Pathways</u> The impact of other pathways is not discussed quantitatively in the literature.

A.5 WASTEWATER TREATMENT PLANT EFFLUENT

A description of the pathways operating in a wastewater treatment plant is complicated by the number of different treatment systems. There are closed tanks and open tanks (with and without mixing). Air emissions from closed tanks occur during venting.

E. C. Jordan[56] and Burns and Roe[57,58] examined the fate of priority toxic pollutants in publicly owned treatment plants. They observed a decrease in organic compound concentrations across the activated sludge process and a lack of pollutant accumulation in the waste-activated sludge. This suggests that organic compounds are substantially air-stripped or biodegraded during secondary treatment. Results from the controlled laboratory experiments of Roberts et al.[59] imply that organic solutes more likely volatilize during wastewater treatment with surface aeration than with bubble aeration. Lurker et al.[60] examined how aeration rate, suspended particle concentration, and detergent concentration influence aerial organic chemical release from an activated sewage treatment process.

The nonaerated open tank system is similar to the nonaerated surface impoundment discussed previously; see Section A.2.1 for a discussion of the corresponding emission rate models. Similarly, open tank wastewater treatment processes with mixing can be estimated from Thibodeaux et al.[61] Hwang[62] went a step further in his activated sludge surface aeration model. His approach was to estimate pollutant removal by degradation, adsorption, and air stripping via a mass balance equation. Like Hwang and Thibodeaux et al., Freeman[63] considered air stripping losses at the air-water interface. Unlike Hwang, however, he viewed the adsorption pathway as insignificant and, thus, ignored it. In an entirely different approach, Freeman[64,65] modeled the mass transfer of a toxic compound into the bubbles of the aerated system (diffused air [subsurface] activated sludge model). The structure of these and other models was critiqued in GCA.[66]

Allen et al.[67] presented models of organic compound losses at each process encountered in wastewater treatment systems. The models include a methodology for estimating the relative importance of competing pathways. Additionally, these investigators compared the loss of volatiles obtained from field tests at several treatment facilities[68] and from these mathematical models. The models predict organic compound losses due to biodegradation or volatilization in close agreement with the field data. Results from other validation studies are not as consistent. Predicted emission rates from aerated surface impoundments at two wastewater treatment plants were generally larger than measured values.[69] The difference between measured and predicted emission rates in Cox et al.[70] appears to be a function of the type of compound and the presence of aerators.

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APPENDIX B

COMPREHENSIVE SOURCE LIST

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APPENDIX C

PROPERTIES FOR COMPOUNDS OF INTEREST

note: these compound properties may be updated. Please check the EPA distribution site for current property sets.

APPENDIX C

PROPERTIES FOR COMPOUNDS OF INTEREST

This appendix contains compound-specific properties of about 500 chemicals, most of which are not included in CHEMDAT8. These data, presented as a source of information, can be easily incorporated into CHEMDAT8. These compounds are stored in a file named "datatwo.wk1". These compound properties greatly increase the utility of CHEMDAT8. These chemicals represent those chemicals that could be encountered in industrial facilities and that are useful for calculating emission rates for the facilities modeled in the body of this report. The list was extracted from the GCA Physical/Chemical Database, WET model stream compositions, and the Industrial Studies Database. Specific chemical properties were updated as additional information became available, especially the Henry's law constants for hazardous volatile chemicals. Missing compound properties were estimated.

The compounds listed in this appendix were not all included in CHEMDAT8 because their inclusion would seriously slow the execution time of the program, and the memory requirements would prevent the program from being run on many machines. Compounds included in the CHEMDAT8 program were selected on the basis of the estimated frequency with which they are found in hazardous wastes and on their position in prioritized lists of pollutants.

It is recognized that biodegradation rates can vary widely from site to site. Therefore, the following priority schedule is provided as guidance in determining the appropriate biodegradation rate constants to be employed in the emission models:

- Use site-specific biodegradation rate data where available.

- Use the rate constants suggested in the following table.

- Estimate the biodegradation rate constants using the following methodology:

  -- Approximate K_{max} from available data for K_{max} for compounds of similar structure and/or functional groups; and

  -- Approximate K_1 either by using the following correlation:

$$K_1 \text{ (L/h/g)} = 0.135 \ \ K_{ow} \quad 0.38$$

where K_{ow} = octanol-water partitioning coefficient

or by using the default (average) value for K_1, which is K_1 = 1 L/h/g, and then calculate K_s as: $K_s = K_{max}/K_1$.

The following properties are given for each chemical listed by name in Table C-1:

- Compound type code
- Molecular weight
- Density
- Vapor pressure at 25 °C
- Solubility
- Henry's law constant
- Diffusion coefficient in water
- Diffusion coefficient in air
- Boiling point

The following properties are given for each chemical listed by name in Table C-2:

- Coefficients for the Antoine equation for estimating vapor pressure at temperatures other than 25 °C.

- LN(OW)
- Kmax biorate (mg/g-hr)
- K1 biorate (L/g-hr)
- rate of hydrolysis (per second)

To estimate vapor pressures at temperatures other than 25 °C, the Antoine equation coefficients are used with the following equation:

$$\log \text{ Vapor Pressure (mm Hg)} = A - \frac{B}{T + C} \qquad (10)$$

where

A, B, and C = the Antoine equation coefficients

T = temperature in °C.

Two approaches may be used to introduce a new compound and its properties into CHEMDAT8. First, the data for one compound in CHEMDAT8 may be replaced with data for the compound of interest in the columns specified above. With this approach, the number of compounds in CHEMDAT8 remains constant. The second approach involves appending the new compound and its properties to the existing list of chemicals in CHEMDAT8. All the equations/calculations must then be copied from one of the existing rows via Lotus 1,2,3 into the appropriate cells in the new row of the spreadsheet. As mentioned above, the inclusion in CHEMDAT8 of all or a large part of the chemicals listed in this appendix could result in increasing the time required to exercise CHEMDAT8 and could prevent its use on some microcomputers.

The properties of interest listed above mimic those in columns B-Q of the CHEMDAT8 spreadsheet.

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
2,4 D	C	221	1.41	0.0828648	0.0000227	0.0000073	0.0231	240.1
2,4,5 T	C	255.48	1.41	5.250e-09	6.348e-12	0.0000067	0.0192	276
50% PEG	H	115	1	0	0.0003	0.0000088	0.0645	0
ACENAPHTHENE	A	154.21	1.07	0.005	0.00771	0.0000077	0.0421	278
ACENAPHTHYLENE	A	152.21	1.02	0.022952	0.000114	0.0000075	0.04386	265
ACETAL	H	118.17	0.8254	41.76573	0.000353	0.0000077	0.0677	102.7
ACETALDEHYDE	O	45.06	0.788	870	0.0000877	0.0000141	0.124	21
ACETALDOL	H	81.11	1	0.1450557	3.350e-08	0.0000108	0.10487	185
ACETAMIDE	N	73.1	1.15	86.06205	1.800e-09	0.0000125	0.1148	80.1
ACETIC ACID	O	60.05	1.05	15.4	0.0000056	0.000012	0.113	118
ACETONE	O	58	0.79	266	0.000025	0.0000114	0.124	56.2
ACETONITRILE	N	41.03	0.78	90	0.0000199	0.0000166	0.128	81.6
ACETOPHENONE	O	120.16	1.03	0.297	0.0000092	0.0000087	0.06	202.3
ACETYL CHLORIDE	C	78.5	1.11	288	0.000199	0.0000115	0.099	52
ACETYLAMINOFLUORENE,2-	A	223.27	1.02	0.0012	0.0000013	0.000006	0.02654	300
ACETYLMETHYLPHTHALATE 4	A	252.22	1.02	0	0.011	0.0000056	0.0226	0
ACETYL-2-THIOUREA,1-	N	118.15	1.15	0	0.1933	0.0000094	0.0585	0
ACIFLUORFEN	A	361	1	0.0022605	0.00151	0.0000044	0.0145	306.0001
ACROLEIN	O	56.1	0.84	244	0.0000822	0.0000122	0.105	53
ACRYLAMIDE	N	71.09	1.12	0.012	2.610e-10	0.0000106	0.097	125
ACRYLIC ACID	O	72.07	0.97	5.2	0.0000002	0.0000106	0.098	141.6
ACRYLONITRILE	N	53.1	0.81	114	0.000098	0.0000134	0.122	77.4
ADENINE	N	135.13	1.15	0.1191207	8.850e-11	0.0000087	0.0487	220
ADIPONITRILE	H	108.14	0.951	0.0018275	1.310e-08	0.0000089	0.0718	295
ALDICARB	P	190.29	1.18	0.0001	3.168e-08	0.0000072	0.0305	287
ALDRIN	P	364.93	1.18	0.000006	0.000496	0.0000049	0.0132	398
ALLYL ALCOHOL	O	58.1	0.85	23.3	0.000018	0.0000114	0.114	97
ALLYL CHLORIDE	C	76.53	0.94	368	0.00927	0.0000108	0.11653	45
ALLYL ETHER, diallyl ether	H	98.14	0.805	58.94663	0.0022624	0.0000085	0.0882	94
ALPHA METHYL STYRENE	A	118.18	1.02	0.076	0.00591	0.0000114	0.264	166
AMETRYN	H	227.35	1	0.0758461	1.880e-11	0.0000059	0.0261	228.4
AMINOBIPHENYL,4-	N	169.23	1.15	0.0004959	0.0000003	0.0000076	0.0361	302
AMINOPHENOL(-o)	N	109.12	1.15	0.511	0.0000037	0.0000086	0.0774	174
AMINOPHENOL(-p)	N	109.12	1.15	0.893	0.0000197	0.0000024	0.0774	164
AMINOPYRIDINE,4-	N	94.12	1.15	0.002	0.1933	0.0000108	0.0802	273
AMYL ACETATE(-n)	O	130.18	0.88	5.42	0.000464	0.0000012	0.064	148.4
ANILINE	N	93.1	1.02	1	0.0000018	0.0000083	0.07	184
ANISIDINE,o-	A	123.15	1.096	0.0551848	0.0000017	0.0000089	0.0565	225
ANTHRACENE	A	178.23	1.25	0.0000013	0.0675	0.0000077	0.0324	0
ANTHRAQUINONE	O	210.24	1.43	3.000e-08	3.200e-09	0.0000076	0.0245	380
AZIRIDINEethylene imine	H	43.1	1	160	0.000454	0.0000158	0.2646	56
BENZAL CHLORIDE	C	127	1.26	0.07	0.00741	0.0000095	0.051	207
BENZALDEHYDE	O	106.13	0.97	1	0.0000423	0.0000091	0.073	178.9
BENZENE	A	78.1	0.87	95.2	0.0055502	0.0000098	0.088	80.1
BENZIDINE	A	184.23	1.02	0.0000004	1.360e-11	0.000015	0.034	400
BENZOFURAN 2,3	A	118.14	1.072	2.009953	0.000237	0.000009	0.0603	174
BENZOIC ACID	O	122.13	1.27	0.00704	1.820e-08	0.000008	0.0536	122.12

TABLE C-1.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
BENZONITRILE	N	103.07	1.15	1	0.0000136	0.0000102	0.0706	0
BENZOPHENONE	O	182.23	0.97	0.0001763	0.00911	0.0000066	0.0353	0
BENZOTRICHLORIDE	C	195.47	1.38	0.2	0.000981	0.0000078	0.0275	221
BENZOYL CHLORIDE	C	113.57	1.41	214	0.000188	0.0000109	0.0567	0
BENZO(A)ANTHRACENE	A	228.3	1.11	0.0000002	1.380e-09	0.000009	0.051	435
BENZO(A)PYRENE	A	252.3	1.11	0.000568	1.380e-09	0.000009	0.043	312
BENZO(B)FLUORANTHENE	A	252.32	1.02	1562.767	0.0000201	0.0000056	0.0226	4
BENZO(k)FLUORANTHENE	A	252.32	1.02	9.590e-11	0.011	0.0000056	0.0226	480
BENZYL ALCOHOL	O	108.15	0.97	0.15	0.0000006	0.000009	0.0712	0
BENZYL CHLORIDE	C	126.6	1.1	1.21	0.000319	0.0000078	0.075	179.4
BIPHENYL	B	154.2	1.18	1	0.000408	0.0000082	0.0404	254
BISPHENOL(A)	O	228.28	0.97	0.0759058	0.00228	0.0000057	0.0264	232
BIS(1,1,2,2-TETRACHLOROPROPYL) ETHER	C	377.7	1.41	875	43.5	0.0000053	0.0116	21.3
BIS(2-CHLOROETHYL)ETHER	C	143	1.22	1.4	0.000013	0.0000075	0.0692	178
BIS(2-ETHYLHEXYL)PHTHALATE	H	390.56	1	0.0000002	0.0000003	0.0000037	0.0351	384
BIS(CHLOROMETHYL)ETHER	C	115	1.32	30	0.0000903	0.0000094	0.0573	104
BROMACIL	H	261.11	1	0.0877172	137.4758	0.0000054	0.021917	239
BROMOBENZENE	C	157.02	1.4952	4.1344	0.00486	0.0000093	0.0355	0
BROMOCHLOROMETHANE	C	129.39	1.41	146.3781	25.9	0.00001	0.0474	0
BROMODICHLOROMETHANE	C	163.8	1.97	59.2	0.2050041	0.0000106	0.0298	90
BROMOFORM	C	252.77	2.89	5.6	0.000532	0.0000103	0.0149	149.5
BROMOMETHANE	C	94.95	1.41	1590	0.0068591	0.0000121	0.0728	4.6
BROMOTOLUENE 4	C	171	1.3959	1.0868	0.00241	0.0000085	0.0326	0
BROMOXYNIL	A	276.92	1	0.0017175	2.140e-08	0.0000052	0.0203	281
BUTADIENE-(1,3)	H	54.09	0.76	2100	0.0713	0.0000108	0.249	-4.4
BUTANE	H	58.12	0.76	1522.124	0.2910089	0.0000112	0.1896	-0.5
BUTANEDINITRILE	N	80.09	1.15	6	0.0000049	0.0000118	0.1008	265
BUTANOL ISO	O	74	0.79	10	0.0000022	0.0000093	0.086	0
BUTANOL(S)	O	74.14	0.97	10	0.0000127	0.0000112	0.1207	0
BUTANOL-1	O	74.1	0.81	6.5	0.0000089	0.0000093	0.08	0
BUTENE	H	56.1	0.6255	2218.377	0.0411	0.0000102	0.2166	-6.47
BUTYL ACETATE(-n)	O	116	0.88	15	0.000164	0.0000081	0.0675	0
BUTYL ACRYLATE	O	128.2	0.8986	5.8	0.000611	0.0000077	0.0584	145
BUTYL BENZENE	A	134.22	1.02	1	0.0883	0.0000081	0.0519	0
BUTYL CARBITOL	H	162.23	0.96	0.00468	0.0811	0.000007	0.0414	0
BUTYL CELLOSOLVE	H	118.2	0.9	1.61	0.0000003	0.0000081	0.0651	170
BUTYLAMINE	N	73.14	0.7327	72	0.0000165	0.0000096	0.1385	77.9
BUTYLENE GLYCOL-(1,3)	O	90.14	1.004	0.06	0.0000036	0.0000102	0.0902	207.5
BUTYLISOBUTYRATE	H	102.13	0.891	68.94406	0.00719	0.0000088	0.0799	90
BUTYRALDEHYDE	O	72.11	0.97	104.2284	0.000258	0.0000114	0.1255	74.8
BUTYRALDEHYDE ISO	O	72.12	0.794	170	0.000147	0.0000101	0.1365	63
BUTYRIC ACID	O	88.1	0.97	0.84	0.0000017	0.0000101	0.0945	163.5
c10 linear	H	168	0.75	2.009953	0.0512	0.0000059	0.0443	174
CAPROLACTAM	N	113.16	1.02	0.0072722	3.600e-09	0.000009	0.06545	270

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
CAPTAN	A	300.57	1	0.00006	0.0000468	0.0000049	0.0183	312.111
CARBARYL sevin	N	201.22	1.232	0.00004	0.0000324	0.0000071	0.0278	274
CARBENDAZIM	H	191.18	1	0.3060232	0.0000025	0.0000065	0.0327	214
CARBON DISULFIDE	S	76.1	1.26	366	0.019152	0.00001	0.104	46.3
CARBON TETRACHLORIDE	C	153.8	1.59	113	0.0302007	0.0000088	0.078	76.8
CARBONYL SULFIDE	O	60	1	3062.283	0.0000991	0.000013	0.1617	-13.11
CATECHOL	A	110	1.02	0.0153211	4.020e-11	0.0000092	0.068	245.5
CHLORACETOPHENONE,2-	A	154.59	1.32	0.044	0.0000009	0.0000087	0.0383	244
CHLORAL	O	147.4	1.51	50	0.00097	0.0000097	0.0385	97.6
CHLORAMBEN	C	171.58	1.41	3.418682	0.0000341	0.0000085	0.0323	147
CHLORAMBUCIL	C	304.23	1.41	0	10.6	0.000006	0.0153	0
CHLORDANE	P	409.8	1.11	0.00001	0.0000367	0.0000044	0.0118	391
CHLORNAPHAZINE	C	268.2	1.41	0	10.6	0.0000065	0.018	0
CHLORO 2 BUTENE,1 trans	H	90.55	0.9295	87.02964	0.00187	0.0000097	0.0926	84
CHLOROACETALDEHYDE	C	78.5	1.11	60	0.000026	0.0000115	0.099	85
CHLOROACETIC ACID	C	94.5	1.41	0.13832	6.480e-08	0.0000121	0.0733	189
CHLOROALLYL ALCOHOL 2	C	92.53	1.41	1.5	0.0000183	0.0000123	0.0755	146
CHLOROANILINE(2)	C	127.6	1.41	1	0.0168	0.0000101	0.0483	0
CHLOROANILINE(3)	C	127.57	1.213	1	0.0168	0.0000093	0.0515	209
CHLOROANILINE,p-	C	127.57	1.41	0.015	10.6	0.0000101	0.0483	232
CHLOROAZOBENZENE	C	216.7	1.41	0.0757537	0.0108	0.0000074	0.0237	0
CHLOROBENZENE	C	112.6	1.11	11.8	0.003762	0.0000087	0.073	132
CHLOROBENZILATE	C	325.2	1.41	0.0000022	9.414e-08	0.0000058	0.0141	400
CHLOROBENZOPHENONE (PARA)	C	216.67	1.41	0.0000026	3.400e-09	0.0000074	0.0237	330
CHLOROBENZOTRIFLUORIDE, P	H	120.53	1	103.0833	0.0652549	0.0000086	0.0605	79.6001
CHLOROBENZYL ALCOHOL -(m)	C	142.59	1.41	0.0050423	0.0000029	0.0000095	0.0415	237
CHLOROBENZYLATE	O	325.2	0.97	2.664e-09	5.080e-10	0.0000046	0.0168	415
CHLOROBUTADIENE,1	H	88.54	0.96	160.0874	0.010102	0.00001	0.0943	68
CHLOROETHANE (ethyl chloride)	C	64.51	1.41	1200	0.0120961	0.0000115	0.271	12.4
CHLOROETHYLENE	C	63.5	1.41	2946.029	0.00544	0.0000154	0.1299	0
CHLOROHYDRIN, a 3 CHLORO 1,2 PROPANEDIOL	H	110.54	1.345	0.024749	5.350e-09	0.0000107	0.06	213
CHLOROMETHYL METHYL ETHER	C	80.51	1.41	223.079	0.0000864	1.34E-5	0.092	59.1
CHLORONAPHTHALENE,2-	C	162.62	1.41	0.017	0.0182	0.0000088	0.0347	256
CHLORONITROBENZENE(-o)	C	157.56	1.52	0.0760185	0.00788	0.0000094	0.0351	242
CHLORONITROBENZENE, p	A	157.57	1.534	0.1022261	0.0000914	0.0000094	0.0349	236
CHLOROPHENOL-2	C	128.6	1.26	1.4	0.0000083	0.0000095	0.0501	175.6
CHLOROPHENOL-3	C	128.6	1.24	0.5	0.0000033	0.0000094	0.0505	214
CHLOROPHENOL-4	C	128.6	1.31	0.18	0.0000011	0.0000097	0.0493	217
CHLOROPRENE	C	88.5	0.958	273	0.0009293	0.00001	0.104	0
CHLOROPROPANE-1	C	78.54	0.89	350	0.013	0.0000103	0.1153	0
CHLOROPROPANE-2	C	78.54	0.87	523	0.017	0.0000101	0.1164	0

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
CHLOROPROPENE 3	C	75.6	1.41	361	0.359	0.0000139	0.1008	0
CHLOROPROPIONITRILE,3-	C	89.53	1.41	2.5	0.0000051	0.0000125	0.0791	0
CHLOROPROPYLENE-2	C	76.53	1.41	0	0.3589956	0.0000138	0.099	0
CHLOROTOLUENE-4	C	126.6	1.07	2.8	0.00466	0.0000087	0.055	162
CHRYSENE	A	228.2	1.11	5.760e-10	1.180e-09	0.0000062	0.0248	488
CRESOL	O	108	1.03	0.3	0.0000016	0.0000093	0.0694	195
CRESOL(-m)	O	108.1	1.03	0.08	0.0000007	0.00001	0.074	202
CRESOL(-o)	O	108.1	1.05	0.24	0.0000016	0.0000083	0.074	190.8
CRESOL(-p)	O	108.1	1.03	0.11	0.0000007	0.00001	0.074	203
CROTONALDEHYDE	O	70.09	0.85	30	0.0000154	0.0000102	0.0903	99
CUMENE HYDROPEROXIDE	H	152.2	1.03	0.733844	0.0000312	0.0000076	0.0436	158
CUMENE (isopropylbenzene)	A	120.2	0.86	4.6	0.0131	0.0000071	0.065	153
CYANOGEN	N	52.04	0.95	3980	0.00496	0.0000137	0.20355	-21.2
CYCLOHEXANE	H	84.2	0.78	100	0.0137	0.0000091	0.0839	81
CYCLOHEXANOL	O	100.2	0.95	1.22	0.0000045	0.0000083	0.214	161
CYCLOHEXANONE	O	98.2	0.95	4.8	0.0000041	0.0000086	0.0784	157
CYCLOHEXYLAMINE	N	99.17	1.15	8.664001	0.0000423	0.0000104	0.0745	0
CYCLOPENTADIENE	H	66.1	0.82	4	19.3	0.0000109	0.1525	40
CYMENE,para	H	134.22	0.86	1.75365	0.0183	0.0000073	0.056	177
DAZOMET	H	162.27	1	0.2642225	0.0000021	0.0000072	0.0406	217
DDE,p,p'-	C	318.03	1.41	0.0000065	0.000068	0.0000059	0.0144	348.111
DDT	P	354.49	1.18	0.0000002	0.114	0.000005	0.0137	260
DIAZINON	H	304.36	1	0.0000118	2.150e-08	0.0000049	0.018	369.2
DIAZOMETHANE	N	42.04	1.15	3811.993	0.000013	0.0000175	0.260532	-23
DIBENZOFURANS	A	222	1.02	0.006698	0.00399	0.000006	0.0267	287
DIBENZOPYRENE1,2,7,8	A	302.4	1.02	0	0.011	0.000005	0.018	0
DIBROMOCHLOROMETHANE	C	208.29	2.451	15	0.000783	0.0000105	0.0196	120.2
DIBROMOETHANE-1,2	C	187.88	1.41	11.78	0.0109	0.0000081	0.0287	0
DIBROMOMETHANE	C	173.85	1.41	48	0.000998	0.0000084	0.0318	0
DIBROMO-3-CHLOROPROPANE,1,2	C	236.36	1.41	0.8	0.0000236	0.000007	0.0212	196
DIBROMO-4-HYDROXYBENZONITRILE, 3,5	A	290.93	1	0.0167509	0.0000005	0.000005	0.0191	244.0
DIBUTYLPHTHALATE	O	278.3	1.043	0.0001	0.0000003	0.0000079	0.0438	340
DICHLORO 2-PROPANOL 1,3	C	129	1.35	0.27	0.00046	0.0000098	0.0484	174
DICHLORO PROPANOL 2,3	C	129	1.35	7	0.0000234	0.0000098	0.0484	182
DICHLOROANILINE 2,3	A	162	1	0.0033803	0.0000005	0.0000072	0.0407	272
DICHLOROANILINE(2,3)	A	162.03	1	0.0114387	0.0000018	0.0000072	0.0407	252
DICHLOROBENZENE(1,2) (-o)	C	147	1.31	1.5	0.00194	0.0000079	0.069	179
DICHLOROBENZENE(1,4) (-p)	C	147	1.29	1.2	0.00317	0.0000079	0.069	173.4
DICHLOROBENZIDINE,3,3'-	C	253.13	1.41	0.0013037	0.0000027	0.0000067	0.0194	287.111
DICHLOROBENZONITRILE,2,6-	P	172.01	1.18	0.0005	0.0000063	0.0000076	0.0349	270
DICHLOROBENZOPHENONE P,P	C	251.11	1.41	0.0000029	0.0000047	6.8E-6	0.0196	353
DICHLOROETHANE(1,1) ethylidenedichloride	C	98.96	1.17	591	0.0056	0.0000105	0.0742	0

TABLE C-1.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
DICHLOROETHANE(1,2)	C	99	1.26	80	0.0011769	0.0000099	0.104	0
DICHLOROETHENE 1,2 trans	C	96.94	1.41	331	0.0644767	0.0000119	0.0707	47.7
DICHLOROETHENE(1,1) vinylidene chloride	C	96.97	1.213	630	0.0259005	0.0000104	0.09	31.9
DICHLOROETHYL ETHER	C	143.02	1.41	8.230494	0.0000205	0.0000095	0.0413	142
DICHLOROETHYLENE(1,2) cis	C	96.95	1.28	200	0.0154982	0.0000113	0.0736	60.7
DICHLOROMONOFLUOROMETHANE	C	102.92	1.41	1360	921	0.0000115	0.0650	9
DICHLOROPHENOL	A	163.01	1	3.600194	0.0000501	0.0000071	0.0404	145
DICHLOROPHENOL 2,5	A	163.01	1	0.1120569	0.0000016	0.0000071	0.0404	211
DICHLOROPHENOL(2,4)	C	163.01	1.41	0.12	0.0000048	0.0000088	0.0346	210
DICHLOROPHENOL(2,6)	C	163	1.41	0.034	0.0000048	0.0000088	0.0347	220
DICHLOROPHENOXYACETIC ACID(2,4)	C	221	1.41	290	0.0621	0.0000065	0.0588	47.2
DICHLOROPROPANE 1,2	C	112.99	1.156	40	0.002862	0.0000087	0.0782	95.5
DICHLOROPROPENE(1,3)	C	111	1.2	43	0.0035499	0.00001	0.0626	112
DICHLOROPROPYLENE,1,2- (cis)	C	110.97	1.41	375.841	0.00898	0.000011	0.0586	92.5
DICHLOROPROPYLENE,1,2-(trans)	C	110.97	1.41	113.8602	0.011	0.000011	0.0586	77
DICHLORO-2-BUTENE 1,2	C	124.9	1.41	0	10.6	0.0000103	0.0498	0
DICHLORO-2-BUTENE(1,4)	C	125	1.19	2.87	0.000259	0.0000081	0.0725	158
DICHLORO-2-BUTENE, 1,4	H	125	1.188	18.3067	0.00165	0.0000093	0.0534	123
DICHLORVOS	A	220.98	1.415	0.012	0.0000003	0.0000073	0.02315	227.111
DIELDRIN	P	380.93	1.18	0.0000002	0.0000584	0.0000047	0.0125	0
DIETHANOLAMINE	N	105.14	1.0881	0.0005463	1.800e-12	0.0000098	0.0704	268.8
DIETHYL AMINE	N	73.14	1.15	224.959	0.00731	0.0000125	0.1147	0
DIETHYL ETHER	O	74.14	0.97	534.1944	0.000265	0.0000086	0.0782	245
DIETHYL SULFATE	S	154.19	1.177	0.0342	0.0000061	0.0000081	0.0409	208
DIETHYL (N,N) ANILINE	N	149.23	0.93	0.00283	5.740e-08	0.0000059	0.0513	0
DIETHYLBENZENE P	A	134.22	1.02	0.9956	0.00671	0.0000081	0.0519	0
DIETHYLENE GLYCOL DIETHYL ETHER	H	162.23	0.909	1.214403	0.0000021	0.0000068	0.0424	185
DIETHYLENE GLYCOL DIMETHYL ETHER	H	162.23	0.937	3.443058	0.0000015	0.0000069	0.0418	162
DIETHYLENE GLYCOL MONOBUTYL ETHER	H	162.23	0.967	7.556084	2.160e-08	0.000007	0.0412	231
DIETHYLENE GLYCOL MONOETHYL ETHER	H	134.18	0.999	0.0501	4.860e-08	0.000008	0.0524	202
DIETHYLENE GLYCOL MONOETHYL ETHER ACETATE	H	192.23	1	0.113302	0.0000006	0.0000065	0.0325	189
DIETHYLENE GLYCOL MONOMETHYL ETHER	H	120.15	1.01	8.298628	4.140e-08	0.0000086	0.0605	194
DIETHYLHYDRAZINE N,N	H	88.2	1	0	0.0003	0.0000103	0.0932	0
DIETHYLTHIOPHOSPHATEBENZO M ETHYL PETHER	H	253.31	1	0.0000095	2.120e-08	0.0000055	0.0227	392.001

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
DIISOBUTYLENE	H	112.22	0.708	44.69303	0.1177248	0.0000073	0.0778	101
DIISODECYL PHTHALATE	H	446.7	1	0.0000001	0.000408	0.0000039	0.0111	451.01
DIISOPROPYL BENZENE (PARA)	A	162.28	1.02	1	0.107	0.0000072	0.0402	0
DIISOPROPYL KETONE	H	114.19	0.806	12.99374	0.000568	0.0000078	0.0717	124
DIISOPROPYLAMINE	H	101.19	0.722	73.17715	0.000307	0.0000078	0.0887	84
DIMETHOXY-(3,3')-BENZIDINE	O	244.32	0.97	0.0758996	0.00244	0.0000055	0.0242	311
DIMETHYL AMINE	N	45.09	1.15	1520	0.0000052	0.0000167	0.2342	6.9
DIMETHYL BENZYLAMINE N,N	N	135.23	1.15	0.07587	0.00135	0.0000087	0.0487	0
DIMETHYL BENZ(A)ANT 7,12	A	212.28	1	0	0.0003	0.0000061	0.0285	0
DIMETHYL CARBAMOYL CHLORIDE	C	107.54	1.168	1.757571	0.0000004	0.00001	0.0662	167
DIMETHYL DISULFIDE	S	94.2	1.046	29.488	0.0000015	0.0000101	0.0834	109
DIMETHYL FORMAMIDE	N	73.09	0.9445	4	0.0000002	0.0000103	0.0939	153
DIMETHYL HYDRAZINE(1,1)	H	60.1	0.791	157	0.0000016	0.0000109	0.106	63.9
DIMETHYL PHTHALATE	A	194.2	1.19	0.0002	0.000001	0.0000063	0.0568	283.8
DIMETHYL SULFATE	S	126.14	1.26	0.1	0.000004	0.0000096	0.0514	188
DIMETHYL SULFIDE	S	62.12	1.26	420	0.00545	0.0000146	0.140	36.2
DIMETHYL TRISULFIDE	H	126	1	2.200398	3.034249	0.0000083	0.057	172
DIMETHYLACETAMIDE	H	45.082	0.688	1483.699	0.0000102	0.0000123	0.286963	7
DIMETHYLAMINOAZOBENZENE,4-	N	212	1.15	0.0006401	7.320e-08	0.0000066	0.0268	298.111
dimethylaniline N,N	N	128	0.956	0.708	0.0000139	0.0000141	0.152982	193
DIMETHYLBENZIDINE 3,3	A	212.28	1.02	0.0000014	1.352e-09	0.0000062	0.0283	384
DIMETHYLBENZ(A)ANTHRACENE(7,12)	A	256.33	1.02	1.620e-09	2.730e-10	0.000005	0.0461	477
DIMETHYLETHYLAMINE	N	73.19	1.11	20	0.000385	0.0000122	0.1163	0
DIMETHYLPHENOL(2,4)	O	122.16	1.04	0.0573	0.000921	0.0000087	0.0584	211.5
DIMETHYLPHENOL(3,4)	O	122.17	0.97	0	0.0072	0.0000083	0.0602	0
DIMETHYLSULFONE	H	94.33	1	0.0923178	2.270e-08	0.0000099	0.0849	238
DIMETHYLSULFOXIDE	H	58.08	1	0	0.0003	0.0000132	0.1696	0
DIMETHYLSULFOXIDE	H	78.13	1	1.008534	0.0000005	0.0000111	0.111	189
DINITROBENZENE M	N	168.1	1.56	0.05	0.000022	0.0000076	0.279	0
DINITROPHENOL 2,4	N	184	1.68	0.014	0.0000051	0.0000091	0.0273	250
DINITROTOLUENE 2,6	N	182.14	1.15	6	0.0000091	0.0000073	0.0327	0
DINITROTOLUENE(2,4)	N	182.1	1.31	0.0051	0.0000072	0.0000071	0.203	0
DINITRO-o-CRESOL(4,6)	N	198	1.15	0.018	0.0000014	0.0000069	0.0293	254.7
DIOXANE(1,4)	O	88.2	1.03	37	0.0000055	0.0000102	0.229	0
DIPHENYLHYDRAZINE(1,2)	B	184.23	1.19	0.000052	0.0000002	0.0000074	0.0317	220
DIPHENYLMETHANE	B	168.23	1.19	0.0003899	0.0000363	0.0000078	0.0358	0
DIPROPYLAMINE	N	101.22	1.15	189.9606	0.000253	0.0000103	0.0724	0
DIPROPYLBUTRAL	H	156	1	0.2041487	0.0000867	0.0000073	0.0428	209.8
DIPROPYLENE GLYCOL	H	146	1.023	0.0388421	1.590e-08	0.0000077	0.0463	206
DI-n-OCTYL PHTHALATE	H	390.56	0.76	4.849e-09	0.137	0.0000036	0.0151	490

TABLE C-1.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
dodecane	H	170	0.75	0.2747982	0.0664	0.0000059	0.0436	216.2
ENDOSULFAN	P	406.95	1.18	0.00001	0.0000191	0.0000046	0.0115	390
ENDRIN	P	380.93	1.18	0.0000002	0.0000004	0.0000047	0.0125	445
EPICHLOROHYDRIN	C	92.5	1.18	17	0.0000335	0.0000098	0.086	117
EPOXYBUTANE 1,2	C	72.11	0.826	207.912	0.000461	0.0000103	0.1343	61
ETHANE	H	30	0.76	2970	0.0494	0.0000167	0.5139	0
ETHANOL	O	46.1	0.79	50	0.0000303	0.000013	0.123	0
ETHANOLAMINE(mono-)	N	61.09	1.02	0.4	0.0000003	0.0000114	0.107	172
ETHOXYETHANOL-2	O	90	0.9	5.4	0.0000064	0.0000096	0.0947	135
ETHYL ACRYLATE	O	100	0.92	40	0.000254	0.0000086	0.077	100
ETHYL CARBAMATE	C	89.09	1.41	0.6218955	1.170e-08	0.0000126	0.0796	183
ETHYL ETHER	O	74.12	0.71	520	0.00068	0.0000093	0.074	34.5
ETHYL MORPHOLINE, ethyl diethylene oxime	H	115.18	1	0.4095041	0.0000002	0.0000088	0.0644	208
ETHYL TOLUENE, 4	H	120.2	0.861	3.44306	0.0128	0.0000078	0.0649	162
ETHYL VINYL ETHER	H	72.11	0.754	573.6588	0.00213	0.0000098	0.1396	33
ETHYLACETATE	O	88.1	0.9	100	0.000128	0.0000097	0.0732	77
ETHYLAMINE	N	45	1.15	1057.349	0.0000256	0.0000168	0.2349	0
ETHYLBENZENE	A	106.2	0.87	10	0.0078806	0.0000078	0.075	136.2
ETHYLENE DIAMINE	N	60.11	1.15	10.18362	0.0000085	0.0000141	0.152523	126
ETHYLENE DIBROMIDE	C	187.88	2.7	14	0.00065	0.0000119	0.0217	131.6
ETHYLENE GLYCOL	O	62.08	1.11	0.126	1.800e-09	0.0000122	0.108	0
ETHYLENE GLYCOL DIMETHYL ETHER	H	90.12	0.867	83.73	0.000035	0.0000094	0.0961	85
ETHYLENE GLYCOL MONOBUTYL ETHER	H	118.18	0.903	0.339572	0.0000005	0.0000082	0.065	171
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	H	176	1	3.416916	0.0000049	0.0000068	0.0365	208
ETHYLENE GLYCOL MONOETHYL ETHER ACETATE	H	148.17	1	1.746256	0.0000018	0.0000076	0.0458	143
ETHYLENE GLYCOL MONOETHYL ETHER Cellosol	H	90.12	0.93	2.746598	0.0000011	0.0000098	0.0932	135
ETHYLENE GLYCOL MONOMETHYL ETHER	H	76.1	1	4.928497	0.0000008	0.0000112	0.114805	124.5
ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE	H	134.14	1	5.066	0.0000022	0.000008	0.0529	124
ETHYLENE GLYCOL MONOPHENYL ETHER	H	138.17	1.102	5.042345	6.840e-08	0.0000084	0.0482	237
ETHYLENE GLYCOL MONOPROPYL ETHER	H	104.16	1	3.072762	0.0000009	0.0000093	0.0739	133
ETHYLENE OXIDE	O	44	0.87	1250	0.0002381	0.0000145	0.104	0
ETHYLENE THIOUREA	N	102.17	1.15	0.3716955	1.520e-10	0.0000102	0.0715	198.222
ETHYLHEXYLACRYLATE,2-	H	184.28	0.88	1.271859	0.00294	0.0000061	0.0364	184
ETHYLPHENOL,3-	P	122.17	1.18	1	0.0000001	0.0000094	0.0553	0
ETHYL(2) HEXANOL	O	130.22	0.8344	0.36	0.0000617	0.0000073	0.0592	184

TABLE C-1.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
FLUORANTHENE	A	202	1.02	0.0177	0.067	0.0000064	0.0302	250
FORMALDEHYDE	O	30	0.97	3500	0.0000003	0.0000198	0.178	-14
FORMAMIDE	O	45	0.97	342.0861	0.0000012	0.0000151	0.2509	0
FORMIC ACID	O	46.03	1.22	42	0.0000007	0.0000014	0.079	100.7
FREON 11, fluorotrichloromethane	C	137.37	1.494	795.2637	0.0527	0.00001	0.0426	23.7
FREON 12 DICHLORODIFLUOROMETHANE	C	120.92	1.41	5000	0.401	0.0000105	0.052	-29.8
FREON 12, dichlorodifluoromethane	C	120.91	1	6768.665	0.7809416	0.0000085	0.0603	-41.001
FUMARIC ACID	O	116.07	0.97	0.0760844	0.0000017	0.0000086	0.0646	0
FURAN	O	68.08	0.94	596	0.00534	0.0000122	0.104	31.4
FURFURAL	O	96.09	1.16	2	0.0000811	0.0000104	0.0872	161.7
Generic Organic material	H	100	1	25	0.000018	0.0000096	0.0782	125
GLUTARIC ACID	O	132.13	0.97	0.0002911	2.060e-08	0.000008	0.0542	340
GLYCERIN (GLYCEROL)	O	92.09	1.25	0.00016	1.300e-08	0.0000115	0.0798	216
GLYOXAL	O	58.04	1.27	221.1501	0.000011	0.0000153	0.1544	51
GLYPHOSATE	H	169.07	1	0.1363822	7.800e-09	0.000007	0.0385	186.001
GUTHION	H	317.34	1	0.0002913	1.680e-09	0.0000048	0.0171	340.001
GYLCIDOL	O	74.08	1.11	0.925	0.0000009	0.0000122	0.114272	162
HEPTACHLOR	C	373.35	1.57	0.0003	0.0023	0.0000057	0.0112	339
HEPTANE ISO	H	100.21	0.76	66	4.35	0.0000071	0.187	0
HEPTANE(-n)	H	100.02	0.68	46	2.01998	0.0000076	0.0926	0
HEXACHLOROBENZENE	C	284.8	2.04	0.0048	0.0017001	0.0000059	0.0542	322
HEXACHLOROBUTADIENE	C	260.8	1.67	0.15	0.0103002	0.0000062	0.0561	215
HEXACHLOROCYCLOHEXANE (GAMMA ISOMER)	C	290.83	1.87	0.0000109	0.0000078	0.0000073	0.0142	390
HEXACHLOROCYCLOPENTADIENE	C	272.77	1.7	0.081	10.6	0.0000072	0.0161	239
HEXACHLOROETHANE	C	237	2.09	0.65	0.0083501	0.0000068	0.0025	186
HEXAFLUOROACETONE	O	166.02	1	57353.46	162.7182	0.0000071	0.0394	-101
HEXAMETHYLENE 1,6 DIISOCYANATE	N	168.27	1.04	0.0382011	0.0000003	0.0000072	0.038	255
HEXAMETHYLPHOSPHORAMIDE	N	179.2	1.03	0.1190317	1.280e-13	6.9E-6	0.0352	233
HEXANE(-n)	H	86.2	0.66	150	0.7680137	0.0000078	0.2	69
HEXANOIC ACID	O	116.06	0.9265	0.0763529	0.0000011	0.0000084	0.0659	205.7
HEXANOL-1	O	102.18	0.82	0.812	0.0000182	0.0000075	0.059	158
HEXEN-2-ONE 5	O	98.16	0.847	10.85701	0.00008	0.0000088	0.0862	128
HYDRAZINE	N	32.06	1.0081	14.4	0.0000007	0.000019	0.4164	113.5
HYDROGEN SULFIDE	C	34.1	1.41	15200	0.023	0.0000161	0.176	-60.2
HYDROQUINONE	O	110.11	1	0.0006957	1.440e-09	0.000009	0.06853	286
HYDROXYACETIC ACID	O	76.05	0.97	189.8651	0.00019	0.000011	0.11638	216.001
INDENO(1,2,3-cd)-PYRENE	N	276.34	1.15	1.000e-09	5.070e-13	0.0000057	0.019	536
ISOBUTYLENE	H	56.11	0.626	2250.243	0.0366	0.0000102	0.216458	-6.9
ISODECANOL	H	152.2	1	0.0264044	0.0000053	0.0000074	0.0442	212
ISOPHORONE	H	138.21	0.92	0.439	0.0000066	0.0000068	0.0623	215
LINDANE hexachlorocyclohexane	C	290.85	1.41	0.0309093	0.0021	0.0000062	0.0162	259

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
MALEIC ACID	O	116.07	1.59	0.075846	1.470e-08	0.0000115	0.0523	260.001
MALEIC ANHYDRIDE	O	98.1	0.93	0.0013406	0.0000002	0.0000111	0.095	200
METHACRYLIC ACID	O	86.1	1.0153	0.1	0.0000113	0.0000105	0.0958	163
METHANOL	O	32	0.79	114	0.0000052	0.0000164	0.15	0
METHOMYL	H	162.2	1	0.00005	0.0000008	0.0000072	0.0407	144.0001
METHOXYCHLOR	O	345.65	0.97	0.0001552	0.000259	0.0000045	0.0156	350
METHYL 1-PENTENE 2	H	84	0.76	270.7512	10.5	0.000009	0.113	0
METHYL ACETATE	O	74.1	0.934	235	0.000102	0.00001	0.104	56.9
METHYL ACRYLATE	O	86.1	0.97	88	0.0000001	0.0000102	0.0976	77
METHYL AMINE	N	31.06	1.15	1520	0.00538	0.000021	0.417	0
METHYL AZIRIDINE 2	N	57.1	1.15	0	0.1933	0.0000145	0.164502	0
METHYL BENZYL ALCOHOL 4	O	122.17	1.015	0.0864688	0.0000139	0.0000086	0.059	215
METHYL CHLORIDE	C	50.5	0.95	3830	0.0088201	0.0000065	0.126	-24
METHYL CHOLANTHRENE 3	A	268.36	1.02	0.000759	0.000134	0.0000054	0.0209	0
METHYL CYCLOHEXANE	H	92.2	0.76	43	0.979	0.0000085	0.0986	0
METHYL ETHERdimethyl ether	O	46.08	0.97	3980	0.00318	0.0000149	0.242	-23.6
METHYL ETHYL KETONE, 2 butanone	O	72.1	0.82	100	0.00013	0.0000098	0.0808	79.6
METHYL FORMATE	O	60.05	0.97	500	0.13	0.0000127	0.1635	0
METHYL HYDRAZINE	N	46.09	0.866	49.6	0.0000004	0.0000139	0.253053	87
METHYL IODIDE	M	141.94	1.65	400	0.00253	0.0000104	0.039	42.4
METHYL ISOBUTYL KETONE	O	100.2	0.8	15.7	0.0003901	0.0000078	0.075	115.8
METHYL ISOCYANATE	N	57.06	1.15	461.743	0.0105	0.0000145	0.1647	39.1
METHYL ISOPROPYL KETONE	H	86.15	0.805	189.8966	0.000458	0.0000092	0.1057	94
METHYL MERCAPTAN	S	48.1	0.999	1728.82	0.00363	0.0000148	0.2244	1
METHYL METHACRYLATE	O	100.1	0.95	39	0.0001409	0.0000086	0.077	101
METHYL MORPHOLINE	H	101.15	0.92	17.7398	0.0000033	0.000009	0.0798	117
METHYL NAPTHALENE(1-)	A	142.19	1.02	0.0539	0.00071	0.0000078	0.048	0
METHYL NAPTHALENE(2-)	A	142.19	1.02	0.06772	0.000058	0.0000078	0.048	0
METHYL PARATHION	P	263.23	1.18	0.0000098	6.789e-08	0.0000059	0.02	0
METHYLENE CHLORIDE, dichloromethane	C	85	1.34	438	0.003	0.0000117	0.101	39.8
METHYLENE DIPHENYL DIISOCYANATE	N	236	1.15	0.0006439	4.860e-08	0.0000062	0.0233	327.111
METHYLENE DIPHENYLAMINE (MDA)	H	198	1	0.000351	2.810e-08	0.0000064	0.0313	337
METHYLENEDIANILINE 4,4	N	172	1.15	0.0004037	0.0000005	0.0000075	0.0353	305.111
METHYLENE-BIS (2-CHLOROANILINE),4,4'-	N	267.15	1.15	0.0000694	0.0000003	0.0000058	0.0199	331
METHYLSTYRENE (-4)	A	118.19	1.02	1.6188	0.00591	0.0000088	0.0616	0
METHYL-TERTIARY-BUTYL ETHER	O	83.1	0.97	185.949	0.0005551	0.0000105	0.1024	64
MONOMETHYL FORMANIDE	O	59.07	1.011	0.7626558	9.670e-10	0.0000132	0.1647	184
MORPHOLINE	N	87.12	1	10	0.0000573	0.0000096	0.091	129
NABAM	H	256.35	1	0.0000004	2.500e-16	0.0000054	0.0224	416.0001
NAPHTHALENE	A	128.2	1.14	0.23	0.0004831	0.0000075	0.059	218

TABLE C-1.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
NAPHTHOL,alpha-	O	144.18	0.97	0.002204	2.540e-08	0.0000076	0.0482	0
NAPHTHOL,beta-	O	144.17	0.97	10	1.390e-08	0.0000076	0.0482	285
NAPHTHYLAMINE,alpha-	N	143.19	1.15	0.0005366	5.000e-08	0.0000084	0.0451	300.8
NAPHTHYLAMINE,beta-	N	143.19	1.15	0.0003781	3.520e-08	0.0000084	0.0451	306.1
NEOPENTYL GLYCOL	O	104	0.97	0.0341692	1.600e-08	0.0000092	0.0751	208
NITRO m XYLENE, 2	A	151.17	1.117	0.1869559	0.000427	0.000008	0.0425	224
NITROANILINE P	N	138.14	1.15	0.0015	0.000227	0.0000086	0.0473	0
NITROBENZENE	N	123.1	1.2	0.3	0.0000239	0.0000086	0.076	0
NITROBIPHENYL,4-	B	199.21	1.19	0.0002913	0.0000073	0.000007	0.0286	340
NITROGLYCERIN	N	227.09	1.6	0.0036	6.000e-19	0.0000078	0.0211	260
NITROMETHANE	N	61.05	1.15	27.8	0.0235	0.000014	0.1491	0
NITROPHENOL,2-	N	139.11	1.15	0.0013423	0.0000001	0.0000085	0.0469	216
NITROPHENOL,4-	N	139.11	1.4	0.0001	1.314e-09	0.0000096	0.043	279
NITROPROPANE 2	N	89.09	0.9876	101.517	0.000119	0.0000101	0.0923	120.3
NITROSODIMETHYLAMINE N	N	74.08	1.15	8	0.0000008	0.0000124	0.1126	152
NITROSOMORPHOLINE	N	116.14	1.15	0.0990759	8.540e-08	0.00001	0.059	225
NITROSO-N-METHYLUREA N	N	103.1	1.15	0.8041194	2.590e-08	0.0000102	0.0706	178
NITROTOLUENE (-p)	N	137.13	1.15	1	0.000408	0.0000086	0.0478	0
NITROTOLUENE, m	A	137.13	1.063	0.1384812	0.0000684	0.0000082	0.0495	230
NITROTOLUENE, o	A	137.14	1.163	0.1778758	0.0000879	0.0000087	0.0475	225
NITROTOLUENE, o	A	137.13	1.163	0.1778758	0.0000879	0.0000087	0.0476	225
NONANOL, n	H	144.26	0.827	0.021735	0.0000045	0.0000069	0.0518	215
OCTANE	H	114.3	0.7	17	3.87	0.0000071	0.0763	125.7
OCTANOL 1	O	130.3	0.8259	0.124	0.0000434	0.0000073	0.0593	0
OCTANOL 2	O	130.3	0.8207	0.15808	0.0000118	0.0000073	0.0595	0
OCTANOL 3	O	130.3	0.8216	0.09424	0.0000071	0.0000073	0.0595	0
OCTANOL 4	O	130.3	0.8192	0.12464	0.0000094	0.0000073	0.0595	0
OIL	H	170	0.76	0	3.5	0.0000059	0.0433	0
OXALIC ACID	O	90.04	1.65	0.0006077	3.600e-09	0.0000137	0.0736	155
PARALDEHYDE	O	132.3	0.99	25.3	0.0000367	0.000008	0.0536	125
PARATHION	P	291.3	1.26	0.0000378	0.0000006	0.0000058	0.017	375
PCB'S (Aroclors)	B	292	1.19	0.0041	0.000864	0.000008	0.0175	306.111
PENTACHLOROBENZENE	C	250.34	1.61	0.0046	0.0073	0.0000063	0.057	277
PENTACHLOROETHANE	C	202.3	1.67	4.4	0.021	0.0000073	0.066	162
PENTACHLORONITROBENZENE	C	295.36	1.41	0.0000991	0.000385	0.0000061	0.0159	357
PENTACHLOROPHENOL	C	266.4	1.98	0.005	0.0000882	0.0000061	0.056	310
PENTADIENE 1,2	H	67.1	0.76	367.458	0.0119	0.0000103	0.154	0
PENTAERYTHRITOL	H	136.15	0.659	0.0098698	3.700e-10	0.0000062	0.0621	227
PHENOL	O	94.1	1.07	0.341	0.0000013	0.0000091	0.082	182
PHENYLCYCLOHEXANONE 4	O	175	0.97	1.4668	0.00875	0.0000067	0.0373	0
PHENYLENE DIAMINE(-m)	N	108.14	1.14	0.028	1.080e-08	0.0000099	0.0663	284
PHENYLENE DIAMINE(-o)	N	108.14	1.15	0.008	1.080e-08	0.0000099	0.066	258
PHENYLENE DIAMINE(-p)	N	108.14	1.15	0.0046	1.260e-09	0.0000099	0.06615	267
PHENYLPHENOL P	O	170.2	0.97	10	0.0032	0.0000068	0.0387	0
PHOSGENE (decomposes)	O	98.92	1	1390	0.0140401	0.0000011	0.108	8.1

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
PHOSPHINE	S	34	1	2000	0.2270003	0.0000182	0.381	-87.78
PHTHALIC ACID	O	166.14	1.59	121	0.0132	0.0000068	0.064	72.6
PHTHALIC ANHYDRIDE	O	148.1	1.33	0.0015	0.0000008	0.0000086	0.071	284
PHTHALIMIDE	N	147.1	1.15	118	0.0114	0.0000083	0.0435	69.5
PINENE(alpha-)	H	136.2	0.86	5	0.0262	0.0000073	0.0549	156
PIPERAZINE	H	86.14	1	3.72	0.0000422	0.0000104	0.091	146
PROPANE	H	44.09	0.76	760	0.022	0.0000132	0.285	0
PROPANE SULTONE,1,3-	H	122.14	1.392	0.0011886	9.010e-09	0.0000103	0.0515	300
PROPANOIC ACID	O	74.08	0.97	8.553405	0.0000018	0.0000112	0.120812	141.1
PROPANOL	O	60.1	0.8037	20.824	0.0000019	0.0000114	0.176	97.2
PROPANOL ISO	O	60.09	0.79	42.8	0.000015	0.0000104	0.098	82.4
PROPENE	H	42.08	0.61	8168.507	0.0427	0.0000119	0.334106	-47
PROPIOLACTONE b	O	72.1	0.97	3.4	0.0000001	0.0000114	0.125	162.3
PROPIONALDEHYDE	O	58.08	0.81	300	0.0000598	0.0000114	0.102	49.5
PROPIONIC ACID	O	74.09	0.97	10	0.0000487	0.0000112	0.1208	0
PROPORUR (Baygon)	N	209.24	1.15	0.0171961	5.770e-08	0.0000067	0.0273	255.111
PROPYL ACETATE ISO	O	102.13	0.87	73.954	0.000317	0.0000087	0.0807	88.2
PROPYL AMINE ISO	N	59.08	0.694	460	0.000358	0.0000105	0.192	33
PROPYL ETHER ISO	O	102.18	0.97	150	0.00224	0.0000093	0.0769	68.4
PROPYLENE	H	42.12	0.76	7600	2.11	0.0000136	0.305	0
PROPYLENE CHLOROHYDRIN	H	94.54	1.103	3.072759	0.0000024	0.0000105	0.0811	133
PROPYLENE GLYCOL	O	76.11	1.04	0.3	0.0000015	0.0000102	0.093	188
PROPYLENE OXIDE	O	58.1	0.83	525	0.0003559	0.00001	0.104	33.9
PROPYLENIMINE 1,22 methyl aziridine	N	57.09	1.15	153.257	0.0000094	0.0000145	0.1645	66
PROPYL(-n) ACETATE	O	102.13	0.89	35	0.000294	0.0000088	0.0799	101.6
PROPYL(-n) BENZENE	A	120.19	0.86	2.5	0.00659	0.0000078	0.065	0
PROPYN-1-OL 2(PROPARLGYL)	O	56.06	0.97	11.6	0.0000086	0.0000133	0.181	113.6
PYRIDINE	O	79.1	0.98	20	0.0000236	0.0000076	0.091	115.5
QUINOLINE	A	129.16	1.02	0.095	0.0000003	0.0000083	0.0546	237.7
QUINONE	N	108.09	1.318	172.1972	0.000001	0.0000107	0.0624	63.111
RESORCINOL	O	110.12	0.97	0.00026	1.880e-08	0.0000087	0.078	280
SILVEX	P	269.51	1.18	0	4420	0.0000058	0.0194	0
SODIUM FORMATE	M	68.01	1.65	0.0007599	1.700e-09	0.0000163	0.11052	0
STYRENE	A	104.2	0.9	7.3	0.0026048	0.000008	0.071	145
STYRENE OXIDE	O	120.15	1.054	0.798015	0.0000893	0.0000089	0.0594	194
SUCCINIC ACID	O	118.09	0.97	0.0007615	1.740e-09	0.0000085	0.0631	0
TAMARON (METHAMIDIPHOS)	H	141.12	1	127.3185	0.0000045	0.0000078	0.0489	69.0001
TEREPHTHALIC ACID	A	166.13	1	0.0039109	1.040e-08	0.0000071	0.0394	296.5
TERPINEOL, ALPHA	H	154.24	1	2.071076	0.000516	0.0000074	0.0434	140
TETRACHLOROBENZENE(1,2,3,4)	C	215.9	1.41	0.019	0.0027	0.0000074	0.0239	254
TETRACHLOROBENZENE(1,2,3,5)	C	215.9	1.41	0.03	0.00426	0.0000074	0.0239	246

TABLE C-1. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, I

COMPOUND NAME		MWT	DENS. g/cc	VP@25C mmHg	HL@25C atm-m3/mol	Dl cm2/s	Dv cm2/s	Bpt deg. C
TETRACHLOROBENZENE(1,2,4,5)	C	215.9	1.86	0.03	0.00426	0.0000088	0.0211	246
TETRACHLORODIBENZO-p-DIOXIN(2,3,7,8)	C	321.96	1.41	0.0000012	0.0000398	0.0000058	0.0143	421
TETRACHLOROETHANE(1,1,2,2)	C	168	1.59	6.5	0.0002495	7.9e-6	0.071	146.2
TETRACHLOROETHENE	C	165.83	1.624	19	0.0177003	0.0000082	0.072	121.4
TETRACHLOROPHENOL(2,3,4,6)	C	231.9	1.41	0.89	0.0000045	0.0000071	0.0217	164
TETRACHLOROPHENOL(2,3,5,6)	C	231.9	1.41	0.01	110.9999	0.0000071	0.0217	0
TETRAETHYL LEAD	M	323.45	1.653	0.35	0.0809	0.0000064	0.0132	200
TETRAETHYLDITHIOPYROPHOSPHATE	S	322.34	1.26	0.0000004	7.200e-09	0.0000055	0.015	335
TETRAETHYLENE PENTAMINE	H	189.31	1	0.0521293	1.500e-13	6.5e-6	0.0331	229.
TETRAFLUOROMETHANE	C	104.46	1	382429.8	60.40877	0.0000093	0.0736	-176.0
TETRAHYDROFURAN	O	72.12	0.88	72.1	0.000049	0.0000105	0.098	67
TETRALIN	H	132.22	1	0.40318	0.00188	0.0000081	0.0534	0
TETRANITROMETHANE	N	196.03	1.15	8	0.1933	0.000007	0.0297	126
THIOUREA	N	76.12	1.41	145	0.00016	0.0000138	0.107	182
THIOUREA,1-(o-CHLOROPHENYL)-	N	186.66	1.15	0.000002	0.1933	0.0000072	0.0317	323
TOLUENE	A	92.4	0.87	30	0.0064201	0.0000086	0.087	110.7
TOLUENE DIAMINE(2,4)	N	122	1.11	1.589889	1.260e-09	0.0000091	0.0569	284
TOLUENE DIISOCYANATE(2,4)	N	174.16	1.2	0.08	0.0000002	0.0000062	0.061	251
TOLUENEDIAMINE(2,6)	N	122.17	1.15	0	0.1933	0.0000092	0.0559	0
TOLUENEDIAMINE(3,4)	N	122.17	1.15	0.0052068	3.280e-09	0.0000092	0.0559	265
TOLUENESULFONYL CHLORIDE	A	190.65	1	0.0042605	0.0000022	0.0000065	0.0328	295
TOLUIC ACID (para-)	O	136.16	0.97	0.00031	5.600e-09	0.0000078	0.052	275
TOLUIC ALDEHYDE	O	120.14	1.03	0.16	0.000253	0.0000087	0.06	204
TOLUIDINE m	A	107.16	0.999	0.1877656	0.0000016	0.0000092	0.0711	203
TOLUIDINE P	A	107.17	1.046	1	0.0000191	0.0000094	0.069758	200.6
TOLUIDINE (-0)	A	107.17	0.989	0.242	0.0000024	0.0000091	0.0714	200.4
TOXAPHENE	H	414	1.11	0.3	0.00489	0.0000043	0.0116	384
TRIBUTYL PHOSPHOROTRITHIOATE SSS	O	314.54	0.97	0.0007587	0.000157	0.0000047	0.0175	470.
TRIBUTYL TIN ACETATE	H	230.4	1	0.0263411	0.00696	0.0000058	0.0257	262.
TRIBUTYLPHOSPHATE	O	266.32	0.97	127	0.007543	0.0000052	0.0216	289
TRICHLOROBENZENE 1,2,3	C	181.46	1.41	0.2169527	0.00787	0.0000082	0.03	221
TRICHLOROBENZENE 1,2,4	C	181.5	1.41	0.18	0.0019201	0.0000082	0.03	213
TRICHLOROBENZENE 1,3,5	C	181.5	1.41	0.23	0.0209	0.0000082	0.03	208.5
TRICHLOROETHANE 1,1,1 methyl chloroform	C	133.4	1.33	123	0.0174002	0.0000088	0.078	75
TRICHLOROETHANE 1,1,2	C	133.4	1.3	25	0.0008239	0.0000088	0.078	74
TRICHLOROETHYLENE	C	131.4	1.4	75	0.0102002	0.0000091	0.079	87
TRICHLOROFLUOROMETHANE	C	137.37	1.49	796	0.0583	0.0000097	0.087	23.8
TRICHLOROPHENOL 2,4,5	P	197.45	1.18	0.0399045	0.0000087	0.000007	0.0291	249
TRICHLOROPHENOL 2,4,6	O	197.46	1	0.0073	0.0000177	0.0000064	0.0314	244.5
TRICHLOROPROPANE 1,1,1	C	147.43	1.41	3.1	0.029	0.0000079	0.071	107

COMPOUND NAME		MWT	DENS.	VP@25C	HL@25C	Dl	Dv	Bpt
			g/cc	mmHg	atm-m3/mol	cm2/s	cm2/s	deg. C
TRICHLOROPROPANE(1,1,2)	C	147.43	1.41	6.64	0.029	0.0000093	0.0396	140
TRICHLOROPROPANE(1,2,2)	C	147.38	1.41	1.37	0.029	0.0000093	0.0397	124
TRICHLOROPROPANE(1,2,3)	C	147.4	1.41	3	0.028	0.0000079	0.071	156
TRICHLORO-1,2,2-TRIFLUOROETHANE,1,1,2-	C	187.38	1.41	270	0.3915875	0.0000081	0.0288	47.7
TRIETHANOLAMINE	N	149.19	1.15	0.01	1.450e-10	0.0000082	0.0427	335.4
TRIETHYLAMINE	N	101.22	0.7326	400	0.000125	0.0000079	0.0881	89.6
TRIETHYLENE GLYCOL DIMETHYL ETHER	H	178.17	0.986	0.277505	4.680e-08	0.0000067	0.0361	216
TRIFLUOROETHANE(1,1,1)	C	84	1.41	9240	84	0.000013	0.0866	-47.3
TRIFLURALIN	N	335.29	1.15	0.0014133	0.00016	0.000005	0.0149	314
TRIISOBUTYLENE	H	170.32	1	0.4095041	0.0917	0.000007	0.0381	208
TRIISOPROPYLAMINE	H	185.34	1	0.216942	0.00343	0.0000066	0.0341	221.001
TRIMETHYL BENZENE, 123	A	120.2	0.89	1.920766	0.0112	0.000008	0.064	175
TRIMETHYLBENZENE (1,3,5)	A	120.2	1.02	2.4	0.147	0.0000087	0.0602	0
TRIMETHYLPENTANE 2,2,4	H	114.22	0.76	40.6	3.338133	0.0000075	0.0733	99.2
TRINITROTOLUENE(2,4,6)	N	227.1	1.15	0.046	0.0000137	0.0000064	0.0245	0
TRIPROPYLENE GLYCOL	H	160.26	1	0.0047115	9.530e-08	0.0000072	0.0413	238
UREA	N	60.06	1.34	6.69	0.000264	0.0000137	0.122	133
URETHANE	N	89.09	1.15	10	0.0000586	0.0000106	0.0866	-40.3
VINYL ACETATE	O	86.09	0.93	115	0.0005078	0.0000092	0.085	73
VINYL ACETYLENE	H	52.08	1	14664.62	0.0962	0.0000141	0.1992	-66
VINYL BROMIDE	C	106.96	1.517	969.1209	0.00674	0.0000118	0.0598	18
VINYL CHLORIDE	C	62.5	0.91	2660	0.0264963	0.0000123	0.106	-13.9
VINYLIDENE CHLORIDE see 1,1dichloroethen	C	96.97	1.213	630	0.0259005	0.0000104	0.09	31.9
WARFARIN	P	308.33	1.18	0.00001	4420	0.0000054	0.0163	356
XYLENE	A	106.2	1.02	8.5	0.00525	0.0000093	0.0714	140
XYLENE(-m)	A	106.16	0.86	8	0.0074341	0.0000078	0.07	139
XYLENE(-o)	A	106.2	0.88	7	0.004878	0.00001	0.087	144.4
XYLENE(-p)	A	106.16	0.86	9.5	0.0074402	0.0000084	0.0769	138.4
XYLENOL(3,4)	O	122.17	0.97	0.019	3.940e-08	0.0000083	0.0602	225
XYLIDINEdimethylaniline	A	121.18	0.98	0.0819225	0.0000028	0.0000084	0.0606	218

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
2,4 D	6.908157	1746.881	193.6385	3.228066	10.76	2.275134	0
2,4,5 T	16.13832	7280.503	273.16	2.854958	10.76	1.64144	0
50% PEG	0	0	0	-4.232786	15.3	0.00332	0
ACENAPHTHENE	7.728	2534.234	245.576	3.92	31.1	4.16815	0
ACENAPHTHYLENE	7.72819	2534.234	245.576	4.07	31.1	2.7	0
ACETAL	6.849664	1279.732	219.7466	2.287809	15.3	0.999325	0
ACETALDEHYDE	8.005	1600.017	291.809	0.43	82.42	0.1966685	0
ACETALDOL	8.206501	2072.293	204.1096	0.1735975	15.3	0.1571452	0
ACETAMIDE	7.156695	1300.449	224.0406	-0.775268	9.7	0.0685	0
ACETIC ACID	7.387	1533.313	222.309	-0.31	14	0.98	0
ACETONE	7.117	1210.595	229.664	-0.24	1.3	1.15	0
ACETONITRILE	7.119	1314.4	230	-0.34	9.7	0.1002612	0
ACETOPHENONE	7.385889	1891.5	217.885	1.58	17.56	0.5379447	0
ACETYL CHLORIDE	6.948	1115.954	223.554	-0.308331	10.76	0.1030783	0
ACETYLAMINOFLUORENE,2-	7.25633	2110.188	182.2596	3.482134	31.1	2.841536	0
ACETYLMETHYLPHTHALATE 4	0	0	0	2.224537	31.1	0.9455041	0
ACETYL-2-THIOUREA,1-	0	0	0	-0.643182	9.7	0.0768	0
ACIFLUORFEN	6.934575	1974.716	181.1196	5.0533	15.3	11.2357	0
ACROLEIN	7.212867	1297.327	246.6905	-0.09	7.8	0.36	0
ACRYLAMIDE	11.29315	3939.877	273.16	0.8008422	9.7	0.2720544	0
ACRYLIC ACID	5.652	648.629	154.683	0.31	17.56	0.1770657	0
ACRYLONITRILE	7.11	1335.674	238.207	-0.92	18	0.75	0
ADENINE	7.221354	1812.02	197.4596	-0.16	9.7	0.1173636	0
ADIPONITRILE	7.213714	2072.084	183.2096	1.675912	15.3	0.5850384	0
ALDICARB	6.927094	1908.791	184.7296	2.174818	15.3	0.9052528	0
ALDRIN	9.357671	4347.02	273.16	5.669268	15.3	19.26059	0
ALLYL ALCOHOL	9.148151	2319.925	273.16	0.17	17.56	0.1566514	0
ALLYL CHLORIDE	7.576274	1493.914	273.16	0.95454	10.76	0.3112157	0
ALLYL ETHER, diallyl ether	6.845911	1250.578	221.3996	2.51897	15.3	1.223344	0
ALPHA METHYL STYRENE	6.92366	1486.88	202.4	3.463532	31.1	2.795661	0
AMETRYN	7.225121	1843.155	195.8636	1.204255	15.3	0.3872162	0
AMINOBIPHENYL,4-	7.500307	2235.337	181.8796	3.605957	9.7	3.166695	0
AMINOPHENOL(-o)	9.228947	2838.639	273.16	0.5815316	9.7	0.2245521	0
AMINOPHENOL(-p)	-3.357	699.157	-331.343	0.5815316	9.7	0.2245521	0
AMINOPYRIDINE,4-	9.589092	3663.803	273.16	0.28	9.7	0.1724783	0
AMYL ACETATE(-n)	8.06791	2186.68	273.16	1.708488	17.56	0.6019543	0
ANILINE	6.9502	1467.242	177.115	0.9	7.1	21	0
ANISIDINE,o-	7.464861	1932.244	196.5096	1.605756	15.3	0.5502056	0
ANTHRACENE	8.91	3761	273.16	4.45	31.1	2.2	0
ANTHRAQUINONE	7.289244	2411.734	167.0596	3.729464	17.56	3.528086	0
AZIRIDINE ethylene imine	9.389235	2142.318	273.16	0.1757197	15.3	0.1574373	0
BENZAL CHLORIDE	9.49223	3174.547	273.16	2.152145	10.76	0.8874708	0
BENZALDEHYDE	8.461938	2523.011	273.16	1.48	17.56	0.4928757	0
BENZENE	6.905	1211.033	220.79	2.15	19	1.4	0
BENZIDINE	7.5424	2625.8	163.256	1.81	31.1	0.6578671	0
BENZOFURAN 2,3	6.88042	1520.652	206.1996	2.625319	15.3	1.342646	0

TABLE C-2. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
BENZOIC ACID	9.033	3333.3	273	1.86	17.56	0.6872873	0
BENZONITRILE	6.74631	1436.72	181	2.046477	9.7	0.8090959	0
BENZOPHENONE	7.34966	2331.4	185	4.525765	17.56	7.08167	0
BENZOTRICHLORIDE	8.326414	2691.007	273.16	2.92	10.76	1.737565	0
BENZOYL CHLORIDE	7.9245	2372.1	273.16	1.959114	10.76	0.7495522	0
BENZO(A)ANTHRACENE	6.9824	2426.6	156.6	5.61	31.1	18.28721	0
BENZO(A)PYRENE	9.245506	3724.363	273.16	5.98	31.1	25.27833	0
BENZO(B)FLUORANTHENE	6.809279	952.6317	238.4996	6.843004	31.1	53.78881	0
BENZO(k)FLUORANTHENE	11.10133	6191.376	273.16	6.84	31.1	53.64763	0
BENZYL ALCOHOL	7.19817	1632.593	172.79	1.675986	17.56	0.5850764	0
BENZYL CHLORIDE	7.53029	1923.019	234.3478	2.3	17.75	1.010042	0
BIPHENYL	7.6317	2167.862	207.61	4.266275	19	5.643243	0
BISPHENOL(A)	8.64308	2910.876	273.16	4.651325	17.56	7.904033	0
BIS(1,1,2,2-TETRACHLOROPROPYL) ETHER	7.812044	1452.055	273.16	4.322158	10.76	5.926039	0
BIS(2-CHLOROETHYL)ETHER	8.210002	2404.325	273.16	1.58	10.76	0.5379447	0
BIS(2-ETHYLHEXYL)PHTHALATE	10.83704	5228.522	273.16	5.3	0.77	0.35	0
BIS(CHLOROMETHYL)ETHER	8.178545	1998.099	273.16	-0.38	10.76	0.0968	0
BROMACIL	6.907701	1743.059	193.8496	8.145402	15.3	168.115	0
BROMOBENZENE	6.86064	1438.817	205.441	3.229374	10.76	2.277738	0
BROMOCHLOROMETHANE	6.49606	942.267	192.587	0.9726127	10.76	0.3161761	0
BROMODICHLOROMETHANE	7.9655	1846.561	273.16	1.88	10.76	0.6994205	0
BROMOFORM	7.988101	2158.654	273.16	2.3	10.76	1.010042	0
BROMOMETHANE	7.566313	1301.449	273.16	1.1	10.76	0.3534569	0
BROMOTOLUENE 4	7.00762	1612.35	206.36	3.536277	10.76	2.979392	0
BROMOXYNIL	7.531281	2171.211	185.8696	1.989251	15.3	0.7695807	0
BUTADIENE-(1,3)	7.216854	1144.753	269.0367	1.871113	15.3	0.6940029	0
BUTANE	3.18243	0	0	1.859488	15.3	0.6869795	0
BUTANEDINITRILE	8.860728	3218.161	273.16	0.35	9.7	0.1833727	0
BUTANOL ISO	7.32705	1248.48	172.92	0.75	7.8	0.11	0
BUTANOL(S)	7.4768	1362.39	178.77	0.75	7.8	0.11	0
BUTANOL-1	7.4768	1362.39	178.77	0.83	7.8	0.11	0
BUTENE	6.805603	918.4548	240.4889	1.865313	15.3	0.6904899	0
BUTYL ACETATE(-n)	7.127	1430.418	210.745	1.79263	17.56	0.6479443	0
BUTYL ACRYLATE	8.141759	2199.925	273.16	2.105592	17.56	0.8520479	0
BUTYL BENZENE	6.98317	1577.965	201.378	4.028965	31.1	4.585114	0
BUTYL CARBITOL	7.74114	2056.904	195.655	2.202231	15.3	0.9272288	0
BUTYL CELLOSOLVE	6.956	1399.903	172.154	1.554456	15.3	0.5260546	0
BUTYLAMINE	8.649454	2025.139	273.16	0.88	9.7	0.2915654	0
BUTYLENE GLYCOL-(1,3)	9.583491	3221.718	273.16	-0.04555	17.56	0.1297253	0
BUTYLISOBUTYRATE	6.84419	1237.194	222.1596	2.53453	15.3	1.240113	0
BUTYRALDEHYDE	6.358544	913.59	185.48	1.125761	17.56	0.3615145	0
BUTYRALDEHYDE ISO	7.983729	1715.402	273.16	1.126484	17.56	0.3617431	0
BUTYRIC ACID	8.064204	2263.387	273.16	0.7236805	17.56	0.2542928	0
c10 linear	6.88042	1520.652	206.1996	4.463722	15.3	6.707476	0
CAPROLACTAM	7.243459	1997.954	187.9596	0.8215773	9.7	0.2770353	0

TABLE C-2. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
CAPTAN	10.25674	4316.929	273.16	2.92452	15.3	1.74445	0
CARBARYL sevin	11.59653	4768.904	273.16	2.36	9.7	1.064485	0
CARBENDAZIM	6.897335	1657.229	198.5996	3.384036	15.3	2.607808	0
CARBON DISULFIDE	6.942	1169.11	241.59	2.16	15.3	0.8935917	0
CARBON TETRACHLORIDE	6.9339	1242.43	230	2.72	1.5	1.5	0
CARBONYL SULFIDE	7.117189	968.5864	241.7505	-0.275866	15.3	0.1060484	0
CATECHOL	7.514789	2030.245	192.6146	0.94	31.1	0.3072813	0
CHLORACETOPHENONE,2-	8.6451	2981.1	273.16	2.594686	15.3	1.307137	0
CHLORAL	7.734462	1799.546	273.16	1.490009	15.3	0.4972112	0
CHLORAMBEN	7.427135	1629.082	211.3296	1.593383	10.76	0.5442809	0
CHLORAMBUCIL	0	0	0	3.274369	10.76	2.3692	0
CHLORDANE	9.300818	4263.922	273.16	2.78	15.3	1.537236	0
CHLORNAPHAZINE	0	0	0	3.950025	10.76	4.279104	0
CHLORO 2 BUTENE,1 trans	6.841615	1217.14	223.2996	1.349343	15.3	0.43963	0
CHLOROACETALDEHYDE	8.360256	1962.524	273.16	-0.219135	10.76	0.1114454	0
CHLOROACETIC ACID	7.55016	1723.365	179.98	-0.621223	10.76	0.0783	0
CHLOROALLYL ALCOHOL 2	9.545546	2793.597	273.16	0.3672189	10.76	0.1861564	0
CHLOROANILINE(2)	7.56265	1998.6	220	0	0.27	0.86	0
CHLOROANILINE(3)	7.55939	2073.75	215	0	0.27	0.86	0
CHLOROANILINE,p-	9.386585	3286.465	273.16	1.83	0.27	0.86	0
CHLOROAZOBENZENE	-1.120589	0	0	5.026951	10.76	10.97962	0
CHLOROBENZENE	6.978	1431.05	217.55	2.5	0.39	10	0
CHLOROBENZILATE	9.669569	4569.931	273.16	6.169221	10.76	29.82998	0
CHLOROBENZOPHENONE (PARA)	11.15672	4991.71	273.16	4.209192	10.76	5.368304	0
CHLOROBENZOTRIFLUORIDE, P	6.839732	1202.451	224.1356	2.560925	15.3	1.269087	0
CHLOROBENZYL ALCOHOL -(m)	8.235456	2309.119	194.2296	2.436677	10.76	1.138353	0
CHLOROBENZYLATE	8.326468	3133.646	160.4096	5.37252	17.56	14.8561	0
CHLOROBUTADIENE,1	6.8348	1163.8	226.3396	2.454152	15.3	1.155892	0
CHLOROETHANE (ethyl chloride)	6.986	1030.01	238.61	1.43	10.76	0.472	0
CHLOROETHYLENE	6.89117	905.01	239.48	0.6267082	10.76	0.2336062	0
CHLOROHYDRIN, a 3 CHLORO 1,2 PROPANEDIOL	8.222207	2199.559	198.7896	-0.956336	15.3	0.0584	0
CHLOROMETHYL METHYL ETHER	6.831054	1134.219	228.0306	-0.21	10.76	0.1123397	0
CHLORONAPHTHALENE,2-	8.657456	3056.778	273.16	4.12	10.76	4.965281	0
CHLORONITROBENZENE(-o)	8.376652	2831.246	273.16	2.603606	10.76	1.317378	0
CHLORONITROBENZENE, p	6.906466	1732.741	194.4196	2.603606	15.3	1.317378	0
CHLOROPHENOL-2	6.877	1471.61	193.17	2.15	15	0.8858069	0
CHLOROPHENOL-3	7.900331	2445.317	273.16	1.403233	10.76	0.4608566	0
CHLOROPHENOL-4	8.510922	2759.663	273.16	2.480466	6.5	1.182815	0
CHLOROPRENE	6.161	783.45	179.7	0.57	10.76	0.2222978	0
CHLOROPROPANE-1	6.92648	1110.19	227.94	0.9487147	10.76	0.3096333	0
CHLOROPROPANE-2	7.771	1582	288	1.048029	10.76	0.3377439	0
CHLOROPROPENE 3	5.29716	418.375	128.168	0.9545268	10.76	0.311212	0
CHLOROPROPIONITRILE,3-	7.32973	1732.55	211.79	0.422814	10.76	0.1954358	0
CHLOROPROPYLENE-2	0	0	0	1.985027	10.76	0.7667412	0
CHLOROTOLUENE-4	8.177249	2304.805	273.16	3.536277	10.76	2.979392	0

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
CHRYSENE	10.68596	5940.981	273.16	5.61	31.1	1.4	0
CRESOL	8.850432	2794.746	273.16	0	23	17	0
CRESOL(-m)	7.508	1856.36	199.07	0.97	23.21	17	0
CRESOL(-o)	7.426974	1744.32	194.444	1.98	22.78	17	0
CRESOL(-p)	7.035	1511.08	161.85	1.94	23.21	17	0
CROTONALDEHYDE	8.536501	2104.827	273.16	1.092311	17.56	0.3510868	0
CUMENE HYDROPEROXIDE	8.191144	1950.172	209.2396	2.308645	15.3	1.017711	0
CUMENE (isopropylbenzene)	6.963	1460.793	207.78	3.497709	31.1	2.880526	0
CYANOGEN	3.59986	0	0	0.8077466	9.7	0.2737029	0
CYCLOHEXANE	6.841	1201.53	222.65	2.529003	15.3	1.234131	0
CYCLOHEXANOL	6.255	912.87	109.13	1.576838	17.56	0.5364586	0
CYCLOHEXANONE	7.84918	2137.192	273.16	0.81	11.49	0.2742431	0
CYCLOHEXYLAMINE	6.68954	1229.42	188.8	1.997921	9.7	0.7754406	0
CYCLOPENTADIENE	6.823	1071	271.6	2.028058	15.3	0.7961605	0
CYMENE,para	6.881701	1530.862	205.6296	4.158295	15.3	5.134476	0
DAZOMET	6.898588	1667.51	198.0296	3.518476	15.3	2.933347	0
DDE,p,p'-	10.32563	4625.263	273.16	5.69	10.76	19.61316	0
DDT	15.19374	6564.769	273.16	6.19	15.3	30.37728	0
DIAZINON	7.284863	2370.844	169.1116	3.821204	15.3	3.822968	0
DIAZOMETHANE	6.800292	864.7323	243.6296	-0.124468	9.7	0.1210698	0
DIBENZOFURANS	6.927094	1908.791	184.7296	5.695732	31.1	19.71178	0
DIBENZOPYRENE 1,2,7,8	0	0	0	8.199224	31.1	176.2214	0
DIBROMOCHLOROMETHANE	7.288803	1733.934	273.16	2.09	10.76	0.035	0
DIBROMOETHANE-1,2	6.72148	1280.82	201.75	1.137044	10.76	0.3651012	0
DIBROMOMETHANE	1.68123	0	0	0.6958743	10.76	0.2481805	0
DIBROMO-3-CHLOROPROPANE,1,2	7.886061	2348.271	273.16	0.2066454	10.76	0.1617557	0
DIBROMO-4-HYDROXYBENZONITRILE, 3,5	7.514083	2024.306	192.8996	2.294361	15.3	1.005071	0
DIBUTYLPHTHALATE	9.386544	3955.114	273.16	5.2	0.4	1	0
DICHLORO 2-PROPANOL 1,3	9.783355	3086.549	273.16	-0.480189	10.76	0.0886872	0
DICHLORO PROPANOL 2,3	6.746815	1759.657	273.16	-0.269502	10.76	0.1066405	0
DICHLOROANILINE 2,3	7.48674	2116.834	187.5796	3.024556	15.3	1.904024	0
DICHLOROANILINE(2,3)	7.47752	2038.121	191.3796	3.024556	15.3	1.904024	0
DICHLOROBENZENE(1,2) (-o)	6.882553	1537.672	205.2496	3.38	2.5	0.58	0
DICHLOROBENZENE(1,4) (-p)	7.199	1690.291	218.09	3.39	6.4	2.3	0
DICHLOROBENZIDINE,3,3'-	7.493614	2176.46	184.7085	3.51	10.76	2.911671	0
DICHLOROBENZONITRILE,2,6-	10.40392	4086.263	273.16	3.75325	15.3	3.602285	0
DICHLOROBENZOPHENONE P,P	10.5374	4794.257	273.16	6.046987	10.76	26.80424	0
DICHLOROETHANE(1,1) ethylidenedichloride	6.992756	1176.864	228.838	1.79	10.76	2.3	0
DICHLOROETHANE(1,2)	7.068385	1292.54	225	1.45	2.1	0.98	0
DICHLOROETHENE 1,2 trans	6.9651	1141.9	231.9	1.48	10.76	0.4928757	0
DICHLOROETHENE(1,1) vinylidene chloride	6.9722	1099.4	237.2	0	10.76	0.9	0

TABLE C-2. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
DICHLOROETHYL ETHER	7.6924	1990.8	235.347	0.685801	10.76	0.2460026	0
DICHLOROETHYLENE(1,2) cis	7.0223	1205.4	230.6	2.202489	10.76	0.9274379	0
DICHLOROMONOFLUOROMETHANE	7.590301	1328.834	273.16	1.83253	10.76	0.6709645	0
DICHLOROPHENOL	7.466021	1635.588	211.7096	3.241122	15.3	2.301272	0
DICHLOROPHENOL 2,5	7.498359	1893.996	199.1696	3.241122	15.3	2.301272	0
DICHLOROPHENOL(2,4)	7.497876	1890.059	199.3596	2.75	25	3.3	0
DICHLOROPHENOL(2,6)	6.899838	1677.797	197.4596	3.241122	10.76	2.301272	0
DICHLOROPHENOXYACETIC ACID(2,4)	8.500344	1800.279	273.16	2.792008	10.76	1.553473	0
DICHLOROPROPANE 1,2	6.98	1380.1	222.8	2.28	17	1.4	0
DICHLOROPROPENE(1,3)	6.80731	1327.64	230.1337	1.98	10.76	0.7633762	0
DICHLOROPROPYLENE,1,2- (cis)	6.845289	1245.558	221.6846	2.735832	10.76	1.478961	0
DICHLOROPROPYLENE,1,2-(trans)	6.838623	1193.779	224.6296	2.568767	10.76	1.277825	0
DICHLORO-2-BUTENE 1,2	0	0	0	0.8726078	10.76	0.2896856	0
DICHLORO-2-BUTENE(1,4)	8.312499	2341.934	273.16	0.8726078	10.76	0.2896856	0
DICHLORO-2-BUTENE, 1,4	6.858446	1347.971	215.8896	0.8726076	15.3	0.2896855	0
DICHLORVOS	9.964257	3543.651	273.16	0.9334952	31.1	0.3055373	0
DIELDRIN	-6.744684	0	0	6.906134	15.3	56.84358	0
DIETHANOLAMINE	8.252672	2454.928	188.1876	-0.66325	9.7	0.0755	0
DIETHYL AMINE	5.8016	583.3	144.1	1.242518	9.7	0.4003997	0
DIETHYL ETHER	6.92032	1064.07	228.8	1.639246	17.56	0.5665672	0
DIETHYL SULFATE	7.838081	2173.876	230.36	-0.29	15.3	0.1048994	0
DIETHYL (N,N) ANILINE	7.466	1993.57	218.5	3.562567	9.7	3.048722	0
DIETHYLBENZENE P	6.9982	1588.31	201.97	4.158206	31.1	5.134077	0
DIETHYLENE GLYCOL DIETHYL ETHER	7.86919	2094.43	231.887	2.934824	15.3	1.760248	0
DIETHYLENE GLYCOL DIMETHYL ETHER	7.083	1556.26	210.37	1.781736	15.3	0.641797	0
DIETHYLENE GLYCOL MONOBUTYL ETHER	8.232163	2281.689	195.3696	2.202231	15.3	0.9272288	0
DIETHYLENE GLYCOL MONOETHYL ETHER	8.216066	2149.489	200.8796	1.33416	15.3	0.4338283	0
DIETHYLENE GLYCOL MONOETHYL ETHER ACETATE	8.208758	2090.436	203.3496	1.267111	15.3	0.4091089	0
DIETHYLENE GLYCOL MONOMETHYL ETHER	8.211577	2113.133	202.3996	0.9001058	15.3	0.2967401	0
DIETHYLHYDRAZINE N,N	0	0	0	0.6255218	15.3	0.2333639	0
DIETHYLTHIOPHOSPHATEBENZO M ETHYL PETHER	6.96702	2275.218	164.7794	4.326276	15.3	5.947427	0
DIISOBUTYLENE	6.84893	1274.031	220.0696	3.671378	15.3	3.353253	0
DIISODECYL PHTHALATE	6.987966	2483.235	153.5677	9.650949	15.3	627.6503	0
DIISOPROPYL BENZENE (PARA)	6.9933	1663.88	194.41	4.928876	31.1	10.07671	0
DIISOPROPYL KETONE	7.177119	1459.448	215.6996	2.171245	15.3	0.9024271	0
DIISOPROPYLAMINE	7.158473	1314.511	223.2996	2.210661	15.3	0.9340937	0
DIMETHOXY-(3,3')-BENZIDINE	7.051436	2436.322	273.16	3.150456	17.56	2.125762	0

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
DIMETHYL AMINE	7.08212	960.242	221.67	0.05483	9.7	0.1416346	0
DIMETHYL BENZYLAMINE N,N	-1.119923	0	0	2.526956	9.7	1.231922	0
DIMETHYL BENZ(A)ANT 7,12	0	0	0	7.456762	15.3	92.02836	0
DIMETHYL CARBAMOYL CHLORIDE	7.197148	1616.599	207.5296	1.044858	10.76	0.3368081	0
DIMETHYL DISULFIDE	6.8257	1303.5	218.4	3.410681	15.3	2.669322	0
DIMETHYL FORMAMIDE	6.928	1400.87	196.43	-0.041408	9.7	0.1301963	0
DIMETHYL HYDRAZINE(1,1)	7.408	1305.91	225.53	0.595338	15.3	0.2272812	0
DIMETHYL PHTHALATE	4.52232	700.31	51.42	1.87	2.2	3.1	0
DIMETHYL SULFATE	7.4455	1843.343	217.055	0.318303	15.3	0.1783568	0
DIMETHYL SULFIDE	7.1509	1195.58	242	1.70649	15.3	0.6009024	0
DIMETHYL TRISULFIDE	6.879565	1513.849	206.5796	5.829383	15.3	22.15714	0
DIMETHYLACETAMIDE	7.124729	1039.441	237.9296	0.05483	15.3	0.1416346	0
DIMETHYLAMINOAZOBENZENE,4-	7.498566	2219.947	182.6185	3.521143	9.7	2.940198	0
dimethylaniline N,N	7.72649	2110.009	242.88	-0.88	9.7	0.0624	0
DIMETHYLBENZIDINE 3,3	7.535748	2561.72	166.2996	4.169629	31.1	5.185646	0
DIMETHYLBENZ(A)ANTHRACENE(7,12)	10.57967	5775.389	273.16	7.456761	31.1	92.02824	0
DIMETHYLETHYLAMINE	7.08212	960.242	221.67	1.126405	9.7	0.3617182	0
DIMETHYLPHENOL(2,4)	8.926483	2930.103	273.16	2.42	10.7	4.7	0
DIMETHYLPHENOL(3,4)	0	0	0	0	5.5	1.05	0
DIMETHYLSULFONE	6.90729	1739.619	194.0396	-0.264333	15.3	0.107124	0
DIMETHYLSULFOXIDE	0	0	0	0.0361875	15.3	0.139343	0
DIMETHYLSULFOXIDE	6.886806	1571.757	203.3496	0.3634962	15.3	0.185551	0
DINITROBENZENE M	4.337	229.2	-137	1.52229	9.7	0.5114555	0
DINITROPHENOL 2,4	7.516903	2048.072	191.7596	1.54	8	0.62	0
DINITROTOLUENE 2,6	4.372	380	-43.6	2.05	9.7	0.8115939	0
DINITROTOLUENE(2,4)	7.981089	3074.44	280.23	2.01	9.7	0.7836799	0
DINITRO-o-CRESOL(4,6)	8.884898	3169.326	273.16	2.85	9.7	1.634334	0
DIOXANE(1,4)	7.350545	1517.53	238.065	1.22037	17.56	0.392715	0
DIPHENYLHYDRAZINE(1,2)	13.8359	5402.621	273.16	3.03	19	1.913115	0
DIPHENYLMETHANE	6.291	1261	105	4.798269	19	8.988508	0
DIPROPYLAMINE	2.278649	0	0	2.110636	9.7	0.8558166	0
DIPROPYLBUTRAL	7.216752	1774.272	199.3976	3.731519	15.3	3.534435	0
DIPROPYLENE GLYCOL	8.218305	2167.685	200.1196	0.1654824	15.3	0.1560334	0
DI-n-OCTYL PHTHALATE	7.001507	2621.431	146.1596	9.2	15.3	423.0154	0
dodecane	6.898254	1664.768	198.1816	5.331716	15.3	14.33503	0
ENDOSULFAN	9.318406	4269.167	273.16	3.55	15.3	3.015383	0
ENDRIN	9.681486	4883.984	273.16	5.6	15.3	18.1279	0
EPICHLOROHYDRIN	8.22943	2086.816	273.16	0.03	10.76	0.1385906	0
EPOXYBUTANE 1,2	6.83185	1140.529	227.6696	1.441351	10.76	0.4764868	0
ETHANE	6.82915	663.72	256.68	0.9913252	15.3	0.3213955	0
ETHANOL	8.321	1718.21	237.52	-0.32	8.8	0.9	0
ETHANOLAMINE(mono-)	7.456	1577.67	173.37	-0.773026	9.7	0.0686	0
ETHOXYETHANOL-2	7.874	1843.5	234.2	0.6863381	17.56	0.2461183	0

TABLE C-2. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
ETHYL ACRYLATE	7.964455	1897.011	273.16	1.5014	17.56	0.5021918	0
ETHYL CARBAMATE	7.364662	1737.454	204.4896	-0.447976	10.76	0.0912	0
ETHYL ETHER	6.92	1064.07	228.8	1.639246	17.56	0.5665672	0
ETHYL MORPHOLINE, ethyl diethylene oxime	6.894822	1636.683	199.7396	1.924971	15.3	0.7274908	0
ETHYL TOLUENE, 4	6.875279	1479.869	208.4796	3.772945	15.3	3.664899	0
ETHYL VINYL ETHER	6.820354	1047.859	232.9896	1.645062	15.3	0.5694574	0
ETHYLACETATE	7.101	1244.95	217.88	0.9244851	17.58	0.303138	0
ETHYLAMINE	7.05413	987.31	220	0.17986	9.7	0.1580087	0
ETHYLBENZENE	6.975	1424.255	213.21	3.15	6.8	2.1	0
ETHYLENE DIAMINE	7.337209	1521.051	215.3196	-0.269471	9.7	0.1066435	0
ETHYLENE DIBROMIDE	7.34485	1675.301	244.82	1.6	10.76	0.5474415	0
ETHYLENE GLYCOL	8.0908	2088.9	203.5	-0.914444	17.56	0.0606	0
ETHYLENE GLYCOL DIMETHYL ETHER	7.232956	1377.29	232.43	1.134076	15.3	0.3641545	0
ETHYLENE GLYCOL MONOBUTYL ETHER	8.19856	2008.895	206.7696	1.554456	15.3	0.5260546	0
ETHYLENE GLYCOL MONOBUTYL ETHER ACETATE	7.2159	1659.2	191.339	1.48746	15.3	0.4961033	0
ETHYLENE GLYCOL MONOETHYL ETHER ACETATE	7.377117	1641.85	209.2748	0.619354	15.3	0.2321078	0
ETHYLENE GLYCOL MONOETHYL ETHER Cellosol	8.177948	1846.634	213.6096	0.2502244	15.3	0.1680427	0
ETHYLENE GLYCOL MONOMETHYL ETHER	8.171905	1799.523	215.6046	0.2522626	15.3	0.1683427	0
ETHYLENE GLYCOL MONOMETHYL ETHER ACETATE	7.52829	1641.851	209.2747	0.185323	15.3	0.1587658	0
ETHYLENE GLYCOL MONOPHENYL ETHER	8.235456	2309.119	194.2296	1.889739	15.3	0.705406	0
ETHYLENE GLYCOL MONOPROPYL ETHER	8.176798	1837.652	213.9896	1.120402	15.3	0.3598234	0
ETHYLENE OXIDE	7.128	1054.54	237.76	-0.3	4.2	0.91	0
ETHYLENE THIOUREA	7.211493	1731.503	201.5974	-0.641652	9.7	0.077	0
ETHYLHEXYLACRYLATE,2-	6.884682	1554.707	204.2996	3.773185	15.3	3.665669	0
ETHYLPHENOL,3-	7.468	1856	187	2.4	15.3	1.102401	0
ETHYL(2) HEXANOL	9.114945	2850.004	273.16	2.643529	17.56	1.364211	0
FLUORANTHENE	6.373	1756	118	5.33	31.1	1.5	0
FORMALDEHYDE	7.195	970.6	244.1	1.94	5	0.25	0
FORMAMIDE	2.602059	19.62512	264.1977	-0.553912	17.56	0.0831	0
FORMIC ACID	7.581	1699.2	260.7	-0.924103	17.56	0.0601	0
FREON 11, fluorotrichloromethane	6.816687	1017.234	234.7566	2.576381	15.3	1.286367	0
FREON 12 DICHLORODIFLUOROMETHANE	3.698946	0	0	2.16	10.76	0.8935916	0
FREON 12, dichlorodifluoromethane	6.795418	806.5787	247.0498	2.402047	15.3	1.104378	0
FUMARIC ACID	-1.118697	0	0	-0.445571	17.56	0.0914	0

TABLE C-2. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
FURAN	6.975	1060.87	227.74	1.853527	17.56	0.6834056	0
FURFURAL	6.575	1198.7	162.8	1.578185	17.56	0.5370913	0
Generic Organic material	6.859312	1354.71	215.5096	0	19	1.1	0
GLUTARIC ACID	6.947832	2093.118	174.6596	0.0219418	17.56	0.1376169	0
GLYCERIN (GLYCEROL)	6.165	1036	28	-1.432496	17.56	0.0385	0
GLYOXAL	8.130124	1472.782	229.5696	-1.11614	15.3	0.0508	0
GLYPHOSATE	8.207067	2076.833	203.9194	-0.494987	15.3	0.0875	0
GUTHION	6.94768	2093.121	174.6594	2.708063	15.3	1.443459	0
GYLCIDOL	9.224102	2760.353	273.16	-0.381763	17.56	0.0966636	0
HEPTACHLOR	8.961409	3722.308	273.16	5.05	10.76	11.20331	0
HEPTANE ISO	6.8391	1335.41	237.2	3.162377	15.3	2.148051	0
HEPTANE(-n)	6.89677	1264.9	216.54	3.161653	15.3	2.146692	0
HEXACHLOROBENZENE	9.55388	3248.572	203.07	5.47	10.76	16.17883	0
HEXACHLOROBUTADIENE	7.485238	1956.415	215.333	3.74	10.76	3.560762	0
HEXACHLOROCYCLOHEXANE (GAMMA ISOMER)	6.966292	2268.189	165.1596	0.936952	10.76	0.3064629	0
HEXACHLOROCYCLOPENTADIENE	8.41529	2834.547	273.16	3.99	10.76	4.431426	0
HEXACHLOROETHANE	7.2284	1347.978	132.91	3.456234	10.76	2.777865	0
HEXAFLUOROACETONE	7.105094	665.0909	258.4496	4.214555	15.3	5.393552	0
HEXAMETHYLENE 1,6 DIISOCYANATE	6.914242	1798.169	190.8096	1.27331	9.7	0.4113342	0
HEXAMETHYLPHOSPHORAMIDE	6.90523	1722.428	194.9896	-0.000432	9.7	0.1349489	0
HEXANE(-n)	6.876	1171.17	224.41	2.727623	15.3	1.468376	0
HEXANOIC ACID	9.477544	3158.919	273.16	1.591822	17.56	0.5435379	0
HEXANOL-1	7.86	1761.26	196.66	1.774724	17.56	0.6378716	0
HEXEN-2-ONE 5	7.178988	1474.01	214.9396	1.344229	17.56	0.4376675	0
HYDRAZINE	8.683764	2243.776	273.16	-1.37	9.7	0.0407	0
HYDROGEN SULFIDE	6.99392	768.13	249.09	1.173106	10.76	0.3768052	0
HYDROQUINONE	9.778832	3857.106	273.16	0.59	17.56	0.2262222	0
HYDROXYACETIC ACID	3.82111	459.9652	273.16	-1.097389	17.56	0.0516	0
INDENO(1,2,3-cd)-PYRENE	9.813007	5609.269	273.16	7.66	9.7	109.9392	0
ISOBUTYLENE	6.805457	917.0536	240.5706	1.796808	15.3	0.6503171	0
ISODECANOL	8.22165	2195.003	198.9796	2.920139	15.3	1.737775	0
ISOPHORONE	7.962584	2480.726	273.16	1.7	15.3	0.5975001	0
LINDANE hexachlorocyclohexane	6.915866	1811.968	190.0496	0.936952	10.76	0.3064629	0
MALEIC ACID	7.956923	2706.393	273.16	-0.445571	17.56	0.0914	0
MALEIC ANHYDRIDE	12.6834	4638.2	273.16	0	4.08	1	0
METHACRYLIC ACID	11.26555	3657.094	273.16	0.6610121	17.56	0.2407243	0
METHANOL	7.897	1474.08	229.13	-0.7	18	0.2	0
METHOMYL	20.8751	7506.508	273.16	-0.301311	15.3	0.1037134	0
METHOXYCHLOR	6.951463	2128.043	172.7596	6.571831	17.56	42.42731	0
METHYL 1-PENTENE 2	6.83529	1121.3	229.687	2.664926	15.3	1.389991	0
METHYL ACETATE	7.065	1157.63	219.73	-0.09	19.87	0.1247767	0
METHYL ACRYLATE	6.838646	1193.779	224.6296	0.9331476	17.56	4.3	0
METHYL AMINE	7.3369	1011.5	233.3	-0.530324	9.7	0.0848	0

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
METHYL AZIRIDINE 2	0	0	0	0.6105353	9.7	0.2303237	0
METHYL BENZYL ALCOHOL 4	9.069858	3021.253	273.16	2.385993	17.56	1.088972	0
METHYL CHLORIDE	7.093	948.58	249.34	1.92	10.76	0.7243333	0
METHYL CHOLANTHRENE 3	-3.119754	0	0	7.430058	31.1	89.90299	0
METHYL CYCLOHEXANE	6.823	1270.76	221.42	2.963777	15.3	1.805412	0
METHYL ETHER dimethyl ether	3.59986	0	0	0.6286275	17.56	0.2339989	0
METHYL ETHYL KETONE, 2 butanone	7.11243	1305.006	229.2666	0.28	2	0.2	0
METHYL FORMATE	3.027	3.02	-11.9	0.0940167	17.56	0.1465752	0
METHYL HYDRAZINE	6.5762	1007.5	181.4	-0.478592	9.7	0.0888	0
METHYL IODIDE	7.657383	1507.3	273.16	1.69	0	0.5922948	0
METHYL ISOBUTYL KETONE	6.672	1168.4	191.9	1.38	0.74	0.4515826	0
METHYL ISOCYANATE	6.822807	1067.989	231.8306	2.84454	9.7	1.626545	0
METHYL ISOPROPYL KETONE	5.483397	955.5712	273.16	0.9050759	15.3	0.2980333	0
METHYL MERCAPTAN	6.808206	942.8276	239.0696	1.173106	15.3	0.3768052	0
METHYL METHACRYLATE	6.5168	1052.176	188.37	1.295875	17.56	4.3	0
METHYL MORPHOLINE	7.173846	1433.993	217.0296	1.357002	15.3	0.4425861	0
METHYL NAPTHALENE(1-)	7.03592	1826.948	195	4.132105	24.03	5.018151	0
METHYL NAPTHALENE(2-)	7.0685	1840.264	198.4	4.132105	31.1	5.018151	0
METHYL PARATHION	-5.008742	0	0	2.04	15.3	0.8045235	0
METHYLENE CHLORIDE, dichloromethane	6.968411	1074.291	222.995	1.25	22	0.4	0
METHYLENE DIPHENYL DIISOCYANATE	6.942754	2048.169	177.1085	3.308513	9.7	2.441051	0
METHYLENE DIPHENYLAMINE (MDA)	6.946537	2082.649	175.2296	3.379612	15.3	2.597734	0
METHYLENEDIANILINE 4,4	7.501696	2247.655	181.2885	2.633374	9.7	1.352142	0
METHYLENE-BIS (2-CHLOROANILINE),4,4'-	7.513116	2350.365	176.3696	4.900831	9.7	9.832447	0
METHYLSTYRENE (-4)	7.0112	1535.1	200.7	3.463532	31.1	2.795661	0
METHYL-TERTIARY-BUTYL ETHER	6.85249	1103.737	222.72	1.90147	17.56	0.712684	0
MONOMETHYL FORMANIDE	7.204987	1679.083	204.2996	-0.678949	15.3	0.0745	0
MORPHOLINE	7.71813	1745.8	235	-1.08	9.7	0.0524	0
NABAM	7.303247	2548.42	160.2196	-1.646165	15.3	0.0319	0
NAPHTHALENE	7.3729	1968.36	222.61	3.37	42.47	1	0
NAPHTHOL,alpha-	7.28421	2077.56	184	3.076284	17.56	1.992183	0
NAPHTHOL,beta-	7.347	2135	183	2.84	17.56	1.620096	0
NAPHTHYLAMINE,alpha-	7.49977	2230.587	182.1076	2.22	9.7	0.9417578	0
NAPHTHYLAMINE,beta-	7.502136	2251.572	181.1006	2.25	9.7	0.9668059	0
NEOPENTYL GLYCOL	8.219421	2176.788	199.7396	0.3583827	17.56	0.1847226	0
NITRO m XYLENE, 2	6.901502	1691.519	196.6996	3.067034	15.3	1.976124	0
NITROANILINE P	9.5595	4039.73	273.16	1.182549	9.7	0.3799313	0
NITROBENZENE	7.115	1746.6	201.8	1.84	11	2.3	0
NITROBIPHENYL,4-	6.947679	2093.118	174.6596	3.945698	19	4.262934	0

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
NITROGLYCERIN	9.636311	3601.771	273.16	0.6459801	9.7	0.2375789	0
NITROMETHANE	7.28166	1446.94	227.6	0.0639644	9.7	0.1427711	0
NITROPHENOL,2-	11.86137	4392.938	273.16	1.79	9.7	0.6464548	0
NITROPHENOL,4-	10.95784	4459.823	273.16	1.91	9.7	0.7180231	0
NITROPROPANE 2	7.271697	1530.544	228.62	1.283951	9.7	0.4151816	0
NITROSODIMETHYLAMINE N	7.5239	1974.062	273.16	-0.47	9.7	0.0894	0
NITROSOMORPHOLINE	7.183389	1813.598	196.5096	-0.44	9.7	0.0918	0
NITROSO-N-METHYLUREA N	7.362276	1718.378	205.4396	0.185811	9.7	0.1588336	0
NITROTOLUENE (-p)	6.9948	1720.39	184.9	2.45499	9.7	1.156741	0
NITROTOLUENE, m	6.903989	1712.12	195.5596	2.45499	15.3	1.156741	0
NITROTOLUENE, o	6.901917	1694.951	196.5096	2.45499	15.3	1.156741	0
NITROTOLUENE, o	6.901917	1694.951	196.5096	2.45499	15.3	1.156741	0
NONANOL, n	8.223319	2208.672	198.4096	3.076832	15.3	1.993139	0
OCTANE	6.918	1351.99	209.15	3.595688	15.3	3.138369	0
OCTANOL 1	12.0701	4506.8	319.9	2.642804	17.56	1.363345	0
OCTANOL 2	6.3888	1060.4	122.5	2.643529	17.56	1.364211	0
OCTANOL 3	5.2215	560.3	64.7	2.643529	17.56	1.364211	0
OCTANOL 4	5.7396	760.5	89.5	2.643529	17.56	1.364211	0
OIL	0	0	0	5.331716	15.3	14.33503	0
OXALIC ACID	16.86465	5987.326	273.16	-1.280351	17.56	0.044	0
PARALDEHYDE	7.286656	1754.238	273.16	2.303315	17.56	1.012976	0
PARATHION	9.10235	4032.563	273.16	3.055472	15.3	1.956233	0
PCB'S (Aroclors)	-6.785018	-5599.125	273.16	7.308553	19	80.83541	0
PENTACHLOROBENZENE	9.054626	3396.595	273.16	5.96656	10.76	24.98281	0
PENTACHLOROETHANE	6.74	1378	197	2.718297	10.76	1.456443	0
PENTACHLORONITROBENZENE	6.954095	2152.518	171.4296	5.645749	10.76	18.86828	0
PENTACHLOROPHENOL	8.119069	3054.752	273.16	5.01	130	3.4	0
PENTADIENE 1,2	6.9182	1104.991	228.85	2.068878	15.3	0.8251115	0
PENTAERYTHRITOL	8.229961	2263.417	196.1296	-1.547323	15.3	0.0348	0
PHENOL	7.133	1516.79	174.95	1.46	97	13	0
PHENYLCYCLOHEXANONE 4	-0.708	106.4	-146.6	3.692797	17.56	3.41669	0
PHENYLENE DIAMINE(-m)	7.984773	2843.732	273.16	0.8427868	9.7	0.2822246	0
PHENYLENE DIAMINE(-o)	9.250531	3383.349	273.16	0.8427868	9.7	0.2822246	0
PHENYLENE DIAMINE(-p)	9.309744	3472.661	273.16	0.8427868	9.7	0.2822246	0
PHENYLPHENOL P	8.6575	3022.8	216.1	3.822525	17.56	3.827388	0
PHOSGENE (decomposes)	6.842	941.25	230	1.179	15.3	0.3787535	0
PHOSPHINE	3.301009	0	0	2.344077	15.3	1.049757	0
PHTHALIC ACID	7.879505	1728.354	273.16	0.8225744	17.56	0.2772771	0
PHTHALIC ANHYDRIDE	8.022	2868.5	273.16	-0.62	17.56	0.0784	0.000555
PHTHALIMIDE	8.300783	1857.213	273.16	0.8427868	9.7	0.2822246	0
PINENE(alpha-)	6.8525	1446.4	208	3.937396	15.3	4.232081	0
PIPERAZINE	8.57357	2386.184	273.16	0.4268957	15.3	0.196135	0
PROPANE	6.80338	804	247.04	1.425412	15.3	0.4698876	0
PROPANE SULTONE,1,3-	7.256331	2110.189	182.2596	-2.82	15.3	0.0114	0
PROPANOIC ACID	6.866276	1409.059	212.4506	0.2895945	17.56	0.1739324	0

TABLE C-2. COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
PROPANOL	7.84767	1499.21	204.64	0.4913113	17.56	0.2075073	0
PROPANOL ISO	8.117	1580.92	219.61	-0.16	15	0.075	0
PROPENE	6.794065	787.2845	248.1896	1.43124	15.3	0.4722896	0
PROPIOLACTONE b	7.982566	2221.617	273.16	0.4909006	17.56	0.2074327	0
PROPIONALDEHYDE	7.2088	1235.771	237.47	0.691664	17.56	0.2472678	0
PROPIONIC ACID	6.403	950.2	130.3	0.2895945	17.56	0.1739324	0
PROPORUR (Baygon)	7.236959	1942.436	190.7885	2.322595	9.7	1.030209	0
PROPYL ACETATE ISO	6.843416	1231.175	222.5016	1.359286	17.56	0.4434716	0
PROPYL AMINE ISO	11.00768	2488.127	273.16	0.894336	9.7	0.2952457	0
PROPYL ETHER ISO	6.834991	1165.131	226.2636	2.653113	17.56	1.375699	0
PROPYLENE	6.77811	770.85	245.51	1.43124	15.3	0.4722896	0
PROPYLENE CHLOROHYDRIN	8.176797	1837.652	213.9896	-0.003456	15.3	0.1345924	0
PROPYLENE GLYCOL	8.208243	2085.9	203.5396	-0.479632	17.56	0.0887	0
PROPYLENE OXIDE	7.0671	1133.267	236.1054	0.235614	17.56	0.1659081	0
PROPYLENIMINE 1,2 2 methyl aziridine	7.1502	1249.718	226.7196	0.6105354	9.7	0.2303237	0
PROPYL(-n) ACETATE	7.016	1282.28	208.6	1.358564	17.56	0.4431913	0
PROPYL(-n) BENZENE	6.95142	1491.297	207.14	3.594934	31.1	3.1363	0
PROPYN-1-OL 2(PROPARLGYL)	8.993223	2364.043	273.16	0.2602102	17.56	0.1695174	0
PYRIDINE	7.041	1373.8	214.98	0.65	35.03	0.238416	0
QUINOLINE	7.3838	2300.405	273.16	2.03	31.1	0.7975147	0
QUINONE	7.148885	1239.346	227.2685	1.016473	9.7	0.3285457	0
RESORCINOL	6.924308	1884.547	186.0596	0.8	17.56	0.271854	0
SILVEX	0	0	0	4.072398	15.3	4.76272	0
SODIUM FORMATE	-3.119232	0	0	-0.439411	0	0.0919	0
STYRENE	6.945357	1437.432	208.38	3.16	31.1	0.11	0
STYRENE OXIDE	6.888923	1588.822	202.3996	2.644778	17.56	1.365701	0
SUCCINIC ACID	-3.118326	0	0	-0.412145	17.56	0.0941278	0
TAMARON (METHAMIDIPHOS)	7.309743	1307.183	226.1496	0.5316042	15.3	0.2149536	0
TEREPHTHALIC ACID	6.930848	1941.731	182.9246	0.8225744	15.3	0.2772771	0
TERPINEOL, ALPHA	8.180823	1869.102	212.6596	3.182377	15.3	2.185972	0
TETRACHLOROBENZENE(1,2,3,4)	8.872679	3158.681	273.16	5.206064	10.76	12.84254	0
TETRACHLOROBENZENE(1,2,3,5)	8.821956	3084.413	273.16	5.206064	10.76	12.84254	0
TETRACHLOROBENZENE(1,2,4,5)	8.821956	3084.413	273.16	4.51	10.76	6.984653	0.42
TETRACHLORODIBENZO-p-DIOXIN(2,3,7,8)	6.977444	2377.268	159.2696	6.64	10.76	45.03498	0
TETRACHLOROETHANE(1,1,2,2)	6.893793	1354.506	192.43	2.56	6.2	0.68	0
TETRACHLOROETHENE	6.976	1386.92	217.53	2.6	6.2	0.68	0
TETRACHLOROPHENOL(2,3,4,6)	9.168764	2748.848	273.16	4.762268	10.76	8.709778	0.35
TETRACHLOROPHENOL(2,3,5,6)	-1.999987	0	0	4.762268	10.76	8.709778	0
TETRAETHYL LEAD	8.56581	2689.922	273.16	2.392857	0	1.095533	0
TETRAETHYLDITHIOPYROPHOSPHATE	11.84911	5454.172	273.16	1.656811	15.3	0.5753421	0

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
TETRAETHYLENE PENTAMINE	7.386298	1913.731	195.7494	0.1216321	15.3	0.15016	0
TETRAFLUOROMETHANE	6.882466	386.9427	272.6996	2.89165	15.3	1.694992	0
TETRAHYDROFURAN	6.995	1202.29	226.25	1.440628	17.56	0.4761852	0.604
TETRALIN	7.07055	1741.3	208.26	3.763707	15.3	3.635396	0
TETRANITROMETHANE	8.350471	2183.276	273.16	0.4822038	9.7	0.2058602	0
THIOUREA	4.247091	621.8834	273.16	0.8612069	9.7	0.2868102	0.46
THIOUREA,1-(o-CHLOROPHENYL)-	11.46513	5117.637	273.16	2.166816	9.7	0.898937	0
TOLUENE	6.954	1344.8	219.48	2.69	73.48	2.4	0
TOLUENE DIAMINE(2,4)	7.492203	2164.173	185.2996	1.454882	9.7	0.4821615	0.07
TOLUENE DIISOCYANATE(2,4)	6.912613	1784.378	191.5696	6.803719	9.7	51.97128	0
TOLUENEDIAMINE(2,6)	0	0	0	1.454882	9.7	0.4821615	0
TOLUENEDIAMINE(3,4)	7.483529	2089.257	188.9096	1.454882	9.7	0.4821615	0
TOLUENESULFONYL CHLORIDE	6.930257	1936.527	183.2096	2.188507	15.3	0.9161608	0
TOLUIC ACID (para-)	10.50106	4177.125	273.16	2.105137	17.56	0.8517082	0.81
TOLUIC ALDEHYDE	9.005018	2922.234	273.16	2.285832	17.56	0.9975978	0
TOLUIDINE m	7.454377	1846.317	200.6896	2.115259	15.3	0.8592852	0
TOLUIDINE P	7.77229	2317.386	273.16	1.39	31.1	0.4555512	0
TOLUIDINE (-0)	7.19724	1682.94	191.138	2.115272	31.1	0.8592948	0
TOXAPHENE	5.707643	1857.691	273.16	3.3	15.3	2.422935	0
TRIBUTYL PHOSPHOROTRITHIOATE SSS	6.901398	2987.955	273.16	4.803134	17.56	9.026857	0
TRIBUTYL TIN ACETATE	6.91708	1822.323	189.4796	5.463342	15.3	16.08485	0
TRIBUTYLPHOSPHATE	6.0038	1755.628	273.16	5.430991	17.56	15.63593	0
TRICHLOROBENZENE 1,2,3	6.900254	1681.226	197.2696	4.445513	10.76	6.601452	0
TRICHLOROBENZENE 1,2,4	7.7056	2242.67	252.836	3.98	10.76	4.392822	0.55
TRICHLOROBENZENE 1,3,5	8.598745	2754.108	273.16	4.445513	10.76	6.601452	0
TRICHLOROETHANE 1,1,1 methyl chloroform	6.827401	1147.14	218.5387	2.49	3.5	0.74	0.39
TRICHLOROETHANE 1,1,2	7.1921	1480.319	229.0943	2.17	3.5	0.74	0
TRICHLOROETHYLENE	6.518	1018.6	192.7	2.29	3.9	0.88	0.12
TRICHLOROFLUOROMETHANE	6.884	1043.004	236.88	2.53	10.76	1.235208	0
TRICHLOROPHENOL 2,4,5	8.577468	2974.575	273.16	4.001704	15.3	4.477043	0
TRICHLOROPHENOL 2,4,6	9.696309	3528.119	273.16	3.69	15.3	0.26	0
TRICHLOROPROPANE 1,1,1	11.56902	3302.916	273.16	0.2066454	10.76	0.1617557	0.07
TRICHLOROPROPANE(1,1,2)	8.218203	2205.203	273.16	1.654597	10.76	0.5742285	0.009
TRICHLOROPROPANE(1,2,2)	11.14517	3282.281	273.16	1.426414	10.76	0.4702994	0
TRICHLOROPROPANE(1,2,3)	6.903	788.2	243.23	0.2066454	10.76	0.1617557	0
TRICHLORO-1,2,2-TRIFLUOROETHANE,1,1,2-	7.637469	1526.226	273.16	3.456217	10.76	2.777823	0
TRIETHANOLAMINE	8.287391	2762.499	175.5336	-1.75	9.7	0.0291	0
TRIETHYLAMINE	6.958867	1271.96	223.262	2.359257	9.7	1.063793	0
TRIETHYLENE GLYCOL DIMETHYL ETHER	6.898169	1664.082	198.2196	2.429506	15.3	1.131232	0
TRIFLUOROETHANE(1,1,1)	3.965647	0	0	2.703412	10.76	1.437597	0

TABLE C-2.   COMPOUND PROPERTIES FOR ORGANIC COMPOUNDS, II

COMPOUND NAME	A	B	C	LN(OW)	Kmax mg/g-hr	k1 L/g-hr	RT HYD 1/s
TRIFLURALIN	6.937691	2002.526	179.5996	5.355146	9.7	14.63195	0
TRIISOBUTYLENE	6.894822	1636.683	199.7396	5.303749	15.3	13.98851	0
TRIISOPROPYLAMINE	6.900255	1681.23	197.2694	4.965421	15.3	10.40413	0
TRIMETHYL BENZENE, 123	6.880847	1524.055	206.0096	3.999725	15.3	4.469296	0
TRIMETHYLBENZENE (1,3,5)	7.07436	1569.22	209.58	3.999725	31.1	4.469296	0
TRIMETHYLPENTANE 2,2,4	6.797857	1249.485	219.7695	3.567022	15.3	3.06063	0
TRINITROTOLUENE(2,4,6)	-1.337234	0	0	0	4.4	0.45	0
TRIPROPYLENE GLYCOL	8.236003	2313.693	194.0396	2.126133	15.3	0.8675004	0
UREA	8.555151	2304.696	273.16	-0.469833	9.7	0.0894	0.15
URETHANE	7.421	1758.21	205	0.4310978	9.7	0.1968575	0.51
VINYL ACETATE	7.21	1296.13	226.66	0.930263	17.56	0.3046745	0
VINYL ACETYLENE	6.790945	726.4801	251.7996	1.652999	15.3	0.5734261	0
VINYL BROMIDE	6.814487	998.5032	235.8396	1.066461	10.76	0.343235	0
VINYL CHLORIDE	6.9907	969.0518	250.5856	0.06	10.76	0.1422767	0.88
VINYLIDENE CHLORIDE see 1,1dichloroethen	6.972	1099.4	237.2	0	10.76	0.9039771	0
WARFARIN	9.979672	4466.33	273.16	5.387373	15.3	15.05042	0
XYLENE	7.940135	2090.317	273.16	3.15	40.8	1.8	0.091
XYLENE(-m)	7.009	1462.266	215.11	3.2	31.1	2.219942	0.07
XYLENE(-o)	6.998	1474.679	213.69	2.95	40.79	1.8	0.12
XYLENE(-p)	6.99	1453.43	215.31	3.15	31.1	2.124915	0
XYLENOL(3,4)	7.07919	1621.45	159.26	0.1	17.56	0.1473445	0
XYLIDINE dimethylaniline	7.461541	1904.87	197.8396	2.727331	15.3	1.468	0

TECHNICAL REPORT DATA

(Please read Instructions on reverse before completing)

1. REPORT NO. EPA-453/R-94-080A	2.	3. RECIPIENT'S ACCESSION NO.

4. TITLE AND SUBTITLE Air Emissions Models for Waste and Wastewater	5. REPORT DATE November 1994
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Emission Standards Division (MD-13) Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	10. PROGRAM ELEMENT NO.
	11. CONTRACT/GRANT NO. 68-D1-0118
12. SPONSORING AGENCY NAME AND ADDRESS Office of Air Quality Planning and Standards U.S. Environmental Protection Agency Research Triangle Park, NC 27711	13. TYPE OF REPORT AND PERIOD COVERED
	14. SPONSORING AGENCY CODE EPA/200/04

15. SUPPLEMENTARY NOTES

16. ABSTRACT

Analytical models are presented for estimating air emissions from waste and wastewater collection and treatment units. Air emission models have been developed for collection and treatment units, aerated and non-aerated surface impoundments, land treatment facilities, landfills, and waste piles. Emission model predictions are compared to available field data.

This report is the documentation for the computer models Chemdat8 (EPA-453/C-94-080B) and Water8 (EPA-453/C-94-080C).

Appendices include a list of physical-chemical properties for approximately 500 compounds and a comprehensive source list of pertinent literature in addition to that cited in the report.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Emission Models Air Emission Models Air Pollution Air Emissions from Waste/Wastewater Waste Wastewater	Air Pollution control	

18. DISTRIBUTION STATEMENT Release Unlimited, available from the OAQPS TTN bulletin board and NTIS	19. SECURITY CLASS *(Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(Page)* Unclassified	22. PRICE

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