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I am submitting herewith a thesis written by Paul Douglas Dunbar entitled " The Feasibility of Predicting the Stripping of Organics in a Biological System Using UNIFAC. " I have examined the final copy of this thesis for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Master of Science, with a major in Chemical Engineering.

Paul R. Bienkowski, Co-Chairperson

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I have read this thesis and recommend its acceptance:

Accepted for the Council:

Vice Provost
and Dean of the Graduate School

The Feasibility of Predicting the Stripping of Organics in a Biological System Using UNIFAC

A Thesis

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Abstract

A simple empirical model based on Henry's law has been developed by Blackburn to predict stripping rate coefficients in biological systems. This research tests the usefulness of this empirical model for accurately predicting the stripping rate coefficients of volatile organics in waste water treatment plants and to serve as an analytic tool in laboratory biodegradation kinetic studies. The stripping rate coefficients of naphthalene from aqueous solutions were predicted by the model and determined experimentally. The empirical model accurately predicted the experimental stripping rate coefficients in water systems. The Henry's law constant for naphthalene was calculated with UNIFAC (Universal Quasichemical Functional Group Activity Coefficients).

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List of Nomenclature

English symbols

a = interfacial area (m^2)
a_{mn} = group interaction parameter resulting from energy interactions between groups m and n
a_{ij} = system's temperature energy function in UNIQUAC
A = parameter used in Wilson's equation evaluated from binary data.
A1,2 = coefficient which depends on nature of solute and solvent functional groups j in Pierotti's equation
b,m = power constants of the equation
B2 = coefficient which depends only on nature of solvent functional groups j
C1 = coefficient which depends only on solute function group
Cs* = dissolved oxygen sat. conc. at 20°C (mg/L)
Cg1 = concentrations in the gas
Cg2 = concentrations in the gas
D = coefficient independent of solute and solvent function groups
D_i = diffusivity constant in water (cm^2 /sec)
d_i = diameter of impeller (m)
D_p = pressure drop (Pa)
do = diameter of orifice (m)
F2 = coefficient which essentially depends only on nature of solvent function group.
f^L = standard state fugacity of the solute in the liquid phase
f^V = standard state fugacity of the solute in the vapor phase
g = acceleration of gravity (9.80 m/sec^2)
gc = gravitational conversion factor (1.0 kg-m/N-sec^2)
g^E = Gibbs excess energy
g_{ij} = energies of interaction between the molecules
G_m = Gibbs energy of mixing
H_c = Henry's law Constant (torr-l/g mole)
H_i = Henry's Law Constant Dimensionless
H_p = Henry's Law Constant (torr)
HP = total aeration horsepower (HP)
$K_{st}ao$ = stripping rate (hr^{-1})
kl_{st} = liquid film mass transfer (m/hr)
kg_{st} = gas film mass transfer coffficient (m/hr)

k = 1,2,.. N(number of groups in solution)
l_i = a parameter drived from Van der Waals constants
kla_{o2} = oxygen reaeration rate constant
lpm = liters per minute (L/min)
m, p = 1,2,...N(number of groups in the solution)
M_b = molecular weight of solvent kg/kmol
M1 = moles
M2 = moles
$n_{1,2}$ = number of moles
N = impeller speed
N1,2 = number of carbon atoms in solute and solvent respectively
No = standard oxygen transfer rate (lbs O_2/HP/hr)
P = total pressure (torr)
P^V = vapor pressure of the solute (torr)
q = molecular area fraction
Qair = air flow (L/min)
r_i = volume parameter from Van der Waals equation
r_{st} = rate of stripping (g/l-hr)
R = Universal gas constant (62.36 torr-l/gmole-K)
Re = Reynolds number
Re_g = Reynolds number of gas
R_k = group volume parameter for group k
T = absolute temperature (K)
T_i = diameter of vessel (m)
Q_k = the group area parameter for group k
q = pure component molecular constant
q' = pure component molecular constant for water and alcohols
V = volume of waste water basin (10^6 L)
V = volume of tank (L)
V = molar volume (L/mole)
V_o = gas velocity through orifice (m/sec)
V_t = Terminal velocity of gas bubble (m/sec)
V = volume of fluid (L)
Vw1 = liquid volume (L)
Vw2 = liquid volume (L)
Vg1 = gas volume (L)
Vg2 = superfical velocity
x_m = mole fraction of group m in the solution
x_i = mole fraction of comp i
x = Association parameter for water
y_i = mole fraction of solute in the vapor
z = power constant used to describe degree of mixing in waste treatment tanks

Greek Symbols

α_{ij} = a function of the solution's randomness.
α,θ = oxygen transfer correction factors
γ_i^{∞} = activity coefficient of the solute at infinite dilution
γ_i = activity coefficient of the solute
γ_i^{c} = combinatorial contribution to the activity coefficient
γ_i^{R} = residual contribution to the activity coefficient
Γ_k = residual activity coefficient of group k at Temp T
$\Gamma_{k(i)}$ = residual reference activity coefficient
θ_i = surface area parameter from Van der Waals equation
θ_m = group area fraction of group m in the solution
θ_i' = surface area parameter for alcohols and water
λ_{ij} = energies of interaction between the molecules.
Λ_{ij} = Wilson's adjustable parameter
μ_g = viscosity of gas (kg/m-sec)
μ_a = solution viscosity (kg/m-sec)
$\nu_{k(i)}$ = number of groups of kind k in molecule i
ν_a = solution molal volume
ρ_l = density of the liquid (g/cm^3)
ρ_g = density of gas (g/cm^3)
$\nu_{m(j)}$ = the number of groups of type m in comp.
$\nu_{p(j)}$ = the number of groups of type p in comp. j
ν = viscosity of water (kg/m-sec)
σ = surface tension (N/m)
υ_l = molar volumes (L/mole)
ϕ_l = liquid phase fugacity coefficient
Φ_i = molecular volume fraction of comp i
Ψ_{mk} = group interaction parameter of kind k
Ψ_i = diffusivity correction coefficient

I. Introduction

The fates of organic chemicals in biological systems are controlled by three mechanisms: stripping into the dispersed air, sorption onto the biomass, and bio-oxidation by the microbial population. All three mechanisms are significant and need to be accounted for in the quantitative prediction of removing chemicals from a wastewater treatment facility. The proper operation of a wastewater treatment facility requires that all of the organic wastes be completely oxidized.

Stripping is an important factor in fate analysis due to a combination of the high air rates in the aerobic fermentations and the large positive activity coefficients exhibited by many nonpolar organic molecules in water. The loss of these organics from aqueous solutions creates a potential air pollution and control problem. In order to properly control a waste treatment facility to minimize air pollution, these stripping rates must be known.

In a commercial wastewater treatment facility, specific chemicals coming into the facility are not measured. Only surrogate variables such as Biochemical Oxygen Demand (BOD) or Chemical Oxygen Demand (COD) are used to indirectlly measure the amount of organics present in the influent and effluent (Benefield, 1987). BOD is the amount of oxygen required by bacteria to degrade organic molecules, and COD is defined as the amount of oxygen required to chemically oxidize organics (Benefield, 1987). Unless more specific

chemical tests are used to measure for non-polar organics and the facilities respond in a manner which minimizes the stripping effect of these volatile organics, they will certainly become an atmospheric pollulant (Barton, 1987). These pollutants are significant enough to raise concern because approximately 10% of the organics in waste water are volatile; therefore, a health hazard to the employees of a wastewater treatment facility as well as to the surrounding community (Roberts b, 1983; Dunavant, 1986). Another solution to the stripping problem would be to enclose the aerobic treatment tanks and recirculate the airflow in order to increase the time for bacterial degradation. Alternately, stripping is a tool which could be used for purging potential drinking water of volatile organics (Roberts a, 1984).

The volatization and stripping of chemicals both involve mass transfer mechanisms where a chemical transfers from the liquid phase to the vapor phase. However, the differences between the stripping and the volatization of chemicals in a wastewater treatment tank should be distinguished. The volatization of a chemical is insignificant compared to stripping (Blackburn, 1984). The volatization of a chemical occurs as it diffuses across the interface of a body of water, such as at the surface of a lake in laminar flow conditions. Stripping occurs when a gas is dispersed into water, such as at the bottom of an aerobic tank, where the bubble diffusers are located in many facilities. The interfacial area is much greater for stripping. Studies (Roberts, 1984) have shown that equilibrium between the volatile organics and the air bubbles is a good assumption; therefore Henry's law is valid for the chemical equilibrium between the gas and liquid phases. Many

aerobic tanks are in excess of 15 feet deep; therefore, the gas in the bubble has had sufficient time to come into equilibrium with the organics in the liquid phase (Benefield, 1987).

The development of biodegradation models from laboratory scale experiments requires a knowledge of the variation of the liquid phase concentration of the organic substrates with time. In many cases these concentrations are so low in the liquid phase that standard GC and HPLC analysis are unable to accurately detect them. The sensitivity for vapor phase analysis is much greater than liquid phase analysis and the concentration of these organics in the reactor offgas can be determined with a great deal of precision. If the vapor phase concentration can be measured and the Henry's law constant is known then the liquid phase concentration is also known. The ability to predict the liquid phase concentration of trace organics from a knowledge of their vapor phase concentrations and the air flow rate would be a valuable research tool.

The following empirical equation (Blackburn, 1984) which correlates stripping rate coefficients with Henry's law constants was used to predict the stripping rates in this paper.

(1) $K_{st}a_o = (Q_{air}/v)\, bH_c^{m}$

Q_{air} = air flow L/min

V = volume of tank L

b,m = power constants of the equation

b = 3.71 x 10-3, m = 1.045

$K_{st}a_o$ = stripping coefficient hr^{-1}

This empirical equation is based on previous stripping experiments of toluene,1-4 dichlorobenzene and methyl ethyl ketone in pure water. These compounds were chosen beause of their wide range of Henry's law constants. Toluene has a high constant of 2769.0 torr-l/gmole; whereas phenol has a very low value of 0.25 torr-l/gmole. In this equation stripping is a function of air flowrate, volume of the system, and the compound's Henry's law constant.

The major assumption is that an equilibrium is reached between the liquid and gas phase concentrations before the gas phase (bubbles) leaves the liquid phase. Studies have shown that equilibrium is reached very quickly in stripping processes in a diffused aeration system with turbulence (Blackburn, 1984). In addition, Henry's law constants vary as much as +/- 35% in complex mixtures such as waste water systems where the presence of salts, surfactants and humic material exists. (Yurteri, 1987) A reasonable goal would be the ability to predict within +/- 50% of the actual value.

II. Background

Polyaromatics in Water Solutions

Many nonpolar organic molecules exhibit low water solubilities resulting from a repulsive force which is generated by the interaction of the intermolecular potentials of water and the organic molecules. These repulsive forces and the resulting dilute solutions cause the organic molecules to exhibit very large positive deviations from ideal behavior. In dilute solutions, the organic molecule is surrounded by water molecules leading to a high energy state for the organic; then the organic molecule is literally pushed out of the liquid phase. The infinite dilution activity coefficients in these situations can be quite large (>1000) (Thomas, 1982). In this dilute region, where the organic is surrounded only by water molecules as nearest neighbors, the activity coefficient is a constant and does not change with solute concentration. Infinite dilution activity coefficients need to be calculated or experimentally determined in order to evaluate the degree of nonideality of the PAH/water solution.

For dilute solutions, the solubility of the dilute species in the liquid phase is correlated with Henry's law (Prausnitz, 1986). The term on the left in equation 2 is the vapor phase fugacity (f^V), and the term on the right is the liquid phase fugacity (f^L). Thermodynamic equilibrium is acheived when the fugacity of the liquid equals the fugacity of the vapor.

(2) $f^V = f^L$

(3) $f^V = \phi_i y_i P$

(4) $f^L = \gamma_i x_i f^o$

At low pressures (atmospheric) $\phi_i = 1.0$ and $f^o = P^V$.

For dilute systems, the liquid phase fugacity can be approximated by $H_p x_i$ where H_p, the Henry's law constant, is defined as

(5) $$H_p = \frac{\text{limit } f^L/x_i}{x_i \to 0} = P^V \gamma_i^\infty$$

A Henry's law constant is derived by substituting equations 3, 4, and 5 into 2 and keeping in mind that we are dealing with dilute systems at atmospheric pressures.

(6) $y_i P = H_p x_i$

Where:

P = total pressure (torr)

H_p = Henry's law (torr)

x_i = mole fraction of solute in the liquid

y_i = mole fraction of solute in the vapor

γ_i^∞ = activity coefficient of the solute at infinite dilution

f^o = standard state of the fugacity

f^L = fugacity of the solute in the liquid phase

P^V = vapor pressure of the solute (torr)

ϕ_i = liquid phase fugacity coefficient

Calculating a Henry's law constant reduces to finding the infinite dilution activity coefficient of the solute. UNIFAC was used to estimate the infinite dilution activity coefficients in this paper.

A dimensionless Henry's law constant is expressed in terms of concentrations and mole fractions in equation 6.

$$(6) \qquad H_i = \frac{Hc}{RT} = \frac{C_{air}}{C_{water}} = \frac{y_i}{x_i}\left[\frac{MW_i/MW_{air}}{MW_i/MW_{water}}\right]\frac{\rho_{air}}{\rho_{water}}$$

R = 62.36 torr-l/gmole-K

Hi = dimensionless Henry's law constant

MWi = molecular weight of compound

MW_{air} = molecular weight of air

MW_{water} = molecular weight of water

ρ_{air} = density of air

ρ_{water} = density of water

Then the vapor phase mole fraction is substituted by equation 7.

$$(7) \qquad y_i = \frac{x_i \gamma_i^{\infty} P^V}{P_T}$$

The result is equation 8 with a Henry's law constant in the units of torr-l/gmol (Arbuckle, 1983; Mackay, 1979).

$$(8) \qquad Hc = 1.0573x10\text{-}6\ \gamma_{i\infty}\ P^V$$

Infinite dilution activity coefficients are probably the most important kind of experimental information when there is limited data for phase equilibrium (Prausnitz, 1986). When both activity coefficients are known in a binary system at infinite dilution, intermediate compositions can then be estimated (Prausnitz, 1986). Solution properties such as solubility limits, octanol-water coefficients, vapor-liquid equilibria, and Henry's law constants can be readily estimated from infinite dilution activity coefficients with known temperature dependence (Lyman, 1982). Activity coefficients can range from less than 1.0 to more than 10^7 (Lyman, 1982). In estimating vapor-liquid equilibria high percentage errors can be tolerated in infinite dilution activity coefficients. A +/- 10% variation in the coefficients does not significantly affect the results (Lyman, 1982).

Equations of Activity Coefficients

The fundamental equation that defines the activity coefficient for a binary system is

$$(9) \quad G_m = G_{ideal} + G_{excess}$$

G_m = Gibbs energy of mixing

$$(10) \quad G_m = RT(n_1 \ln x_1 + n_2 \ln x_2) + RT(n_1 \ln \gamma_1 + n_2 \ln \gamma_2)$$

G_{ideal} represents the Gibbs free energy for an ideal mixture while G_{excess} (G^E) represents the excess Gibbs energy of mixing (Prausnitz, 1986; Lyman, 1982). Activity coefficients are a function of the change in excess Gibbs energy with the mixture's composition. Equations 11 and 12 show this relationship which is in contrast with infinite dilution activity coefficients.

$$(11) \quad (\delta G^E / \delta n_1) = RT \ln \gamma_1$$

$$(12) \quad (\delta G^E / \delta n_2) = RT \ln \gamma_2$$

Several equations, such as the two-suffix Margules equations, that relate activity coefficients and mole fractions have been developed for binary systems.

$$(13) \quad RT \ln \gamma_1 = A x_2^2$$

$$(14) \quad RT \ln \gamma_2 = A x_1^2$$

There are many other examples of equations developed for binary systems such as Three Suffix Margules, Four Suffix Margules and Van Laar (Prausnitz, 1986). The Margules equations account for enthalpic effects and have shown usefulness in estimating solubility limits in low solubility systems. The Van Laar equations have been useful in predicting vapor-liquid equilibrium. However, these equations do not account for entrophic effects; whereas the Wilson, NRTL (Non-Random Two Liquid), and UNIQUAC account for both effects. Wilson was the first to account for excess entrophy, S^{EX} ,which is also known as the theory of local compostion. The Wilson equation follows.

(15) $g^E/RT = - x_1 \ln(x_1 + \Lambda_{12}x_2) - x_2 \ln(x_2 + \Lambda_{21}x_1)$

(16) $\ln\gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2[\Lambda_{12}/x_1 + \Lambda_{12}x_2 - \Lambda_{21}/\Lambda_{21}x_1 + x_2]$

(17) $\ln\gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) + x_1[\Lambda_{12}/x_1 + \Lambda_{12}x_2 - \Lambda_{21}/\Lambda_{21}x_1 + x_2]$

Wilson's two adjustable parameters Λ_{12} and Λ_{21} are derived from

(18) $\Lambda_{12} = \upsilon_2/\upsilon_1 \exp[(-\lambda_{12} - \lambda_{11})/RT]$

(19) $\Lambda_{21} = \upsilon_1/\upsilon_2 \exp[(-\lambda_{12} - \lambda_{22})/RT]$

where υ_i are molar volumes and λ_{ij} are energies of interaction between the molecules.

Activity coefficients are a function of composition and temperature in the Wilson equation. This model works well for a variety of miscible mixtures, especially for solutions of polar or associating components in nonpolar solvents. A disadvantage of Wilson's equation is its failure to predict phase separation (Prausnitz, 1986).

The NRTL equation is also based on the theory of local compostion; however, it is capable of describing partially miscible systems and is most applicable for extremely non-ideal systems.

(20) $g^E/RT = x_1x_2[\tau_{21}G_{21}/(x_1 + x_2G_{2,1}) + \tau_{12}G_{12}/(x_2 + x_1G_{12})]$

(21) $\tau_{12} = (g_{12}-g_{22})/RT \qquad \tau_{21} = (g_{21} - g_{11})/RT$

(22) $G_{12} = \exp(-\alpha_{12}\tau_{12}) \qquad G_{21} = \exp(-\alpha_{12}\tau_{21})$

(23) $\ln\gamma_1 = x_2^2[\tau_{21}(G_{21}/(x_1+x_2G_{21})^2 + \tau_{12}(G_{12}/(x_2+x_1G_{12})^2]$

(24) $\ln\gamma_2 = x_1^2[\tau_{12}(G_{12}/(x_2+x_1G_{12})^2 + \tau_{21}(G_{21}/(x_1+x_2G_{21})^2]$

The g_{ij} is similiar to λ_{ij} in Wilson's equation while α_{ij} is a function of the solution's randomness (Prausnitz, 1986).

UNIQUAC

The UNIQUAC equation was derived for the purpose of retaining the advantages of Wilson's equation and to be applicable for nonmiscible mixtures. Abrams essentially extended Guggenhein's Quasichemical theory for nonrandom mixtures of molecules of equal size to unequal size molecules (Prausnitz, 1986). The unique variables of the UNIQUAC method were functional group concentrations instead of molecule concentrations (Fredenslund b, 1977). The UNIQUAC equation for Gibbs energy, g^E, consists of combinatorial and residual terms. The combinatorial term is a function of entropy calculated from pure component data which describes differences in molecular size and shape. The residual term is a function of intermolecular forces calculated from binary mixture data. The combinatorial part of the equation is estimated from the Flory-Huggins equation, and the residual component is essentially Wilson's equation (Fredenslund b, 1977). The UNIQUAC equations are given for a binary system.

(25) $g^E = g^E\text{(combinatorial)} + g^E\text{(residual)}$

(26) $$g^{E(comb)}/RT = x_1\ln(\Phi/x_1) + x_2\ln(\Phi/x_2) + (z/2)[q_1x_1\ln(\theta_1/\Phi_1) + q_2x_2\ln(\theta_2/\Phi_2)]$$

(27) $$g^{E(resd)}/RT = - q_1 x_1 \ln(\theta_1' + \theta_2'\tau_{21}) - q_2x_2\ln(\theta_2' + \theta_1'\tau_{12})$$

(28) $\Phi_1 = x_1r_1/(x_1r_1 + x_2r_2)$ $\Phi_2 = x_2r_2/(x_1r_1 + x_2r_2)$

(29) $\theta_1 = x_1q_1/(x_1q_1 + x_2q_2)$ $\theta_2 = x_2q_2/(x_1q_1 + x_2q_2)$

(30) $\theta'_1 = x_1q_1/(x_1q_1 + x_2q_2)$ $\theta'_2 = x_2q_1/(x_1q_1 + x_2q_2)$

r, q and q' are pure component molecular constants.

(31) $\tau_{12} = \exp(-\Delta u_{12}/RT) = \exp(-a_{12}/T)$

(32) $\tau_{21} = \exp(-\Delta u_{21}/RT) = \exp(-a_{21}/T)$

a_{ij} gives the system's temperature energy function. The activity coefficients are given by

(33) $\ln\gamma_1 = \ln(\Phi/x_1) + (z/2)q_1\ln(\theta_1/\Phi_1) + \Phi_2(l_1 - (r_1/r_2)l_2) - \theta'_2q_1\ln(\theta'_1 + \theta'_2\tau_{21}) + \theta'_2q_1[\tau_{21}/(\theta'_1 + \theta'_2\tau_{21}) - \tau_{12}/(\theta'_2 + \theta'_1\tau_{12})$

(34) $\ln\gamma_2 = \ln(\Phi/x_2) + (z/2)q_1\ln(\theta_1/\Phi_1) + \Phi_2(l_1 - (r_1/r_2)l_2) - \theta'_2q_1\ln(\theta'_1 + \theta'_2\tau_{21}) + \theta'_2q_1[\tau_{21}/(\theta'_1 + \theta'_2\tau_{21}) - \tau_{12}/(\theta'_2 + \theta'_1\tau_{12})$

where:

(35) $l_1 = (z/2)(r_1 - q_1) - (r_1 - 1)$

(36) $l_2 = (z/2)(r_2 - q_2) - (r_2 - 1)$

The equation is applicable to a wide variety of nonelectrolyte liquid mixtures. Its main advantages are the simplicity of only two parameters and a wide range of applicability.

UNIFAC

UNIFAC is a combination of the UNIQUAC and ASOG (Analytical Solution of Groups) methods. UNIFAC's combinatorial contribution to the activity coefficient is known as the Stavermann-Guggenheim equation (Danner, 1987). The residual contribution to the activity coefficient is from the ASOG method, whereas UNIQUAC uses Wilson's method. The equations for **UNIFAC** (**UNI**quac **F**unctional **A**ctivity **C**oefficients) are

(37) $\ln\gamma_{ic} = \ln\gamma_{ic} + \ln\gamma_{iR}$

(38) $\ln\gamma_{ic} = \ln(\Phi/x_i) + 5q_i\ln(\theta/\Phi) + l_i - \Phi/(x_i\Sigma_j x_i l_j)$

$j = 1,2,...N$ (number of components in the solution)

(39a) $\Phi_i = r_i x_i / \Sigma_j r_j x_j$

(39b) $\theta_r = q_i x_i / \Sigma_j q_j x_j$

(39c) $l_i = 5(r_i - q_i) - (r_i - 1)$

(39d) $r_i = \Sigma_k \nu_{k(i)} R_k$

$\nu_{k(i)}$ = number of groups of kind k in molecule i

R_k = group volume parameter for group k

k = 1,2,.. N(number of groups in solution)

$q_i = \Sigma_k \nu_{k(i)} Q_k$ (surface area parameter from Van der Waals equation)

Q_k = the group area parameter for group k

Φ_i = molecular volume fraction of comp i

x_i = mole fraction of comp i

θ = molecular area fraction

l_i = a parameter derived from Van der Waals constants

r_i = volume parameter from Van der Waals equation

(40) $\ln\gamma_{iR} = \Sigma_{k\,(i)} [\ln\Gamma_k - \ln\Gamma_{k(i)}]$

Γ_k = residual activity coefficient of group k at Temp T

$\Gamma_{k(i)}$ = residual reference activity coefficient.

(41) $\ln\Gamma_k = Q_k[1-\ln(\Sigma_m\theta_m\Psi_{mk})-\Sigma_m(\theta_m\Psi_{km}/(\Sigma_p\theta_p\Psi_{pm})]$

m, p = 1,2,...N(number of groups in the solution)

θ_m = group area fraction of group m in the solution

Ψ_{mk} = group interaction parameter of kind k

Q_k = group area parameter

(42) $\theta_m = Q_m x_m / (\Sigma_p Q_p x_p)$

x_m = mole fraction of group m in the solution

(43) $x_m = \Sigma_j \nu_{m(j)} x_j / (\Sigma_j \Sigma_p \nu_{p(j)} x_j)$

$\nu_{m(j)}$ = the number of groups of type m in comp. j

$\nu_{p(j)}$ = the number of groups of type p in comp. j

(44) $\Psi_{mn} = \exp(-a_{mn}/T)$

a_{mn} = group interaction parameter resulting from energy interactions between groups m and n.

The method for obtaining a_{mn} consists of many steps. The first step is calculating activity coefficients from experimental VLE data. UNIFAC group interaction parameters are derived from over 2500 binary isotherms and isobars (Fredenslund a, 1977). After activity coefficients have been calculated they are usually checked to be thermodynamically consistent by the Gibbs-Duhem equation. Next, the interaction parameter amn is determined from several binary data sets for a particular group-to-group interaction such as COH in an alcohol and a CH_2 in an alkane. Data from several different alcohols and alkanes must be analyzed in order to find the best interaction parameter amn to fit the data with least error. Over 85 molecular

functional groups have been correlated to find interaction parameters and the number continues to grow.

ASOG has been found to be as useful as UNIFAC; however, it has largely been supplanted due to UNIFAC's stronger theoretical basis (Lyman, 1982). Other methods exist which predict Henry's law constants and infinite dilution coefficients (Dilling, 1977; Treybal, 1979; Thomas, 1984; Kojima, 1979), but UNIFAC is preferred because only the molecular structure of the compound is required. The model developed by Thomas and Eckert gives excellent results but cannot be applied to aqueous systems (Eckert, 1982).

Pierotti's Empirical Correlation

Pierotti developed an empirical correlation which is not predictive, but it is very simple to use. His equation is as follows (Lyman, 1982):

$$(45)\quad \log\gamma_1^{\infty} = A_{1,2} + B_2 N_1/N_2 + C_1/N_1 + D\cdot(N_1-N_2)^2 + F_2/N_2$$

where 1 refers to solute and 2 to solvent

$A_{1,2}$ = coefficient which depends on nature of solute and solvent functional groups j

B_2 = coefficient which depends only on nature of solvent functional groups j

C_1 = coefficient which depends only on solute function group

D = coefficient independent of solute and solvent function groups

F_2 = coefficient which essentially depends only on nature of solvent function group.

$N_{1,2}$ = number of carbon atoms in solute and solvent respectively.

There have been many updates and correction factors on these coefficients to make this equation work quite well (Lyman, 1982; Pierotti, 1959).

Methods for Determining Henry's Law Constants and Activity Coefficients Experimentally

Several experimental methods have been devised to determine activity or infinite dilution activity coefficients and Henry's law constants. However, because the composition ratio y/x varies appreciably in this region causing major uncertainties, the use of infinite dilution activity coefficients has been unattractive in the past. A gas chromatography method by Eckert is the quickest method available for determing infinite dilution coefficients. However, it is not accurate when $\gamma^{\infty} > 100$; neither is it accurate for non-polar molecules or for aqueous systems (Eckert a, 1982). Differential eubulliometry has been shown to be very accurate for aqueous systems with $\gamma^{\infty} > 400$ (Eckert b, 1982). These methods are superior to imprecise VLE

extrapolations in the infinite dilution regions (Eckert b, 1982). However, VLE measurements are a standard method for ascertaining Henry's law constants and activity coefficients (Prausnitz, 1986). A current VLE method for measuring Henry's law constants called EPICS (Equilibrium Partitioning In Closed Systems) was developed by Gosset et al. This method has been reported to have a high degree of precision with the novel approach of measuring relative concentrations rather than absolute.

(46) $$Hc = \frac{(V_{w2} - [(C_{g1}/M_1)/(C_{g2}/M_2)]V_{w1})}{([(C_{g1}/M_1)/(C_{g2}/M_2)]V_{g1} - V_{g2})}$$

where:

V_{w1}, V_{w2} = liquid volume

C_{g1}, C_{g2} = concentrations in the gas

M_1 , M_2 = moles

V_{g1}, V_{g2} = volume of the vapor space

Some classical methods of limited scope for determining activity coefficients include osmotic pressure, freezing point depression, boiling point elevation, and vapor pressure lowering (Walas, 1985).

Empirical Stripping Model

Stripping of chemicals in a wastewater treatment system is a very complicated subject due to the many variables which affect the mass transfer rate. Some mass transfer theory is presented, but it is not the primary focus because of its practical limitations in such a complex mixture. The goal of this study is to determine if equation 1 can be used to predict the stripping rate of organics in a wastewater treatment plant and to serve as an analytic tool in laboratory reactors.

The stripping rate is controlled by the rate of mass transfer through the liquid and gas phases as well as the interfacial area and the concentration driving force. The two-film model describes the overall mass transfer coefficient (Mackay, 1977; Liss, 1974).

$$(47) \quad K_{st}a_o = \frac{a}{V}\left[\frac{1}{k_{lst}} + \frac{RT}{Hck_{gst}}\right]^{-1}$$

$K_{st}a_o$ = stripping coefficient (hr^{-1})
or overall mass transfer coefficient

k_{gst} = gas phase mass transfer coefficient (m/hr)

k_{1st} = liquid film mass transfer coefficient (m/hr)

a = interfacial area (m^2)

a_o = interfacial area per unit volume (m^2/m^3)

R = Universal gas constant (torr-l/K-gmole)

Hc = Henry's law constant (torr-l/g mole)

The overall mass transfer coefficient and interfacial area combine with the concentration gradient resulting in the stripping of the chemical from the liquid to the gas (equation 48). The two-film model and the overall stripping equations are general and apply to either the stripping or volatization mechanisms. The numerical value of the Henry's law constant gives an indication whether the liquid or gas phase resistance is the rate controlling factor. A general rule of thumb is when H_c is greater than 3500 torr-l/g mole, 95% of the mass transfer resistance lies in the liquid phase coefficient. When H_c is less than 10 torr-l/g mole, over 95% of the resistance lies in the gas phase resistance. When $10 < H_c < 3500$ torr-l/g mole, both mass transfer resistances are significant (Smith, 1981). Smith developed a method of predicting stripping in wastewater treatment systems, but it has not shown to be very accurate (Blackburn, 1984).

Stripping can be predicted from diffusivities by the following equations (Barton, 1988)

(48) $r_{st} = K_{st}a_o(C^* - C)$

(49) $K_{st}a = \psi_i K_l a_{o2}$

(50) $\psi_i = (D_i/D)^z$ where z varies

$z = 0.5$ for complete mixed

$z = 0.61\text{-}0.66$

(51) $K_l a_{o2} = (.454 N_o H P \alpha \theta^{T-20})/C_s^* V$

N_o = standard oxygen transfer rate (lbs O_2/HP/hr)

HP = total aeration horsepower (HP)

α,θ = oxygen transfer correction factors

V = volume of the basin (10^6 liters)

C_s^* = dissolved oxygen sat. conc. at 20 C (mg/L)

$K_{la\ o2}$ = Oxygen reaeration coefficient (hr^{-1})

(52) $D_l = (7.4 \times 10\text{-}8\ (18x)^{1/2}\ T)/\mu V^{0.6}$

D_l = diffusivity constant in water (cm^2/sec)

V = molar volume (L/mole)

T = absolute temperature (K)

μ = viscosity of water (centipoise)

x = association parameter for water

Estimating of Ksta

Only predictive methods based upon experimental extrapolations used by environmental engineers have been looked at so far, but there are standard engineering methods used to calculate mass transfer coefficients in aerated systems. Empirical equations from Mass Transfer Operations were used to estimate the overall mass transfer coefficient for naphthalene in the experimental system (Treybal, 1980) for comparison purposes. The system consisted of air bubbling through an orifice above a flat blade impeller in a contained vessel (see figure 1). Empirical correlations were used to estimate

bubble diameters from orifice size, terminal velocity of the bubble, interfacial area, diffusivity of the compound in water, and effective film thickness. Equations 53 through 60 apply for any system where gas bubbles rise from an orifice or sparager in a liquid system. The gas flow rate and the degree of mixing determined which equations were used. Equation 53 was used to estimate the diameter of bubbles at low flowrates. Equation 54 was used for intermediate flow rates only on the condition that the specifications of equation 55 were met.

(53) $d_p = [(6d_o\sigma g_c)/(g\Delta p)]^{1/3}$

d_p = diameter of the bubble (m)

d_o = diameter of the orifice (m)

σ = surface tension (N/m)

Δp = pressure drop (Pa)

g = gravity (9.80 m/sec^2)

g_c = gravitational constant (1.0 kg-m/N-sec^2)

(54) $d_p = 2.312[(\mu_l Q_{Go})/(\rho_l g)]$

μ_l = viscosity of the liquid (kg-m/sec)

Q_{Go} = volumetric gas flow rate through orifice (m^3/sec)

(55) $Q_{Go} > [20(\sigma d_o g_c)^5/(g\Delta p)^2 \rho_l^3]^{1/6}$

but $Q_{Go} < 2100$

(56) $Re_g = d_o V_o \rho_g/\mu_g$

Equation 57 was used to calculate bubble diameters at large gas rates when the Reynolds number was between 10,000 and 50,000.

(57) $d_p = .0071\ Re_g^{-0.05}$

ρ_l = density of the liquid (kg/m^3)

V_o = velocity through orifice (m/sec)

μ_g = viscosity of gas (kg-m/sec)

ρ_g = density of gas (kg/m^3)

Depending on bubble size, terminal velocity can be estimated from the following equations.

(58) $V_t = (g d_p^2 \Delta p)/ 18\mu l \quad d_p < 0.7$ mm

For 0.7 mm < dp < 1.4 mm estimate graphically in Mass Transfer Operations.

(59) $V_t = [(2\sigma g_c)/(d_p \rho l) + g d_p/2]^{1/2}$ 1.4 mm <dp < 6mm,

dp > 6mm

For the orifice used in these experiments, equation 59 applies.

In a mechanically agitated vessel with aeration, the impeller shears the bubbles into smaller sizes creating more interfacial area. The position and size of an impeller is very important to acheive good

gas dispersion into the liquid. It has been shown that the optimal size for the impeller's diameter should be in the range di/T = 0.25 to 0.40 and that its position away from the vessel's bottom should approximately equal its diameter (Treybal, 1980). At low to moderate impeller speeds, the increase in interfacial area is neglible. The impeller speeds were low in all experiments performed in this study. Equations 60 through 63 apply for vessels containing flat-blade turbines. Equation 61 was applicable to the experimental conditions since it met the specifications in equation 60. a_o is the interfacial area created by the gas fed to the vessel.

(60) If $Re^{0.7} (Nd_i/V_g)^{0.3} < 30{,}000$

then

(61) $a_o = 1.44 [(\rho_g/\mu_l)^{0.4} (\rho_l/\sigma^3 g_c)^{0.2}] (V_g/V_t)^{0.5}$

If the left-hand side of equation 62 is greater than 30,000, then the interfacial surface area is due largely to the shear on the bubbles from the impeller, and equation 63 should be used to calculate the interfacial surface area in the system.

If

(62) $Re^{0.7} (Ndi/Vg)^{0.3} > 30{,}000$

then

(63) $a/a_o = 8.33 \times 10\text{-}5\ Re^{0.7} (Ndi/Vg)^{0.3} - 1.5$

a = interfacial area created by impeller shear (m^2)

a_o = interfacial area created by the gas volume (m^2)

V_t = Terminal velocity (m/sec)

N = impeller speed (rpms)

d_i = diameter of impeller (m)

V_g = superfical velocity (m/sec)

T = diameter of the vessel (m)

The diffusivity is needed for estimating the mass transfer coefficient.

(64) $D_l = [(117.3 \times -18)(xM_b)^{0.5} T]/\mu v_a^{0.6}$

M_b = molecular weight of solvent (kg/kmol)

μ_a = solution viscosity (kg/m-s)

x = association factor (2.26 for water)

v_a = solution molal volume

The estimation of a mass transfer coefficient has been shown by Higbie, Danckwerts and Dobbins to be a function of the diffusivity where $k_l \alpha D^n$ (n varies from 0.0 to 0.9) (Treybal, 1980). One of these

methods should be used to obtain an accurate mass transfer coefficient. However, only a rough order of magnitude estimation is desired in this study. The film thickness is given by an approximate value (Levenspiel) where

(65) $K_{st} = D_i/x$ x = film thickness

This has been shown to be a good rough estimate. Combining equation 61 with 65, a stripping rate coefficient was estimated.

(66) $K_{st}\, a_o = D_i/x\, a_o$

This method was used to obtain a rough estimate of the overall mass transfer coefficient which can be used to estimate the stripping rates for comparative purposes.

III. Experimental

Description of Experiments

The experiments consisted of naphathalene stripping from pure water solutions and various contaminated water solutions. Table 1 presents a complete list of the experiments which were performed. Most of the experiments consisted of stripping from pure water (distilled water) solutions in a batch reactor. Studies (Blackburn, 1984) have shown that it is irrelevant whether the water is tap water or distilled, de-ionized, or double distilled. Most pure water experiments were done in triplicate while the experiments involving contaminants were not.

The buffer stripping experiments were performed because most wastewater treatment systems are highly buffered with salts. Glycine (an amino acid) and sucrose experiments were performed since there are many sugars and proteins contained in wastewater systems. Two common organics, m-cresol and phenol, were also present in some experiments to determine their effect on the stripping rate. A 1% solution (1000 mg/l) is a high dissolved solids concentration for wastewater (Benefield). A filtered sludge experiment was done to determine the combined effect of buffers and organics on the stripping rate without any absorption mechanism present to interfere. All solutions were at a concentration of 1%, except for the stripping from filtered sludge that contained both buffers and organics. The sludge was filtered by a 0.2 um teflon filter to remove biomass. The

Table 1. List of Experiments

Solution	Agitation Speed	Air Flow Rate			Naphthalene concentrations
	Rpms	lpm			(mg/l)
water	100	0.1	0.2	0.3	12.0
water	200	0.1	0.2	0.3	12.0
water	300	0.1	0.2	0.3	12.0
1% phenol	300	0.1	0.2	0.3	saturated
1% m-cresol	300	0.1	0.2	0.3	saturated
glycine	300	0.1	0.2	0.3	saturated
sucrose	300	0.1	0.2	0.3	saturated
buffer(1)	300	0.1	0.2	0.3	saturated
sludge(2)	260	0.1			
buffer	260	0.1			

1. Buffer solution contains:
   8.0 g/l $NaNO_3$, 12.0 g/l KH_2PO_4, 1.0 g/l Na_2HPO_4,
   0.001 g/l $FeCl_3$-$6H_2O$, 0.4 g/l $MgSO_4$-$7H_2O$,
   0.02 g/l $CaCl_2$-$2H_2O$

2. Sludge solution was filtered with a 0.2 um filter to remove all of the bacteria. The TOC count was 375 ppm.

filtrate contained a total organic carbon (TOC) of 375 mg/l, which is quite high for a treatment plant (Benefield).

In addition, the stripping data of biphenyl and 4-chlorobiphenyl in pure water, in the same vessel at batch conditions, was obtained from a co-worker (Pettigrew, 1988). These experiments were performed for the purpose of quantifying stripping rate data so that the rates of biodegradation could be backed out. If accurate predictive methods already existed, these experiments would not be necessary. The amount of chemicals absorbed is also required to calculate biodegradation rates in laboratory experiments. This data was used to test the predictive capabilities of equation 1.

Experimental Apparatus

A one liter New Brunswick Bioflow Bench Top Chemostat was used to simulate a wastewater treatment facility at batch conditions. To prevent adsorption on the apparatus only Teflon, glass, and stainless steel came into contact with the solutions. The impeller velocity was varied in a range of 100-400 rpms and the air flow rates were varied from 0.10-0.30 lpm. The chemostat vessel is shown in Figure 1.

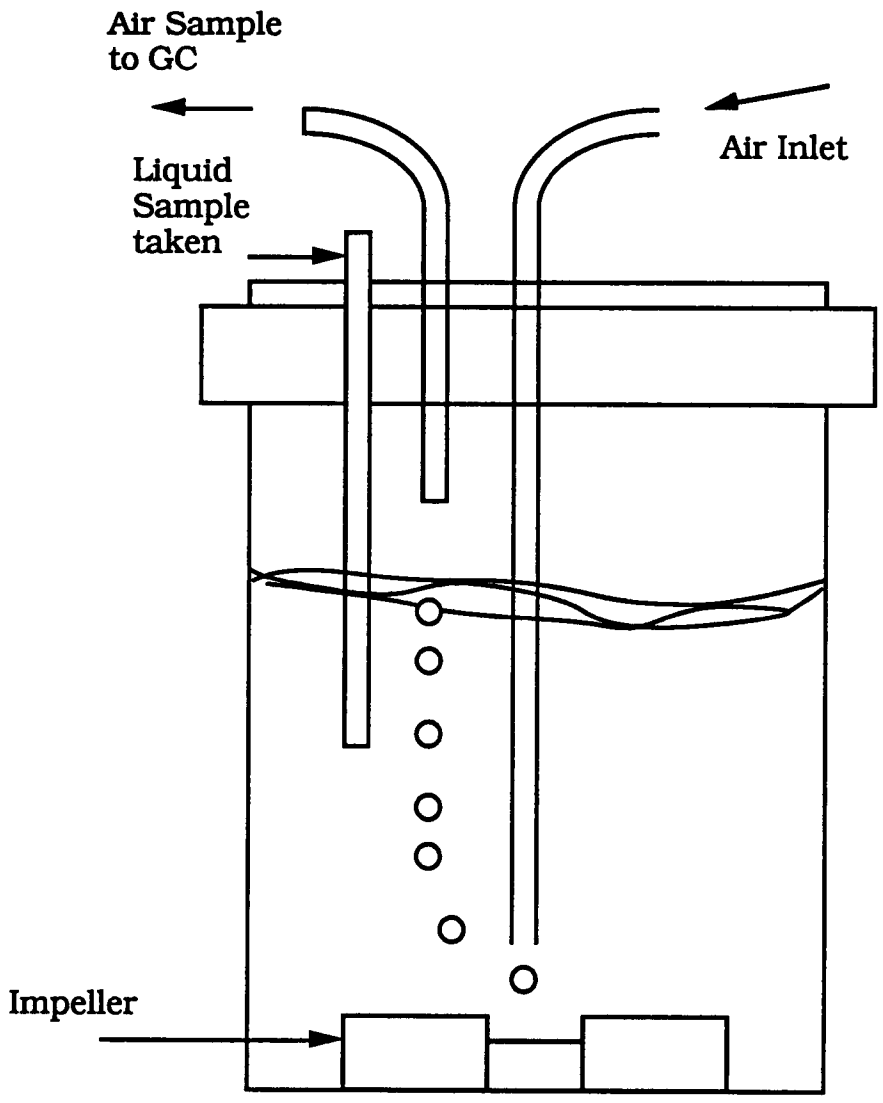

Figure 1. Chemostat Vessel

The impeller's location is not within acceptable engineering geometrical design range for the ratio of di/T. However, at low mixing conditions where the shear rate on the gas bubbles is insignificant, the vessel essentially becomes a bubble column. The impeller's location is irrelevant at these conditions. The liquid is well mixed, but the gas bubbles are not really affected. The impeller does not shear the bubbles; therefore, the gas flow through the orifice determines the amount of interfacial area. The purposes of geometrical design ranges for mixing vessels include scaling up and comparison.

The experiments were performed isothermally (25° C) by means of a heating finger and either cooling water or a Fisher Scientific IsoTemp Refrigerated Circulator Model 900. The air flow rate was measured to an accuracy of +/- 3ml before and after every experiment by bubbling air into an inverted graduated cylinder filled with water to insure that there was a constant flowrate during the experiment.

Naphthalene concentrations in the vapor and liquid phases were measured using a Shizmadzu GC-9AM Gas Chromatograph, which has a detection limit of about 500 ppb using a FID. A standard curve of naphthalene concentration and peak area is shown in figure 2. Naphthalene standards were injected by a syringe in triplicate and the area averaged at each concentration point. Liquid samples were taken through a stainless steel tube by a plastic syringe and quickly injected into a glass storage vial with a teflon septum. Gas samples were taken from the vapor phase of the vessel by sampling through a stainless steel tube into a 7.7 ml sample loop and then injecting onto a packed column using a Valco sampling valve.

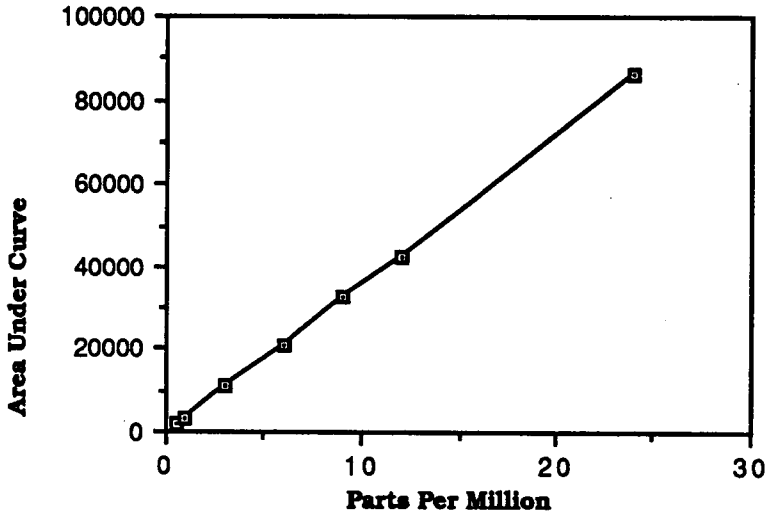

Figure 2. Gas Chromatograph Standard FID Curve For Naphthalene

A mass balance was calculated for some experiments. The results are given in Table 2. In experiments 38 and 39, 117 percent of the mass in the liquid phases was accounted for. In experiment 40, 125.1 percent of the mass was accounted for. In experiment 41, 104.4 percent of the mass was accounted for. These results demonstrate that the mass was not being adsorbed onto the experimental apparatus and that all the naphthalene was either being stripped or was remaining in the liquid phase. The mass balance numbers are slightly high due to extrapolation of the liquid phase chromatograph areas to gas phase chromatograph areas. This is discussed further in the following procedure.

Table 2. Mass Balance Experiments

Exp. no.	Mg accounted For in the liquid	Mg accounted for in the gas	% Accounted For
38	2.97	3.48	117.0
39	2.77	3.25	117.0
40	2.70	3.37	125.1
41	2.50	2.62	104.4

Procedure

Naphthalene calibration standards were prepared by adding 30 mg to 100 ml of methanol in a volumetric flask. Volumes of the resulting 300 ppm solution were then added to six other 10 ml volumetric flasks (ex. 400 microliters of standard were added to 9.6 ml of MeOH to give a 12 ppm solution) to produce a standard curve. Eastman Chemicals manufactured the naphthalene Lot no. A928. A Mettler AM100 balance measured the quantity of naphthalene used in the standards .

Gas standards were attempted, but results were never consistent. A known quantity of naphthalene was added to a 10-liter stainless steel vessel and allowed to equilibrate. The vessel was connected to the gas chromatograph with stainless steel piping using a Valco valve, which controlled the loading of the gas into the sample loop and the injecting onto the column. However, this did not prove to be consistent; therefore, the gas phase concentrations were extrapolated from liquid phase standards. The reasons why the gas phase concentrations were never consistent is not fully understood.

Naphthalene solutions were prepared in sealed vessels and allowed to equilibrate for a day before being added to the chemostat. After adding the solution to the chemostat, the agitation and air flow were turned on and allowed to run for about 15 minutes before taking initial liquid samples through a stainless steel tube submerged in the vessel (see Figure 1). Teflon Tape sealed this tube and a 3 cc syringe was used to extract samples. Samples were put in 2 ml vials and

stored at 4° C. A Hamilton microliter syringe (glass) #701 was used to inject 0.2 ml samples into the GC. Gas samples were taken from the sealed chemostat. A manometer on the offgas trap was used to insure that the vessel was sealed. A pressure differential of about 1" of water indicated a good seal on the vessel.

Data Analysis

Stripping has been modeled by first order irreversible kinetics in the literature (Blackburn, 1984). The reaction rate constant has been substituted by the overall mass transfer coefficient.

(67) $r_{st} = -dCA/dt = K_{st}a_o(t)(CA)$

The change in concentration of the compound with time equals the product of the overall mass transfer coefficient and the compound's liquid phase concentration.

(68) $$r_{st} = \int_{CAo}^{CA} \frac{-dCA}{CA} = \int_0^t k_{st}a_o \, dt$$

Equation 69 is the result of integrating from CAo to CA over time.

(69) $r_{st} = \ln(CAo/CA) = K_{st}a_o \, t$

The stripping rate constant equals the slope of the plot Ln(CAo/CA) on the ordinate and time on the abscissa (See Figure 3).

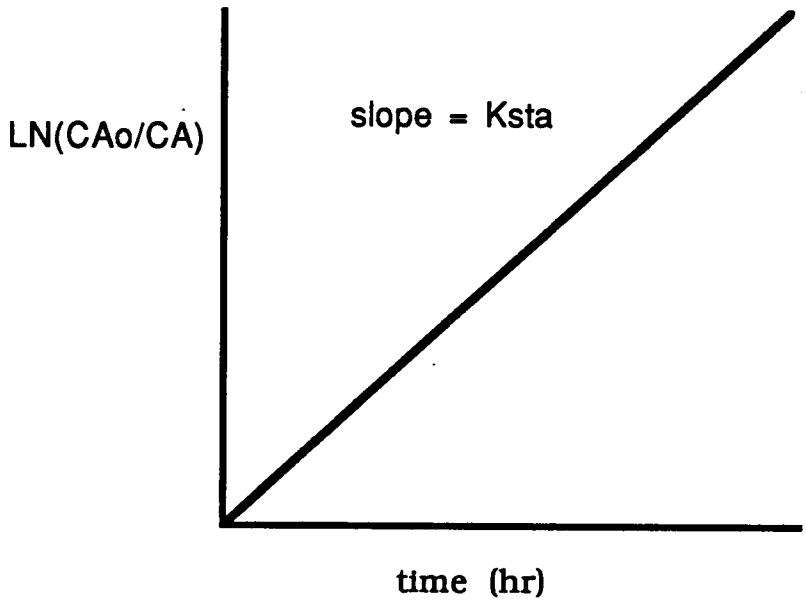

Figure 3. Data Analysis of Stripping

IV. Results and Discussion

A comparison made between infinite activity coefficients found in the literature and those predicted by UNIFAC is followed by a comparison between the Henry's law constants found in the literature and those predicted by UNIFAC. Experimental stripping rates determined in this paper were compared to stripping rates predicted with equation 1 using Henry's law constants predicted by UNIFAC. Stripping rates calculated using estimated diffusitives and bubble diameters were compared with experimental stripping rate constants determined in this paper.

Infinite Dilution Activity Coefficients

Table 3 shows the comparison between infinite dilution activity coefficients from the literature and values predicted by UNIFAC. All values in the table are at 25° C. In general, the more soluble the organics are in water, the closer the literature and UNIFAC values are in comparison. The lower the solubility, the more uncertainty there is in the y/x ratio, leading to greater uncertainty in the infinite dilution activity coefficients. As an example, the benzene and ethylbenzene UNIFAC values compare well to literature values, with errors of 4.95 and 8.64% respectively. Naphthalene and biphenyl are less soluble, and the percent errors are 97.0 and 106.5 respectively. Phenanthracene and anthracene have an order of magnitude lower solubility than naphthalene and biphenyl and have comparative errors

of 304.5% and 286.7% respectively. Phenol is the exception to this rule: It is very soluble in water and has a high comparative error of 82.7%. Despite the error in comparison, all literature and UNIFAC values are of the same order of magnitude.

Table 3. Comparison of Infinite Dilution Activity Coefficients.

Compound	UNIFAC Dimensionless [A]	Literature [B]	%Error $\frac{B - A}{B} \times 100\%$
Naphthalene	1.35×10^5	6.83×10^5 [a]	+97.1
Benzene	3.34×10^3	2.46×10^3 [b]	+5.0
Ethyl Benzene	3.29×10^4	3.74×10^4 [b]	+8.6
Toluene	1.17×10^5	9.86×10^4 [b]	+24.1
Phenol	1.10×10^1	6.60×10^1	+82.7
Biphenyl	1.01×10^0	4.90×10^6 [a]	+106.5
4-PCB	6.79×10^6	-------	------
Phenanthracene	7.11×10^6	1.76×10^6 [a]	+304.3
Anthracene	7.11×10^6	1.84×10^6 [a]	+286.7
o-xylene	5.46×10^4	-------	------
4-Cl-biphenyl	6.79×10^6	-------	------
Cl-benzene	1.84×10^4	-------	------

a (Mackay a)

b (Mackay b)

Vapor Pressures and Solubilities

A list of selected compounds' vapor pressures and solubilities studied in this paper are in the appendix. In summary, the compounds with high vapor pressures had relatively high solubilities in water, whereas low vapor pressures coincided with low solubilities. However, phenol was the exception: It had a low vapor pressure and high water solubility, which is a result of mutual attraction between hydroxyl groups. As a result, phenol strips very little in aqueous solutions (see Table 13). Naphthalene and biphenyl has very similiar vapor pressures and solubilities. Naphthalene has a vapor pressure of 0.088 mm Hg with a solubility of 34 mg/L, and biphenyl has a vapor pressure of 0.091 mm Hg with a solubility of 7. 5 mg/L.

Henry's Law Constants

While there is a paucity in the literature on PAH activity coefficients, Henry's law constants are much more abundant. Tables 4 and 5 present comparisons between Henry's law constants from the literature, calculated with Dilling's equation, and those predicted from UNIFAC. The total average error for the Dilling's law in comparison to the literature was 19.5%; while the total average error for the UNIFAC method was 37.5 %. In general, Dilling's law tended to underpredict the Henry's law constant; while UNIFAC gave both positive and negative deviations. Based on the limited

comparison in Tables 4 and 5, Dilling's equation gave a better representation of the literature values.

The compounds' Henry's law constants grouped into low, medium, and high categories. Phenol was the only compound with a low Henry's law constant. Naphthalene, biphenyl, phenanracene, anthracene, and 4-cl-biphenyl had medium Henry's law constants. Benzene, ethylbenzene, o-xylene, and chlorobenzene, and 1-4 chlorobenzene had high Henry's law constants. The literature value for Naphthalene was 0.0198 (dimensionless). Dilling's law predicted 0.0176, and UNIFAC gave 0.012. The percent difference was 39.4 for the UNIFAC value compared to the literature value. Headspace analysis at the Center for Environmental Biotechnology has shown that the literature value is accurate. The UNIFAC value for Biphenyl was 41.2% under the literature value. The UNIFAC values of Henry's law for phenanthracene and anthracene fared quite well with the literature values--having 14.5 and 23.8% differences respectively--even though the activity coefficients calculated from UNIFAC had much higher percent errors. The UNIFAC value for Benzene compared well with the literature, having only a 5.8% error. For Ethylbenzene, UNIFAC predicted 3.0% below the literature value; whereas Dilling's law was 23.6% below. In the case of toluene, UNIFAC was 29.5% above the literature value and the Dilling value was 45.3% below. UNIFAC value for o-xylene was greater than the literature value by 130%.

Table 4. Henry's Law Constants Comparing UNIFAC and the Literature

	UNIFAC		Literature		% Differ
Compound	Non-dim $\times 10^{-3}$	Units $\frac{\text{torr-l}}{\text{gmole}}$	Non-dim $\times 10^{-3}$	Units $\frac{\text{torr-l}}{\text{gmole}}$	
Naphthalene	12.0	223.6	19.8	367.1	39.4
Biphenyl	9.8	182.5	16.7	310.1	41.2
Phenanracene	5.1	95.1	4.4	85.0	14.5
Anthracene	1.4	27.4	1.1	22.1	23.7
4-Cl-Biphenyl	6.1	113.5	-----	-----	-----
Benzene	240.3	4467.0	227.0	4218.0	5.8
EthylBenzene	330.9	6152.0	344.8	6406.0	4.0
Phenol	0.005	0.089	-----	-----	----
o-xylene	404.0	7511.0	175.0	3252.0	130.0
Toluene	351.6	6537.0	271.6	5046.0	29.5
Cl-benzene	230.9	4294.0	154.2	2865.0	49.8
1-4,Cl-benzene	104.8	1948.0	-----	-----	----

Table 5. Henry's Law Constants Comparing Dillings Law and Literature Values

	Dilling's		Literature		% Differ
Compound	Non-dim $\times 10^{-3}$	Units $\frac{\text{torr-l}}{\text{gmole}}$	Non-dim $\times 10^{-3}$	Units $\frac{\text{torr-l}}{\text{gmole}}$	
Naphthalene	17.6	327.8	19.8	367.0	11.1
Biphenyl	10.1	188.4	16.7	310.1	39.5
Phenanracene	3.3	60.5	4.4	85.0	25.0
Anthracene	1.3	24.9	1.1	22.1	18.2
4-Cl-Biphenyl	3.6	67.0	-----	-----	----
Benzene	227.0	4218.0	227.0	4218.0	0.0
EthylBenzene	263.1	4890.0	344.8	6406.0	23.7
Phenol	0.6	11.4	-----	-----	----
o-xylene	163.8	3044.0	175.0	3252.0	6.4
Toluene	149.9	2769.0	271.6	5046.0	44.8
Cl-Benzene	143.3	2663.0	154.2	2865.0	7.0
1-4 Cl-Benzene	6.2	1149.0	-----	-----	----

(a) torr-L/gmole

Stripping Experiments

Tables 6, 7, and 8 present the average stripping rate coefficients in the pure water experiments and in the other solutions listed in Table 1. In Table 6, the stripping rate coefficient increased slightly as the agitation speed increased. This slight increase (less than 2% in any case) in the stripping rate coefficient does not demonstrate that equilibrium is reached in this system because the agitation rates are so low that the bubbles are not significantly sheared into smaller ones. Further experiments are needed at higher agitation rates to prove equilibrium has been reached at these flow conditions in this vessel. As the air flow rate increased the stripping rate increased due to gas volume and interfacial area increase.

Table 6. Experimental Stripping Rate Constants of Naphthalene in Pure Water

	$K_{st}a_o$ hr^{-1}				
Agitation rpms	Airflow rate lpm			Temp = 25° C	
	0.10	0.15	0.20	0.25	0.30
260	0.25	---	---	---	---
300	0.27	0.48	0.60	0.72	0.95
400	----	----	0.63	0.70	0.97

Table 7 presents naphthalene stripping data in solutions of 1% phenol, Sucrose, Glycine, m-cresol, and buffers. The stripping was performed at constant temperature and a constant agitation speed. The gas flow; however, varied from 0.1 to 0.3 lpm. The results in Tables 6 and 7 are compared later in Tables 8 and 9.

Table 7. Stripping Rate Constants of Naphthalene in Organic and Buffer Solutions

	$K_{st}a_o$ hr^{-1}		
Solution	Air Flow rate** lpm		Temp = 25° C
	0.10	0.20	0.30
1% Phenol	0.21	0.49	0.76
1% Sucrose	0.32	0.80	1.11
1% Glycine	0.35	0.45	0.97
1% m-cresol	0.41	0.60	0.87
Buffer	0.44	0.79	1.34

**Experiments were done at constant rpm of 300

Figure 4 presents naphthalene stripping data in water at different air flow rates. The largest stripping rate is at the highest air flow rate, and the smallest stripping rate at the lowest air flow rate. In Figure 4, the slope at 0.3 lpm air flow rate is .99 with an R-squared value of 99.8%. For linear regression models in statistics, R-squared describes how well the data fits the linear model. An R-squared value of 100% means that the data is perfectly linear. At 0.2 lpm the slope is 0.59 with an R-squared value of 99.3%. At 0.1 lpm the slope is 0.30 with a R-squared value of 98.3%.

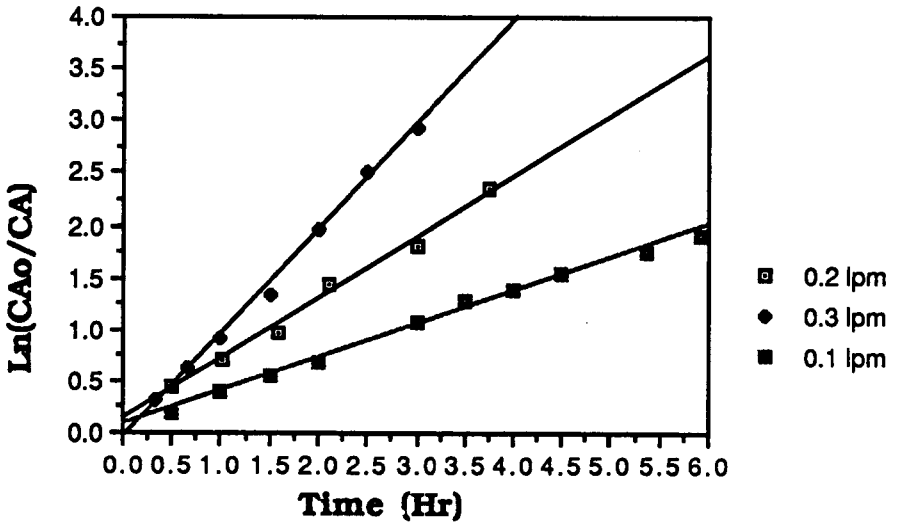

Figure 4. Stripping of Naphthalene in Water

In Table 8A, the stripping rate of naphthalene decreased on the average of 20.5% in the 1% phenol solution in comparison to the rate

in pure water. In Table 8B, the stripping rate in buffers increased on the average of 45.2%. The observance of increased stripping rates has been called the "salting out effect" (Blackburn, 1984). It is postulated that this effect is related to the compound's decreased solubility in the presence of salts. The stripping rate of naphthalene in 1% sucrose solutions is presented in Table 8C. The stripping rate increased on the average of 22.9% compared to stripping in pure water solutions.

Table 9A and 9B present naphthalene stripping data in the presence of m-cresol and glycine, respectively. The results of whether either chemical has a negative or positive effect on the stripping rate is inconclusive. When the air flow is at 0.1 lpm, the stripping rate is +53.3% in the m-cresol solution and +30.7% in the glycine; whereas when the air flow rate increases to 0.2 lpm, the stripping rate is nearly the same for the m-cresol solution and pure water solution. The stripping rate in the glycine solution is -24.7 percent at 0.2 lpm in comparison to the pure water solution. At 0.3 lpm, both the glycine solution and the m-cresol solution had stripping rates which were close to the stripping rates in pure water. The reasons for inconsistency in these experiments is not understood. These experiments should have been done in triplicate to reach a conclusive result.

The naphthalene stripping rate in filtered sludge was 75.2% higher for the same conditions in pure water. The results are in Table 9C. This is an example where stripping rate coefficients are generally higher in the presence of highly buffered systems.

Table 8. Comparison of Stripping Rate Coefficients of Naphthalene in water and Various Solutions: (A) 1% Phenol, (B) Buffer, and (C) 1% Sucrose

	$K_{st}a_o$		
Air flow lpm	Water	Solution	%Difference
		A	
0.10	0.27	0.21	-21.6
0.20	0.60	0.49	-19.2
0.30	0.95	0.76	-20.8
		B	
0.10	0.27	0.44	+64.0
0.20	0.60	0.79	+31.4
0.30	0.95	1.34	+40.3
		C	
0.10	0.27	0.32	+19.7
0.20	0.60	0.80	+32.5
0.30	0.95	1.11	+16.4

Table 9. Comparison of Stripping Rate Coefficients of Naphthalene in Water and Various Solutions: (A) 1% m-cresol, (B) 1%Glycine, (C) Filtered Sludge

	$K_{st}a_o$		
Air flow lpm	Water	Solution	%Difference
		A	
0.10	.27	.42	+53.5
0.20	.60	.59	- 0.6
0.30	.95	.87	- 8.9
		B	
0.10	0.27	0.35	+30.7
0.20	0.60	0.45	- 24.7
0.30	0.95	0.97	+ 1.5
		C	
0.10	0.25	0.44	75.2

Figure 5 demonstrates the stripping rate variability of a compound in the presence of contaminants. Stripping rates in buffer, water, and 1% Phenol solutions are plotted at conditions of a constant air flow rate of 0.1 lpm and 300 rpms. The highest stripping rate was in the Buffer solution (a slope of 0.99 with an R-squared value of 97.7%). The intermediate rate was in water (a slope of 0.30 with an R-squared value of 98.3%). The lowest rate was in the presence of phenol (a slope of 0.21 and an R-squared value of 99.3%).

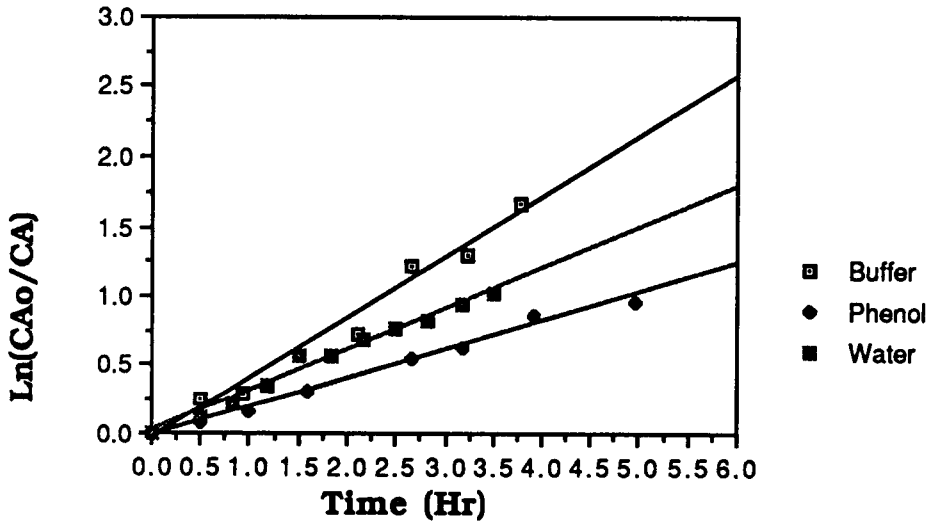

Figure 5. Stripping of Naphthalene in Water and Contaminants

Comparison of the Model to Experimental

Table 10 compares experimental stripping rate coefficients of naphthalene in pure water to stripping rate coefficients predicted by the empirical model using an UNIFAC predicted Henry's law constant. Table A2 in the Appendix contains stripping rate coefficients predicted by equation 1 using literature values of Henry's law constants.

Equation 1 using UNIFAC values was consistently closer to experimental stripping rate coefficients than equation 1 using literature values. The error of equation 1 using UNIFAC values averaged 7.2%; while the error of equation 1 using literature values averaged 71.9%. When the air flow was 0.1 lpm and the agitation speed was 260 rpms, equation 1 using UNIFAC had only 20.8% error; while equation 1 using a literature value had 103.2% error. When the agitation speed was 300 rpms and airflow was 0.1 lpm, the percent errors were 11.9% for UNIFAC and 88.1% for literature values.

The results using the UNIFAC Henry's law constants incorporated into the model are quite accurate. However, it must be remembered that this is a pure water system and stripping rates will be greater in real systems containing buffers.

Table 10. Comparison of Predicted Stripping Rate Coefficients of Naphthalene using Equation 1 and Experimental Stripping Rate Coefficients.

Air Flow lpm	Agitation Rpms	Experimental $K_{st}a_o$	UNIFAC $K_{st}a_o$	% Error
0.10	260	0.25	0.30	+20.8
0.10	300	0.27	0.30	+11.9
0.15	300	0.47	0.45	-4.8
0.20	300	0.60	0.61	+0.3
0.20	400	0.63	0.61	-3.2
0.25	300	0.72	0.76	+5.0
0.30	300	0.95	0.91	- 4.9
0.30	400	0.97	0.91	-6.4

Table 11 presents biphenyl and 4-chlorobiphenyl stripping rate coefficients. Experimental results were compared with values predicted by equation 1. The experiments were performed by Pettigrew in the same system. Again, equation 1 using a UNIFAC predicted Henry's law constant did a better job of predicting the stripping rate coefficients. The average percent error using the UNIFAC values was 10.2%; while the percent error using literature values was 73.5%. In the case of 0.40 lpm air flow rate and 300 rpms, the percent error for UNIFAC was +13.7; while using a literature value was 102.3% for the model. For the case of 0.2 lpm and 300 rpms, the UNIFAC method gave a -4.67% error, while a literature value gave a +65.9% error.

These biphenyl stripping rate coefficients (an average comparative error of 10.2%) compared quite well with naphthalene stripping rate coefficients (an average comparative error of 7.2%). These results demonstrate the potential usefulness of equation 1 to serve as an analytic tool in laboratory biodegradation experiments.

There was no literature Henry's law constants found for 4-chlorobiphenyl. Therefore, only experimental results will be compared to predictions by equation 1 using a UNIFAC predicted Henry's law constant. Equation 1 did not do well in this case. The predicting stripping rate coefficients for each of the experiments were in error by -65.9% and -47.9%. This might indicate that 4-chloroBiphenyl has a higher activity coefficient than UNIFAC predicts or that the literature value for the vapor pressure could be incorrect.

Table 11. Comparison of Experimental Stripping Rate Cofficients of Biphenyl and 4-Cl Biphenyl in Water and Rate Coefficients Predicted by Equation 1.

Air Flow lpm	Experimental $K_{st}a_o$	UNIFAC $K_{st}a_o$	%Error
Biphenyl Experiments With UNIFAC Comparison			
0.10	0.28	0.25	-12.2
0.20	0.51	0.49	- 4.7
0.40	0.84	0.98	+13.7
Biphenyl Experiments With Literature Comparison			
0.10	0.28	0.43	+52.3
0.20	0.51	0.85	+65.9
0.40	0.84	1.70	+102.3
4-ChloroBiphenyl Experiments			
0.10	0.44	0.15	-65.9
0.20	0.57	0.30	-47.9

Table 12 compares experimental stripping rate coefficients for naphthalene with contaminants in the solution. The coefficients predicted by equation 1 using UNIFAC predicted Henry's constants. Equation 1 underpredicted the stripping rate coefficients in all cases by an average of 23.2%. Experiments performed in buffer and sludge solutions were the least accurately predicted. The least accurately predicted stripping rate coefficient had an error of -46.6%.

The results in Tables 10, 11, and 12 demonstrate that the correlation will give reasonably accurate results in small scale laboratory experiments. All predicted stripping rate coefficients using UNIFAC predicted Henry's law constants were within a range of +20.8% and -46.6%.

Table 13 presents a comparison of stripping experiments found in the literature and predicted stripping rates at same conditions by the equation 1 using UNIFAC predicted Henry's law constants. The results were not satisfactory: There were large errors for several of the experiments. Toluene stripping in pure water experiments, the percent error was +190.0 on one and +145.4 on another. The percent errors for phenol stripping in water experiments were -45.3 and -56.7. Errors for 1-4 diclorobenzene stripping in water experiments were +135.5, +65.5, +55.2, +35.62, -4.72, and -10.6%. These results indicate that only an order of magnitude stripping estimates are feasible for predicting stripping in wastewater treatment tanks.

Table 12. Comparison of Experimental Stripping Rate Coefficients of Naphthalene in Systems of Contaminants With Coefficients Predicted Using Equation 1 Incorporating Henry's Law Constants Predicted by UNIFAC.

Solution	Experimental $K_{st}a_o$	UNIFAC $K_{st}a_o$	%Error
Buffer	0.44	0.30	-46.6
Buffer	0.79	0.61	-31.1
Buffer	1.34	0.91	-32.3
Sludge	0.44	0.30	-31.1
1% m-cresol	0.42	0.30	-27.2
1% m-cresol	0.60	0.60	- 1.0
1% m-cresol	0.79	0.91	-14.8
1% sucrose	0.32	0.30	- 5.6
1% sucrose	0.80	0.60	-24.3
1% Sucrose	1.11	0.91	-18.2

Table 13. Comparison of Previous Stripping Rate Coefficients Found in the Literature with Rates Predicted Using Equation 1

Compound-Solution	Actual Rate $K_{st}a_o$	Equation 1 $K_{st}a_o$	%Error
Toluene/Water	1.09(a)	2.67	+145.4
Toluene/Water	1.84	5.336	+190.0
Phenol/Water	8.1x10-5	4.4x10-5	- 45.3
Phenol/Water	5.1x10-5	2.2x10-5	- 56.7
1-4 Cl-benzene/Water	0.32	0.75	+135.3
1-4 Cl-benzene/Water	0.91	1.51	+ 65.5
1-4 Cl-benzene/Water	1.94	3.01	+ 55.2
Toluene/surfactant	1.09	2.04	+ 87.2
Toluene/surfactant	1.84	4.07	+121.2
1-4 Cl-benzene/Water	0.32	0.44(b)	+ 35.6
1-4 Cl-benzene/Water	0.91	0.84(b)	- 4.7
1-4 Cl-benzene/Water	1.94	1.73(b)	- 10.6

(a) all experiments in literature were done by Blackburn et al.

(b) The Henry's law constant was estimated by Dilling's law

Table 14 presents a comparison of the experimental data and stripping rate coefficients estimated by equations 53 through 66, which are found in Treybal's Mass Transfer. The results were quite good, with all of the estimated rates higher than the experimental by an average of +19.0%. Although this is an accurate method of stripping estimation, we would prefer a simpler model to work with.

Table 14 Comparison of Experimental Stripping Rate Coefficients and Predicted From Estimated Diffusivities and Bubble Diameters

Air Flow lpm	Agitation Rpms	Experimental $K_{st}a_o$	Estimated $K_{st}a_o$	% Error
0.10	260	0.25	0.44	+43.0
0.10	300	0.27	0.46	+41.6
0.15	300	0.48	0.57	+17.6
0.20	300	0.60	0.66	+ 8.7
0.20	400	0.63	0.74	+18.0
0.25	300	0.72	0.73	+ 1.8
0.30	300	0.95	0.80	+15.8
0.30	400	0.97	0.90	+ 6.8

V. Conclusions

Equation 1 using UNIFAC predicted Henry's law constants proved to be fairly reliable, giving accurate stripping rate predictions for most compounds. Equation 1 will be a useful analytic tool for small scale reactor biodegradation experiments in laboratories. The model predicted within an average of 7% of the stripping of naphthalene in pure water, and the stripping rate prediction for biphenyl in water was within 13% of the experimental value. The presence of small amounts of organic contaminates can have a dramatic effect on the stripping rate of naphthalene by either increasing or decreasing its infinite dilution activity coefficient. Stripping rates were significantly increased in the presence of buffers--by as much as 40%--and appear to override any negative effects by organics. Stripping rates in biological systems will probably be larger than those predicted by the model.

Equation 1 is useful for predicting within an order of magnitude range the stripping rate in a wastewater treatment plant. In the larger systems found in the literature, the equation 1 predicted the stripping rates within an average of 79% error, with errors as high as 190%.

UNIFAC did an adequate job of predicting Henry's law constants for this research. However, it would be helpful to have more accurate infinite dilution activity coefficients for PAHs than those present in the literature.

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Appendix

Table A1. List of Vapor Pressures and Solubility Data of Selected Compounds

Compound	Vapor Pressure (mm Hg) Temp. = 25 °C	Solubility (mg/L) Temp. = 25 °C
Naphthalene	8.8×10^{-2} d	3.4×10 a
Biphenyl	9.1×10^{-2}	7.5×10^{0} a
Phenanthracene	6.8×10^{-4}	1.3×10 a
Anthracene	1.9×10^{-4}	7.3×10^{-2} a
4-Cl-Biphenyl	8.5×10^{-4}	2.4×10
Benzene	$9.7 \times 10^{+1}$ d	1.8×10^{3} b
Ethyl Benzene	9.5×10 d	2.1×10^{2} c
Phenol	4.0×10^{-1}	7.4×10^{5} e
o-xylene	7.0×10	1.7×10^{2} d
Toluene	$2.8 \times 10^{+1}$ d	5.2×10^{2} d
Chlorobenzene	$1.1 \times 10^{+1}$ d	4.7×10^{2} d
Acenaphthene	2.8×10^{-3}	3.9×10 d
1-4 Cl-Benzene	6.0×10^{-1} e	7.9×10^{1} e

a (Mackay a) b (May) c (Bohon) d (Mackay c)

e (Blackburn a) f (Arbuckle)

Table A2. Predicted Stripping Rate Constants using Equation 1. With Literature values for Hc and Experimental Stripping Rate Constants

Air Flow lpm	Agitation Rpms	Experimental $K_{st}a_o$	Literature $K_{st}a_o$	% Error
0.10	260	0.25	0.51	+103.0
0.10	300	0.27	0.51	+88.1
0.15	300	0.48	0.76	+59.9
0.20	300	0.60	1.02	+68.3
0.20	400	0.63	1.02	+62.4
0.25	300	0.72	1.27	+76.3
0.30	300	0.95	1.52	+59.6
0.30	400	0.97	1.52	+57.2

(a) stripping units in Hr-1

Vita

Paul Douglas Dunbar was born August 25, 1963, and raised on a small farm outside of Millington, Tennessee. He attended elementary and Junior High School at Tipton Academy in Brighton. He attended High School at Memphis Briarcrest and graduated in May 1981. He attended Memphis State University for two years and transferred to The University of Tennessee at Knoxville, where he received his B.S. with a major in Chemical Engineering in June of 1986. In the fall of 1986, he returned to UTK and to enroll in graduate school and start work for the Center for Environmental Biotechnology as a graduate research assistant. He received his M.S. in Chemical Engineering in October of 1989, and will continue in the Chemical Engineering program and pursue a Ph.D.