활성슬러지 하수처리장에 유입된 Polycyclic Aromatic Hydrocarbons의 농도분포를 예측하기 위한 수학적 모형의 개발

A Mathematical Model for Prediction of the Fate of Polycyclic Aromatic Hydrocarbons in Activated Sludge Processes : Steady State and Dynamic Simulation

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要　　旨

본 연구에서는 활성슬러지 하수처리장에 유입된 PAHs의 일종인 anthracene을 대상으로 이의 농도 분포, 물리적 혹은 생물학적 변환을 예측하기 위한 수학적 모형을 제안하였다. 이 수학적 모형은 유입 anthracene의 volatilization, biodegradation 및 adsorption/desorption과 같은 반응을 고려한 5개의 연립미분방정식으로 구성되어 있으며, 이들에는 7개의 kinetic rate constants와 18개의 input variables 를 포함하고 있다.

　Steady state simulation의 결과 유입된 anthracene은 1차 침전지에서의 슬러지 배출로 인하여 약 33%가 포기조에서 발생한 volatilization에 의하여 약 61%가 제거되어, 총괄적인 anthracene의 제거율은 약 97%정도이었다. Dynamic simulation의 결과로 본 연구대상 system의 경우에 system이 steady state에 도달하는 시간은 약 160시간 정도로 예측되었다. 이와 아울러 본 연구에서 제안된 수학 적 모형의 활용 가능성이 각종 simulation의 결과로 비교적 구체적으로 규명되었다.

Abstract

　A mathematical model was proposed to predict the predominant reactions and transport pathways of anthracene in a conventional activated sludge wastewater treatment system. The model consists of five differential equations with seven kinetic parameters and eighteen input variables. Volatilization, biodegradation, adsorption/desorption as well as the convective inputs and outputs are included in the model. The steady state calculations showed that volatilization (61%) in aeration tank and the withdrawal of primary sludge (33%) were two major pathways for removal of anthracene from the system. The overall removal was about 97%. The system reached a practical steady state at about 160 hours via dynamic modeling. The proposed model can give plausible predictions of the fate of priority organic

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pollutants in activated sludge processes.

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1. Introduction

Wastewater treatment plants do receive hazardous organic chemicals despite enforcement of regulations, and undesirable discharging to the plants is likely to continue for some time[12]. These organic chemicals are present in varying degree in the liquid, solids and off-gas phases of activated sludge processes. They can be transferred from one phase to another and they may undergo transformations. A problem of considerable significance has been their accumulation in the suspended solids and the transference of these substances to the sludge disposal areas.

The behavior of the organic priority pollutants in a conventional activated sludge system was investigated[2, 6, 12, 24]. Even if the studies showed the overall percent removals of the compouds, they could not delineate what kinds of physical, chemical or biological processes controlled the fate of the compounds. A model for their fate in activated sludge processes has not been reported. The fates of polycyclic aromatic hydrocarbon (PAHs) in a conventional activated sludge system are of special interest, since PAHs from natural and anthropogenic sources are widely distributed in the environment and cause potential health problems to humans and aquatic life.

The system in this study was assumed to be well-operated at steady state conditions. The mixed liquor in an aeration basin was completely mixed with sludge recycle. The expermental verification of the proposed model is not part of this research.

2. Reactions and Kinetic Formulations

2.1 Volatilization

It is generally accepted as consisting of diffusion of solutes such as gases and some hydrophobic organic pollutants from the bulk of the water to the interface, followed by transfer across the interface, and finally diffusion from the interface to the bulk of the air phase[13]. A material balance with a simple first-order rate expression[5, 18, 25] in water bodies is given by

$$V\frac{dC}{dt} = K(C_\infty - C)A \qquad (1)$$

where C_∞ is the solute or oxygen concentration in the water in equilibrium with the solute or oxygen concentration in the atmosphere at steady state conditions, C is the concentraion in the water at time t, V is the volume, A is the surface area, K is either the volatilization rate constant for the organic solute or the reaeration rate constant for oxygen. For the organic solutes it is assumed that the substances are exhausted away from the water body as soon as they volatilize so that the concentraions in the atmosphere above the water surface are zero. Thus, the equilibrium concetrations in the water are also zero. For oxygen, C_∞ is the saturation concetration for the appropriate temperature and baromatric pressure.

Several suggestions[10, 11, 13, 18] have been made to estimate volatilization rate of compounds from water, using theoretical consideratons, laboratiory measurements and field studies. It is demonstrated that the ratio of the substrate volatilization rate to the oxygen reaeration rate constant can be measured in the laboratory[30, 31]. The volatilization rate of the substrate in a real body for which the oxygen

$$(K_C)_{env} = (K_O)_{env} \left(\frac{K_C}{K_O} \right)_{lab}$$

$$= U_{CO} (K_O)_{env} \qquad (2)$$

where K_C is the rate constant of hydrophobic organic compounds for the body of water under investigaion, and K_O is the reaeration rate constant of oxygen. The consistency of the ratio, U_{CO}, between two constants was established for those material that have a volatility similar to oxygen, i.e., for those materials whose resistance is mainly in the liquid layer[18]. Several studies confirmed the consistency of the ratio, U_{CO} ($=K_C/K_O$ in laboratory), and found that the ratio is independent of turbulence levels[15, 22, 25, 26, 32], of the presence of surfactants[32], of aeration system[15], of dissolved solids[1, 27], or of temperature[32].

2.2 Adsorption and Desorption.

Sorption includes any process whereby organic substrates are physically or chemically bound to a solid surface. It is postulated that sediments, soils, suspended solids and biota act as sinks for sorbed materials, removing them from the water column. However, the substrates can also be released (desorbed) from the suspended solids at a later time.

Sorption studies have been conducted with natural sediments and hydrophobic organic compounds having a water solubility less than several parts per million. The sorption isotherms appear to be linear over a range of dissolved phase concentration[8, 31, 34]. The linear partition coefficient[8], K_P, is given by

$$X = K_P C \qquad (3)$$

where X denotes the concentration of sorbate on the sediment, relative to dry weight (conveniently expressed as ppb), C is the equilibrium solution sorbate concentration (ppb) and K_P is the partition coefficient. The linear partition coefficient are relatively independent of sediment concentrations and ionic strength in the suspensions. Sorbates in a mixture of the sediments and organic substrates sorb independently[8].

The organic carbon content of the sediment[8, 9, 31, 34] and octanol-water partition coefficient of the chemical[8, 9] are the most reliable predictors of sorption capacity. As sorption is keyed soly to organic carbon, the partiotion coefficient is normalized for the fraction of organc carbon in the sorbent, expressed by

$$K_{OC} = K_P/OC \qquad (4)$$

where OC is the fractional mass of organic carbon in the sediment and K_{OC} is the partition coefficient normalized to the organic carbon content.

It was experimentally shown that the K_{OC} is directly proportional to the octanol-water partition coefficients, K_{OW}[8].

$$K_{OC} = 0.63 \ K_{OW} \qquad (5)$$

$$\text{or log } K_{OC} = 1.00 \text{ log } K_{OW} - 0.21 \qquad (6)$$

Two material balance equations are suggested to describe adsorption and desorption kinetics of pesticides in lake waters[16, 19, 28]. They are formulated for the dissolved phase and particulate phase, separately, taking into account the interactions with each other.

$$\frac{dC}{dt} = -K_f \ X \ C + K_r \ C_P \qquad (7)$$

$$\frac{dC_p}{dt} = K_f X \ C - K_r C_p \qquad (8)$$

where C and C_P are the concentration of the chemical in the dissolved phase and particulate phase, respectively, in the system at time, t. K_f and K_r are the adsorption rate constant and desorption rate constant, respectively. X indicates the concentration of suspended solids.

2.3 Biodegradation

The techniques used in evaluating the biodegradability of organic substrates have varied extensively, and it is doubtful that any one procedure can be used to indicate susceptibilities to biodegradation in aquatic environments[30]. The phenomena are too complex and varied with some of the substrates that are difficult to de-

grade. It is recognized that problems associated with assessing the biodergradative fate of PCBs in the environment are numerous and relate to low solubility, volatilization, photodecomposition and particulate matter[29]. It appears that without precise knowledge or careful control of the factor mentioned above, it is virtually impossible to estimate the true biotransformation rate of hydrophobic organic compounds.

Typically, the Monod expression for substrate utilization has been used to describe the biodegradation kinetics of PAHs and pesticides[20, 21, 23, 30, 31].

$$\frac{dC}{dt} = -\frac{U_m}{Y}\frac{C}{K_s+C}X \qquad (9)$$

where C is the concentration of the chemical at time, t, U_m is the maximum growth rate, Y is the yield coefficient in biomass produced per unit C metabolized, K_s is the concentration of the chemical supporting a half-maximum growth rate and X is the biomass per unit volume.

When the chemical concentration is much lower than K_s, then the Eq.9 is reduced to

$$\frac{dC}{dt} = -\frac{U_m}{YK_s}C\ X = -K\ C\ X \qquad (10)$$

where K is a second-order rate constant with units of volume/time/biomass for removal of the chemical by biomass when X is expressed in biomass/volume. The rate expression is used to depict the biodegradation of hydrophobic organic chemicals in natural waters[16, 17].

3. Process Model

The purpose of a model building in this study is to follow the path of a chemical through activated sludge processes, not to determine the effects of the chemical on biological reactions occurring in the various segments of the activated sludge processes. The compartmental analysis, based on the kinetic formulations and the principle of continuity or mass balance, has been used for visualizing the movement and distribution of the chemical in the system.

Anthracene is chosen for study because it is commercially important PAH which is produced in large quantities and used extensively as a reagent in organic synthesis. Also, it is distributed among the liquid, solid and gaseous phase of the system. The major physical and chemical properties are shown in Table 1 as well as those for naphthalene and phenanthrene.

3.1 Physical Configuration and Notation

A conventional activated sludge treatment system has been chosen for modeling. The system is assumed to be preceded by screening, grit removal and primary sedimentation. The activated sludge section consists of a single aeration basin and a final clarifier. The system is assumed to be well-operated at steady state conditions (with a fixed ratio maintained between the rate at which nutrient are utilized and the rate of bacterial growth). The mixed liquor in the aeration basin is completely mixed with sludge recycle. A portion of the mixed liquor is directly withdrawn form the aeration basin as waste sludges.

The schematic configuration of the system used in this study is shown in Figure 2 and the numerical values in the figure is further discussed in the following section. The symboles (i. e., Q, S, X, C, C_P, C_S, C_t) and the subscripts (i.e.,

Table 1. Properties of the PAHs

Properties	Anthracene	Naphthalene	Phenanthrene
Mol.wt.(g/g−mol)	178.23	128.19	178.23
Henry's Constant (dimensionless)	0.067	0.017	0.006
Vapor Pressure (mm Hg)	0.04	0.87	0.0034
Solubility (mg/L)	0.075	30	1.18
Octanol−Water(log Kow) Partition Coefficient	4.45	3.37	4.46

References : EPA−430/9−78−009 and EPA−440/4−79−029b

o, u, i, a, r, w, e, m)are initially defined as shown in Appendix. However, some of them are redefined in the course of the text, since BOD_5 and TSS are not readily available variable for the consideration of real-time dynamic simulations. The rest of the symboles which do not above are explained in the section where they first appear.

3.2 Primary Clarifier

The objective of primary sedimentation is to remove readily settleable solids and floating material and thus to reduce the suspended solids content. The major mechanisms are the physical separation of suspended solids and some reduction of the influent soluble substrates. Efficiently designed and operated primary sedimentation tanks should remove from 50% to 70 % of the suspended solids[14].

Assume that the equilibrium has been reached between the dissolved and suspended solids phase of a chemical before the chemical in the influent enters the clarifier. A mass balance for the total suspended solids in the primary clarifier can be written as

$$Q_o X_o - Q_i X_i - Q_u X_u = 0 \qquad (11)$$

Define that f_u is the fraction of the total suspended solids removed from the primary clarifier and U is equal to Q_u/Q_o.

$$f_u = \frac{Q_u X_u}{Q_o X_o} \qquad (12)$$

$Q_i X_i$ can be then expressed as

$$Q_i X_i = (1 - f_u) Q_o X_o \qquad (13)$$

Substituting Eq. 13 for $Q_i X_i$ in Eq. 11 yields

$$U Q_o X_u = Q_o X_o - (1 - f_u) Q_o X_o \qquad (14)$$

and $$U = f_u \frac{X_o}{X_u} \qquad (15)$$

Q_u is then expressed by

$$Q_u = U Q_o = \frac{f_u X_o}{X_u} Q_o \qquad (16)$$

Using the relationship of $Q_o = U Q_o + Q_i$, Q_i is given in terms of f_u and X_u, as

$$Q_i = \left(\frac{X_u - f_u X_o}{X_u} \right) Q_o \qquad (17)$$

Substituting Eq. 17 for Q_i in Eq. 13, then

$$X_i = \frac{(1 - f_u) X_o X_u}{X_u - f_u X_o} \qquad (18)$$

Suppose that C_{so} is the amount of the chemical in the influent suspended solids in mass of the chemical per unit mass of the total suspended solids,

$$C_{po} = C_{so} X_o \qquad (19)$$

Assume that mass of the chemical in the suspended solids getting into and out of the primary clarifier is unchanged (i.e., $C_{si} = C_{so}$). C_{pi}, which is equal to $C_{si} X_i$, can be expressed by

$$C_{pi} = C_{so} \frac{(1 - f_u) X_o X_u}{X_u - f_u X_o} \qquad (20)$$

3.3 Aeration Basin : Mathematical Formulations of Fate Model

The kinetic formulations investigated in natural aquatic system was used to postulate a compartmental model of the distribution, transport and fate of PAHs in an activated sludge process. The schematic presentation of the movement of a chemical in an aeration basin shown in Figure 1.

The aeration basin was modeled as having three compartment : liquld, particulate and gaseous. Each compartment represents the entire volume and mass of the particular physical phase. Furthermore, the contents of each compartment were assumed to be homogenous, thus enabling each compartment to be modeled as a completely stirred reactor. The complete model of the aeration basin consists of five material balance equations, each formulated as an ordinary differential equation, as follows : (1) parent compound in the liquid phase, (2) non-parent compound in the liquid phase, (3) parent compound in the particulate phase, (4) non-parent compound in the particulate phase, and (5) parent compound in the gaseous phase. Non-parent compound in the gas phase is assumed to
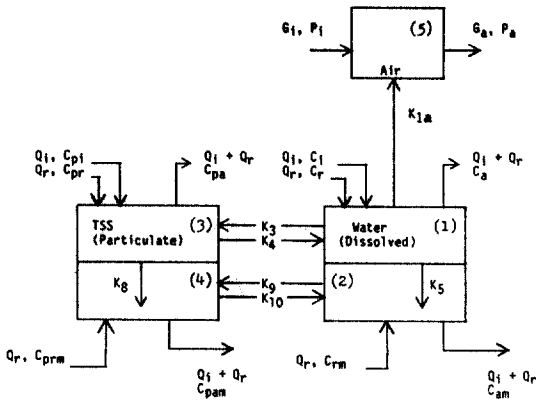
Figure 1. Compartmental Model for the Movement of a Chemical in an Aeration Basin.

be negligibly small. If experimental data should indicate that it should be included, all that is required is to write one more differential equation.

The mass balance equation for a PAH (C_a) in the dissolved phase is given by

$$V\frac{dC_a}{dt} = Q_iC_i + Q_rC_r - (Q_a+Q_w)C_a - K_1A(C_a$$

$$-(\frac{P_a}{H})M) - K_3X_aC_aV + K_4C_{pa}V - K_5X_aC_aV \tag{21}$$

where t is the time elapsed in hour as an independent variable in the system, V is the volume of the liquid (e.g., the liquid-air bubble mixture) in the aeration basin in L, and A is the interfacial mass transfer area of the liquid-air mixture. K_1 is the volatilization rate constant of the chemical which has the dimensions of velocity, K_3 is the adsorption rate constant in L/ mg of TOC/hr, K_4 is the desorption rate constant in hr^{-1}, K_5 is the biodegradation rate constant in the dissolved phase in L/mg of TOC/hr. X is the TOC concentration of total suspended solids in mg of TOC/L, P_a is the partial pressure in the gas phase in atm, H is the Henry's law constant in atm $m^3/g-mol$, and M is the molecular weight of the PAH in mg/g−mol. The rest of the symbols are the same as previously

defined and presented in Appendix.

Substituting R Q_i for Q_r and (1+R) Q_i for (Q_a +Q_w) in Eq.21, and dividing the Eq.21 by V, the Eq.21 can then be expressed by

$$\frac{dC_a}{dt} = \frac{C_i}{t_o} + \frac{RC_r}{t_o} - \frac{(1+R)C_a}{t_o} - k_{1a}(C_a$$

$$-(\frac{P_a}{H})M) - K_3X_aC_a + K_4C_{pa} - K_5X_aC_a \tag{22}$$

where $t_o(=V/Q_i)$ is the hydraulic retention time of wastewater in the aeration basin in hour, and $K_{1a}(=K_1A/V)$ is the volatilization rate constant of the chemical in hr^{-1}.

Under the same assumption and procedures above, the mass balance for the PAH in the suspended solids phase, C_{pa}, is also given by

$$\frac{dC_{pa}}{dt} = \frac{C_{pi}}{t_o} + \frac{RC_{pr}}{t_o} - \frac{(1+R)C_{pa}}{t_o}$$

$$+ K_3X_aC_a - K_4C_{pa} - K_8C_{pa} \tag{23}$$

where K_8 is the biodegradation rate constant in the suspended solids phase in hr^{-1}.

For the air compartment, the mass balance for the PAH in the gas phase can be given as

$$\frac{M}{R_gT}V_g\frac{dP_a}{dt} = \frac{M}{R_gT}(G_iP_i - G_aP_a) +$$

$$K_{1a}V(C_a - (\frac{P_a}{H})M) \tag{24}$$

where R_g is the constant in std atm $m^3/g-mol$ °K, T is the temperature in °K, G is the air flow rate in L/hr, and V_g is the volume of the gas in the aeration basin in L.

The mass balance for the non-parent compound (metabolites) in the dissolved phase is

$$\frac{dC_{am}}{dt} = \frac{RC_{rm}}{t_o} - \frac{(1+R)C_{am}}{t_o}$$

$$+ K_5X_aC_a - K_9X_aC_{am} + K_{10}C_{pam} \tag{25}$$

where K_9 is the adsorption rate constant for the metabolite in L/mg of TOC/hr and K_{10} is the desorption rate constant for the metabolite in hr^{-1}. The index m indicates metabolite. The terms with K_9 and K_{10} have been included in Eq. 25 under the assumption that the rate expression describing the adsorption and desorption for

parent compounds may be directly used for depicting the behavior of the non-patrent compounds.

The mass balance for the non-parent compound in the particulate phase is

$$\frac{dC_{pam}}{dt} = \frac{RC_{prm}}{t_o} - \frac{(1+R)C_{pam}}{t_o}$$
$$+ K_8 C_{pa} + K_9 X_a C_{am} - K_{10} C_{pam} \qquad (26)$$

Photolysis may account for transformation of hydrophobic organic chemicals in dilute solution. As sunlight passes down through a water body, its intensity decreases and marked changes in its spectral distribution occur. It is clear that photolysis is not a major transport pathway of anthracene in mixed liquors in aeration basins. PAHs do not contain groups amenable to hydrolysis. Hydrolysis is not thought to be a significant fate process for anthracene, either. As a practical matter, neither photolysis nor hydroysis is considered in mathematical formulation as described above.

The mathematical model, consisting of Eq.22 through Eq.26, is also directly applicable, without any change of the notation previously used, to an activated sludge system where waste sludges are discharged from returned sludge line, since it is a matter of the location of waste sludges discharging points.

4. Discussion of Results

4.1 Steady State Simulations

A conventional activated sludge system with a single aeration basin, preceded by primary sedimentation was modeled. This study considered that 10 ug of anthracene per liter of water in the dissolved phase (C_o) is found in the influent into the primary clarifier. Provided that the major mechanism in it is the physical separation of total suspended solids and no reduction of the influent BOD_5 (S_o), X_i and C_{pi} in the primary clarifier effluent can be predicted using Eq. 18 and 20 under presumed operational con-

Table 2. Operational Conditions in Primary Clarifier

Variable	Value
C_o	10 ug/L
S_o	240 mg of BOD_5/L
X_o	0.00025 kg of TSS/L (250mg/L)
Q_o	157,725 L/hr (1 MGD)
f_u	0.6
X_u	0.04 kg of TSS/L (40,000mg/L)
K_{oc}	16,000 for anthracene
OC	0.3 for raw sewage
OC	0.45 for mixed liquor

Related assumptions : $C_i = C_o$; $C_{si} = C_{so}$.

ditions shown in Table 2.

The partition coefficient, K_{oc}, normalized to organic carbon is 16,000 for anthracene[23]. It was assumed that organic carbon contents (OC) are 0.3 and 0.45 for the total suspended solids in raw sewage and mixed liquor, respectively. It was also assumed that instantaneous partitioning of anthracene in between the dissolved phase and the particulate phase has been established in the sewer before the raw sewage reaches the plant. Determination of the concentrations, C_i, C_{si} and C_{pi} in the effluent from the primary clarifier was made and summarized in Table 3.

Consider the proposed fate model consisting of the five differential equations (Eq.22 through

Table 3. Variables Calculated from the Known Operational Conditions

Variables	Value	Applicable Equation
U	0.0375	Eq.15
Q_u	591 L/hr(0.00375 MGD)	Eq.16
Q_i	157,134 L/hr(0.99625 MGD)	Eq.17
X_i	0.00010038kg of TSS/L(100.38 mg/L)	Eq.18
K_p	4,800(ug/kg of TSS)/(ug/L)for raw sewage	Eq.4
K_p	7,200(ug/kg of TSS)/(ug/L)for mixed liquor	Eq.4
C_{so}	48,000ug/kg of TSS	Eq.3
C_{po}	12 ug/L	Eq.19
C_{to}	22 ug/L	—
C_i	10 ug/L	—
C_{si}	48,000ug/kg of TSS	—
C_{pi}	4.82 ug/L	Eq.20
C_{ti}	14.82 ug/L	—

Eq.26). Under steady state conditions (i.e., $dC_a/dt = 0$, $dC_{pa}/dt = 0$, $dP_a/dt = 0$, $dC_{am}/dt = 0$, and $dC_{pam}/dt = 0$), the fate model has five algebraic equations with five unknown state variables. The steady state simulation of the fate of anthracene in the aeration basin can be possible with known kinetic rate constants and input variables.

Experiments with hexachlorobenzene, PCB, DDE and chlordane yielded rates of volatilization that are 20% − 30% of the oxygen reaeration rate[1]. The ratios of the chemical volatilization rate constants to the oxygen reaeration rate constant range between 0.14 to 0.71 for the hydrophobic compounds. The ratio that for anthracene is not available. Assuming a value in the middle of this range, for lack of better information, gives a ratio of 0.4. Assuning the reaeration rate constant is 10.8 hr^{-1}[4] gives an estimated volatilization rate constant for anthracene, K_{1a}, of 4.32 hr^{-1}.

A biodegradation rate constant was estimated to be 0.021 mL/g of biological mass/hr using ^{14}C−labeled trichlorobiphenyl[16]. Provided that the biological mass is the total suspended solids in mixed liquor and total organic carbon (TOC) content in the total suspended solids is 45%, K_8 was assumed to be about 5.25 $\times 10^{-5}$ hr^{-1} and K_5 was about 2.34×10^{-8} L/mg of TOC/hr, which is actually a half of K_8.

Based on the review of results from sorption kinetic studies of several PAHs in many streams[33], K_3 and K_4 were assumed to be 2.34×10^{-3} L/mg of TOC/hr and 0.32 hr^{-1}, repectively. K_9 and K_{10} were considered as half of K_3 and K_4. The seven kinetic rate constants for anthracene in the aeration basin are given in Table 4.

In addition, the fourteen input variables in Table 5 were assumed to represent the activated sludge treatment system for steady state simulation. It is noted that the gas flow rate, G_a,

Table 4. Kinetic Rate Constants for Anthracene in Aeration Basin

Rate constant	Value
K_{1a}	4.32 hr^{-1}
K_3	2.84×10^{-3} L/mg of TOC/hr
K_4	0.32 hr^{-1}
K_5	2.34×10^{-8} L/mg of TOC/hr
K_8	5.25×10^{-5} hr^{-1}
K_9	1.42×10^{-3} L/mg of TOC/hr
K_{10}	0.16 hr^{-1}

Table 5. Input Variables for the Proposed Fate Model

Variable	Value
f_x	4
R	0.3199
H	1.16108×10^{-3} atm m^3/g−mol
G_a	9.0509×10^7 L/hr
M	178,230 mg/g−mol
R_g	8.2054×10^{-5} atm m^3/g−mol
V	942,800 L
V_g	10,180 L
X_a	1,125 mg of TOC/L (2,500mg of TSS/L at a 45% OC)
t_o	6 hr
T	293 °k
C_i	10 ug/L
C_{pi}	4.82 ug/L
P_i	0.0 atm

was selected, based on a rate of 1.6 L air/min per liter of reactor volume[7]. Furthermore, if one assumed that the following relationships are valid : $C_r = C_a$; $C_{pr} = f_x C_{pa}$, where $f_x = X_r/X_a$; $C_{rm} = C_{am}$; $C_{prm} = f_x C_{pam}$; and $G_i = G_a$, the solution at the steady state conditions were as follows : $C_a = 0.87$ ug/L; $C_{pa} = 10.97$ ug/L; $P_a = 3.16 \times 10^{-9}$ atm; $C_{am} = 2.49 \times 10^{-3}$ ug/L; and $C_{pam} = 0.027$ ug/L.

A total suspended solids content of 12.06mg TOC/L (as 26.8mg of TSS/L) in the final clarifier effluent was calculated assuming that the fraction of TSS removed from the final

$C_o=10.$ $C_i=10.$ $C_a=0.87$
$C_{po}=12.$ $C_{pi}=4.82$ $C_{pa}=10.97$
$C_{BO}=48,000$ $C_{Bi}=48,000$ $C_{Ba}=9,751$
$X_o=2.5\times10^{-4}$ $X_i=1.0038\times10^{-4}$ $X_a=1,125$
$S_o=240.$ $S_i=240.$ $S_a=15.$
$Q_o=157,725$ $Q_i=157,134$ $Q_a=198,143$

$C_u=10.$ $C_r=0.87$ $C_e=0.54$
$C_{pu}=1,920$ $C_{pr}=43.88$ $C_{pe}=0.12$
$C_{Bu}=48,000$ $C_{Br}=9,751$ $C_{Be}=9,751$
$X_u=0.04$ $X_r=4,500$ $X_e=12.06$
$S_u=240.$ $S_r=15.$ $S_e=15.$
$Q_u=591.$ $Q_r=50,275$ $Q_e=147,868$

$C_w=0.87$
$C_{pw}=10.97$
$C_{Bw}=9,751$
$X_w=1,125$
$S_w=15.$
$Q_w=9,266$
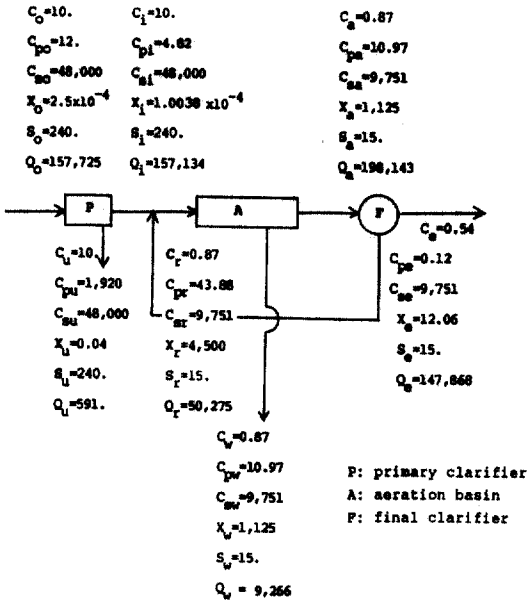
P: primary clarifier
A: aeration basin
F: final clarifier

Figure 2. Schematic Configuration of an Activated Sludge Treatment System, and Mass Balances for Anthracene, TSS and BOD₅, and Flow Rates : X_o, X_i and X_u in kg TSS/L; X_a, X_r and X_w in mg TOC/L.

Table 6. Mass Fluxes for Anthracene (g/day)

Sources for Loss	Rate (g/day) of Removal	Percent of Removal
Volatilization	50.93	61.16
In primary sludge	27.39	32.89
In waste sludge	2.63	3.15
In final clar. efflu.	2.33	2.80
Biodegradation	0.0136	—

Figure 3. Schematic Diagram of Mass Fluxes (g/day) of Anthracene in the Activated Sludge Treatment System.

clarifier is about 99.2%, and the TOC content in the TSS is 45%. The substrate concentration, S_a, in the aeration basin was assumed to be 15mg BOD₅/L.

Mass balances for anthracene, TSS and BOD ₅, and flow rates at the points of interest in the activated sludge system are shown in Figure 2. Note that the concentrations, C_e and C_{pe}, were calculated under the assumption that instantaneous partitioning of anthracene in between the dissolved phase and the particulate phase were achieved when the mixed liquor leaving the aeration basin was put out of forced aeration conditions.

On the basis of the mass balances in Figure 2, the fate of anthracene (83.28 g/day as an input load into the system) are summarized in Table 6 and shown in Fugure 3 as a schematic diagram of mass fluxes.
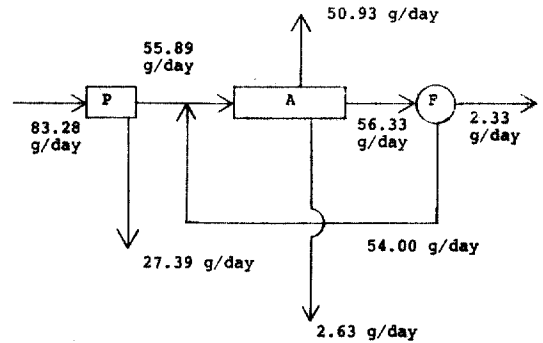
Under the steady state assumptions and the conditions previously described, volatilization (61%) and disposal of primary sludge (33%) were two major losses of anthracene from the system. Mass fluxes in waste sludges and final clarifier efluent or biodegradation were minor pathways for removal of anthracene from the system. The overall removal of anthracene was about 97% in the system.

It seems remarkable that the mass flux in the internally recycled sludges accounted for 54.00 g/day of the input load (83.28 g/day) into the system. It is due to the results that anthracene was partitioned between the dissolved phase(C_r =0.87 ug/L) and the particulate phase (C_{pr}= 43.88ug/L) in the returned sludges.

Since experimental results are not available, it is impossible to quantitatively compare them with the steady state calculations.

However, field surveys[12] and an investi-

gation of the behavior of spiked organic chemi-cals[24] has shown a coincidence that primary sedimentation is one of the major removal path-ways in a conventional activated sludge wastewater treatment system. The results in Table 6 also suggest that hydrophobic organic chemicals entering the system would be present in varying degree in the liqiud, solids and off-gas phase in activated sludge processes.

It is noted that the results from the steady state simulations are considered to be prelimi-nary in nature. Nonetheless, the present study has offered a useful mathematical modeling approach to determine the major transport path-ways of hydrophobic organic chemicals in acti-vated sldge processes.

4.2 Dynamic Simulation

Dynamic simulations of the proposed fate model were conducted to investigate the transi-ent behavior of the system. This study considers that 10 ug/L and 4.82 ug/L anthracene in the dissolved phase and the particulate phase, re-spectively, were found in the primary effluent.

The seven kinetic rate constants and fourteen input variables with the conditions provided for the steady state modeling were assumed to re-present the activated sludge system for dynamic simulations. As shown in Equation 22 through Equation 26, the model is composed of the five initial value ordinary differential equations and was integrated simultaneously using the numeri-cal method[3]. The initial values for the five state variables were assumed to be zero for this dynamic modeling. The calculation results show that all of the five responses eventually reach the steady state values at the time shown in Table 7.

The system reaches a practical steady state at about 160 hours since the solutions for C_{am} and C_{pam} are extremely small, and the times re-quired for C_{am} and C_{pam} to reach steady con-ditions are longer than those for C_a and C_{pa} by a

Tabel 7. Responses at Steady State via Dynamic Modeling

Response	Concentration at Steady State	Time Required to Reach Steady State
C_a	0.8709 ug/L	80 hr
C_{pa}	10.97 ug/L	49 hr
P_a	3.162×10^{-9} atm	55 hr
C_{am}	2.492×10^{-3} ug/L	420 hr
C_{pam}	2.734×10^{-2} ug/L	510 hr

factor of 5 or more. 2.734×10^{-2} ug/L of non-parent compounds seems to be a very small con-centration. However, it could not be ignored since the concentration is equivalent of 10.936 ug of the non-parent compounds residing in 1kg of dried TSS, assuming the TSS concentration is about 2,500 mg/L.

5. Conclusions

A mathematical fate model for anthracene has been developed and applied to a con-ventional activated sludge wastewater treat-ment system. Under the steady state assumptions and the conditions given, volatilization (61%) and removal of primary sludges (33%) are two major pathways for dis-appearance of anthracene from the system.

The anthracene mass fluxes in Figure 3 show that mixed liquor suspended solids can adsorb anthracene in primary effluent. The aeration process does significantly strip anthracene into the atmosphere. However, the mass flux in in-ternally recycled sludges remarkably contains a significant amount of input loads of anthracene into the system. The formulated mathematical model (Eq.22 through Eq.26) is also directly applicable, without any change of the symboles used in this study, to an activated sludge sys-tem where waste sludges are discharged from recycle lines.

In this study, kinetic approach was used to describe adsorption and desorption of an-

thracene onto total suspended solids in the system. As a practical matter, experimental results may show that sorption process is rapid and may not be rate-limited, in which cases an appropriate modification should be made in the model. However, it is not part of this study. It is expected that the model will have broad application to a majority of the organic priority pollutants entering wastewater treatment works.

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Appendix-Notaion

The following symbols are used in this paper.

C = concentration of chemical in dissolved phase, ug/L.

C_p = concentration of chemical in suspended solid phase, expressed in ug of chemical per unit volume of wastewater, ug/L.

C_s = concentration of chemical in suspended solid phase, expressed in ug of chemical per unit weight of suspended solids, ug/kg of TSS(i.e., $C_P = C_S X$).

C_t = total chemical concentration in wastewater, ug/L (i.e., $C_t = C + C_p$)

Q = wastewater flow rate, L/hr

S = concentration of soluble organic substrate, readily available for bacterial growth and maintenance, mg of BOD_5/L.

X = concentration of total suspended solids : X_0, X_i and X_u have units of kg of TSS/L, but X_a, X_r, X_w and X_e are expressed in mg TOC/L.

Subscripts

a = effluent from aeration basin to final clarifier.

e = final clarifier effluent.

i = effluent from primary clarifier to aeration basin.

m = metabolite

o = raw sewage i.e., influent into primary clarifier.

r = recycle flow.

u = underflow from primary clarifier.

w = waste sludge from aeration basin.