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Removal mechanisms of VOCs in an activated sludge process

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Abstract

This study investigated the factors in plant operating parameters effecting volatile organic compound (VOC) removal and elucidated each individual mechanism in an activated sludge process (ASP). The results suggest that stripping increase with an increase in Henry's law constant with the exception of toluene, which differed because of the effect of biodegradation competition. The emission rate can be controlled by increasing the active biomass concentration (X_b) in the aeration basin, hydraulic retention time (HRT), and oxygen transfer efficiency (OTE). Increasing X_b enhances total VOC removal and biodegradation, which reduces the fraction of the stripping removal. Longer HRT can reduce stripping removal significantly if other variables such as oxygen requirement and OTE are held constant. For the same volatile compound, a process with higher air-to-water ratio requires a higher active biomass concentration to reduce stripping removal. Increasing OTE decreases the air-to-water ratio requirement, which reduces the gas-phase transfer of VOCs into the atmosphere. The results show a reasonable agreement between measured and predicted stripping values. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Activated sludge process; Biodegradation; Oxygen transfer; Stripping; Volatile organic compound

1. Introduction

Many different industries generate wastewater streams that contain volatile organic compounds (VOCs). Among wastewater treatment processes, the activated sludge process (ASP) is one of the most significant VOC emission sources. The ASP removes VOC through stripping, adsorption and biodegradation. The adsorption mechanism is

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not as important as stripping and biodegradation [1]. For example, Bhattacharya et al. [2] studied the removal and fate of 11 selected RCRA compounds in a pilot-scale activated sludge system. They showed that sorption of the 11 compounds into primary and secondary sludge ranged from 0.6% to 5.1%. Namkung and Rittmann [3] estimated the VOC emissions from publicly owned treatment works (POTW) using a general fate model. They concluded that biodegradation was the major mechanism for the removal of nonchlorinated VOCs including toluene, benzene, ethylbenzene, and methylene chloride, and stripping was the main removal mechanism for chlorinated compounds such as chloroform, tetrachloroethylene, and trichloroethylene. Other investigators [4,5] essentially report a similar phenomenon, i.e., chlorinated VOCs tend to be stripped to a greater extent than nonchlorinated compounds; the latter VOCs are biodegraded substantially.

Biodegradation removal is a function of the biological rate constant (k_b) and active biomass concentration (X_b) in the reactor. Namkung and Rittmann [3] indicated that the total VOC removal reached a maximum level when k_b was above $0.1 \text{ m}^3/\text{g VSS-d}$. In other words, if VOCs were acclimated to achieve k_b values beyond $0.1 \text{ m}^3/\text{g VSS-d}$, biodegradation would be the control mechanism for VOC removal. The fate of 1,4-dichlorobenzene (DCB) was examined in a bench-scale activated sludge system by Melcer and Bedford [6]. They indicated that DCB removal mechanisms shift between stripping and biodegradation depending on the degree of acclimation afforded to the biomass. Initially, DCB is preferentially removed by stripping. The stripping of DCB declines with increasing acclimation until the major portion of the DCB loss is attributed to biodegradation. However, the lack of k_b values available in the literature is a major detriment for evaluating biodegradation loss. Other investigators [4,5] further demonstrated that the extent of VOC stripping increased at the airflows and lower oxygen transfer efficiencies (OTEs) typically encountered in the coarse diffusers. The objective of this study is to illustrate the effect of plant operating parameters on VOC removal and to elucidate the significance of competing removal mechanisms using a developed mathematical model.

2. Theory of removal mechanisms

2.1. General fate model

The general fate model has been applied to the study of VOC and semi-VOC (SVOC) removal mechanisms in an activated sludge treatment process using diffused aeration. A mass balance on an individual VOC in a completely mixed aeration basin is [3]

$$V \frac{dC_L}{dt} = Q_L C_{LI} - Q_E C_L - Q_W C_L - r_{\text{ads}} - r_m - r_{\text{bio}}, \quad (1)$$

where V is volume of aeration basin (m^3); C_L is target compound effluent concentration (mg/l); C_{LI} is target compound influent concentration (mg/l); t is time (d); Q_L is wastewater flow rate (m^3/d); Q_E is effluent flow rate (m^3/d); Q_W is wasted sludge flow rate (m^3/d); r_{ads} is adsorption rate (g/d); r_{bio} is biodegradation rate (g/d); and r_m

is stripping rate (g/d). The following sections describe the estimation of three removal rates in Eq. (1).

2.2. Stripping rate

Matter-Muller et al. [7] indicated that the mass transfer rates of VOCs in diffused aeration depend upon the mass transfer coefficient as well as the VOC saturation in the exit air bubbles. Roberts and Munz [8] estimated the stripping rate by solving the degree of saturation of the air bubbles in a diffused aeration using the equation given by Matter-Muller et al. [7]

$$r_m = Q_G Hc C_L S_d, \quad (2)$$

where Q_G is air flow rate (m^3/d); Hc is Henry's law constant (dimensionless); S_d is VOC saturation in exit bubbles which is calculated by $[1 - \exp(-\phi)]$ (dimensionless); ϕ is saturation parameter which is estimated by $(K_L a_{\text{voc}} V)/(Q_G Hc)$ (dimensionless); and $K_L a_{\text{voc}}$ is VOC mass transfer coefficient ($1/\text{d}$).

The stripping rates of VOCs during aeration can be estimated using the two-film theory that has been widely used to estimate the oxygen transfer rate in aeration systems. Smith [9] used a simple laboratory procedure to obtain the ratio of the mass transfer coefficient of the VOC to the oxygen transfer coefficient. If the oxygen transfer coefficient can be estimated or measured in a natural water body or wastewater treatment unit, then the mass transfer coefficient of the VOC under those same conditions can be estimated by multiplying the values of the ratio and oxygen transfer coefficient. Roberts and Dandliker [10] indicated that the mass transfer rate of six VOCs was shown to be proportional to that of oxygen in an agitated vessel, with a proportionality coefficient of approximately 0.6 for the six VOCs studied. Rathbun and Tai [11] simultaneously measured the mass transfer coefficient of VOCs and oxygen in a laboratory-scale stirred tank over a wide range of mixing conditions. They showed that the proportionality of mass transfer coefficients of 1,1,1-trichloroethane, 1,2 dichloroethane to oxygen transfer coefficients were 0.60 ± 0.03 and 0.62 ± 0.01 , respectively. This proportionality was essentially independent of the mixing conditions. These studies demonstrated that the mass transfer coefficient of VOCs and oxygen measured in the laboratory to be constant over a wide range of conditions. Thus, a proportional relationship of the mass transfer coefficients between VOCs and oxygen is defined as Ψ for estimating the VOC stripping rate from the oxygen transfer rate. This application, however, is only valid for highly volatile compounds and may not be applied to SVOC. In this study, a modified Ψ value corrected for liquid resistance referred to as Ψ_m [12,13] was applied for predicting stripping rates of VOCs with widely varying volatility. Since the oxygen transfer is controlled by liquid-phase resistance, one can assume that the overall oxygen transfer coefficient ($K_L a_{\text{O}_2}$) is equal to the liquid-phase oxygen transfer coefficient ($k_L a_{\text{O}_2}$). The relationship between the Ψ_m and Ψ values is described as follows

$$\Psi_m = \frac{K_L a_{\text{voc}}}{K_L a_{\text{O}_2}} = \frac{K_L a_{\text{voc}}}{k_L a_{\text{O}_2}} = \frac{k_L a_{\text{voc}}}{k_L a_{\text{O}_2}} \frac{K_L a_{\text{voc}}}{k_L a_{\text{voc}}} = \left(\frac{D_{\text{LVOC}}}{D_{\text{LO}_2}} \right)^n \frac{R_L}{R_T} = \Psi \frac{R_L}{R_T}, \quad (3)$$

where Ψ_m is modified Ψ value (dimensionless); $k_L a_{\text{voc}}$ is liquid-phase VOC mass transfer coefficient (1/d); Ψ is $((D_{\text{LVOC}})/(D_{\text{LO}_2}))^n$ (dimensionless); D_{LVOC} is liquid-phase diffusion coefficient of VOC (cm^2/s); D_{LO_2} is liquid-phase diffusion coefficient of oxygen (cm^2/s); R_L and R_T is liquid-phase and total resistance, respectively (dimensionless); and n is 0.5 for diffused aeration system. Consequently,

$$\Psi = \Psi_m \frac{R_T}{R_L}. \quad (4)$$

Eq. (4) can be applied to estimate the stripping rate for intermediate and low volatility compounds as long as the mass transfer coefficient of oxygen and liquid-film resistance fraction are known. This application improves the stripping rate estimation for SVOC by incorporating liquid-phase resistance. In order to estimate the stripping rate of a particular compound, Eq. (3) can be rearranged as

$$K_L a_{\text{voc}} = \Psi_m K_L a_{\text{O}_2}. \quad (5)$$

The oxygen transfer coefficient ($K_L a_{\text{O}_2}$) is estimated from the oxygen requirement using a mass balance:

$$K_L a_{\text{O}_2} = \frac{R_{\text{O}_2}}{(C_{\text{LO}_2}^* - C_{\text{LO}_2})V}, \quad (6)$$

where R_{O_2} is dissolved oxygen requirement in the aeration basin (g/d); $C_{\text{LO}_2}^*$ is DO concentration in equilibrium with the atmosphere (mg/l); and C_{LO_2} is DO concentration in the aeration basin (mg/l).

2.3. Biodegradation rate

The biodegradation rate is independent of the VOC concentration (zero-order) at high VOC concentrations. For very dilute concentrations, the Monod kinetics rate becomes a first-order relationship with respect to VOC. In this study, the first-order relationship suggested by Namkung and Rittmann [3] was used to express the biodegradation rate (r_{bio}) as

$$r_{\text{bio}} = k_b X_b V C_L, \quad (7)$$

where k_b is apparent first-order biological rate constant ($\text{m}^3/\text{g VSS-d}$); and X_b is active biomass concentration (g VSS/ m^3).

2.4. Adsorption rate

Adsorption is the process in which organic compounds are bound to solids surface, of which biological solids are a primary example. The rate of VOC removal via adsorption is expressed with the concentration of VOC adsorbed on the sludge when biomass is wasted from the system [3]

$$r_{\text{ads}} = Q_w X_w k_p C_L, \quad (8)$$

where X_w is concentration of wasted cells (g VSS/ m^3); and k_p is partition coefficient ($\text{m}^3/\text{g VSS}$).

The partition coefficient (kp) is proportional to the octanol/water partition coefficient, K_{ow} [14], which is a ratio of a compound concentration in the octanol phase to its concentration in the water. Karickhoff et al. [14] found that this proportionality for organic compounds is

$$kp = (6.3 \times 10^{-7}) f_{oc} K_{ow}, \quad (9)$$

where f_{oc} is fraction of organic carbon in solids (g organic carbon/g VSS); and K_{ow} is octanol/water partition coefficient (m^3/m^3 octanol).

For biological cells, $f_{oc} = 0.53$ when cells are presented by $C_5H_7NO_2$, then Eq. (8) can be simplified to

$$r_{ads} = 3.35 \times 10^{-7} Q_W X_W K_{ow} C_L. \quad (10)$$

The ASP system is assumed to be steady-state, thus the accumulation term, $V(dC_L)/(dt)$, is equal to zero in Eq. (1). In addition, the liquid outflow ($Q_E + Q_W$) is assumed to equal the inflow (Q_L). Thus, Eq. (1) is simplified to

$$Q_L(C_{LI} - C_L) - r_{ads} - r_{bio} - r_m = 0, \quad (11)$$

where $r_{ads} = AC_L$; $r_{bio} = BC_L$; $r_m = EC_L$; $A = 3.35 \times 10^{-7} Q_W X_W K_{ow}$; $B = k_b X_b V$; and $E = Q_G HcS_d$.

Eq. (11) can be rearranged to provide the equation for the effluent target compound concentration

$$C_L = \frac{C_{LI}}{1 + R_{ads} + R_{bio} + R_m}, \quad (12)$$

where R_{ads} is adsorption fraction ($(A)/(Q_L)$, dimensionless); R_{bio} is biodegradation fraction ($(B)/(Q_L)$, dimensionless); and R_m is stripping fraction ($(E)/(Q_L)$, dimensionless).

The total fraction of VOC removed from the liquid phase using three different mechanisms (stripping, biodegradation and adsorption) is expressed as the total loss fraction (TLF):

$$TLF = 1 - \frac{C_L}{C_{LI}} = \frac{R_{ads} + R_{bio} + R_m}{1 + R_{ads} + R_{bio} + R_m}. \quad (13)$$

The emission factor (EF), the fraction of the total mass loading of the influent liquid stream, which is stripped from the process, can be estimated by the stripping fraction as

$$EF = \frac{R_m}{1 + R_{ads} + R_{bio} + R_m}. \quad (14)$$

2.5. Competing removal mechanism

The removal competition between stripping and biodegradation can be conceptually expressed using the concept of “competing point” (CP), where the biodegradation rate competes equally with the stripping rate. The required active biomass concentration at

the CP is then termed as the competing active biomass concentration (CB). Thus, for a given VOC with higher volatility, it requires a higher active biomass concentration to compete with the stripping mechanism. At the CP, the stripping removal is equal to the biodegradation removal, or Eq. (2) equals Eq. (7). Thus, CB and the biological rate constant at the CP are calculated as follows

$$CB = \frac{Q_G HcS_d}{K_b V}, \quad (15)$$

$$k_{b,CP} = \frac{Q_G HcS_d}{X_b V}. \quad (16)$$

where $k_{b,CP}$ is biological rate constant at the CP (m^3/g VSS-d).

2.6. Selected organic chemicals and operational parameters

The 10 organic compounds, with diverse volatility, evaluated in this study are perchloroethylene (PCE), 1,1,1-trichloroethane (111TCA), trichloroethylene (TCE), toluene (TLN), chloroform (CLF), methylene chloride (MC), styrene (STR), 1,2-dichloroethane (12DCA), naphthalene (Naph), and methyl ethyl ketone (MEK). The properties and biological rate constants of these compounds are summarized in Table 1. The Hc values of these 10 VOCs range from 0.0018 to 1.17. Three compounds (1,2-DCA, Naph, and MEK) can be considered as SVOC and the remaining seven compounds as VOC. These 10 chemicals are frequently observed in synthetic organic chemicals manufacturing industrial waste streams. PCE, 111TCA, TCE, CLF, MC and 12DCA are chlorinated VOCs and the remaining four compounds are nonchlorinated compounds.

Table 2 provides the operating parameters for an industrial wastewater plant located in southern Taiwan. An average 25°C water temperature in the aeration basin was used throughout this study. A ratio of gas-phase to liquid-phase mass transfer coefficient of 10 was used to estimate the mass transfer coefficient of VOC in diffused aeration as

Table 1
Properties of 10 selected chemicals (25°C)

VOCs	Hc (–)	K_{ow} (–)	k_b (m^3/g VSS-d)	D_L (10^5 cm^2/s)
PCE	1.170	398	0.016	0.82
111TCA	0.701	309	0.018	0.88
TCE	0.371	195	0.021	0.91
TLN	0.268	490	0.058	0.86
CLF	0.138	91	0.019	1.0
MC	0.130	18	0.01	1.17
STR	0.115	1445	0.003	0.8
12DCA	0.049	28	0.024	0.99
Naph	0.0196	2344	0.024	0.75
MEK	0.0018	1.9	0.005	0.98

Source: USEPA [15].

Table 2
Operational parameters of wastewater treatment plant

Parameters	Unit	Value
Wastewater flow rate, Q_L	m^3/d	17,800
Air flow rate, Q_G	m^3/d	623,000
Air to water ratio, Q_G/Q_L	–	35
Aeration tank volume, V	m^3	6000
Depth of basin, Z_d	m	7.2
Wasted cells concentration, X_W	$\text{g VSS}/\text{m}^3$	7500
Wasted sludge flow rate, Q_W	m^3/d	950
Solid retention time, SRT	d	3.3
Hydraulic retention time, HRT	h	8
Oxygen requirement	kg/d	12,500
Oxygen transfer efficiency, OTE	%	7.9
Oxygen transfer coefficient, $K_L a$	d^{-1}	387

suggested by Hsieh et al. [13]. The average mixed liquor suspended solids (MLSS) was 3400 mg/l with $X_b = 2040$ mg/l.

3. Results and discussion

The approach presented above is used to simulate a competing VOC removal mechanism in an ASP. Table 3 shows the results of CB, $k_{b,CP}$ as well as the fraction distribution of three VOC removal mechanisms for ten VOCs at $X_b = 2040$ mg/l.

3.1. Effect of active biomass concentration

Figs. 1–3 present the effects of varying X_b on the distribution of the individual removal fraction for PCE, TLN, and Naph. As X_b increases, biodegradation removal further increases and the corresponding VOC removal by stripping decreases. The general trend of VOC removal by each mechanism is similar with little removal by

Table 3
Result for three individual removal mechanisms at $X_b = 2040$ mg/l

VOCs	CB (mg/l)	$k_{b,CP}$ (m^3/g VSS-d)	R_m (%)	R_{bio} (%)	R_{ads} (%)	TLF (%)
PCE	6300	0.050	73.8	23.9	0.1	97.8
111TCA	3930	0.034	64.0	33.2	0.1	97.3
TCE	1830	0.019	45.6	50.8	< 0.1	96.5
TLN	490	0.014	18.9	79.0	0.1	98.0
CLF	465	0.0071	25.8	68.8	< 0.1	94.7
MC	1440	0.0067	37.7	54.1	< 0.1	91.7
STR	680	0.0059	57.5	25.8	2.4	85.7
12DCA	220	0.0025	9.2	85.5	< 0.1	94.7
Naph	90	0.0010	3.8	89.3	1.5	94.5
MEK	40	0.0001	1.5	75.4	< 0.1	76.9

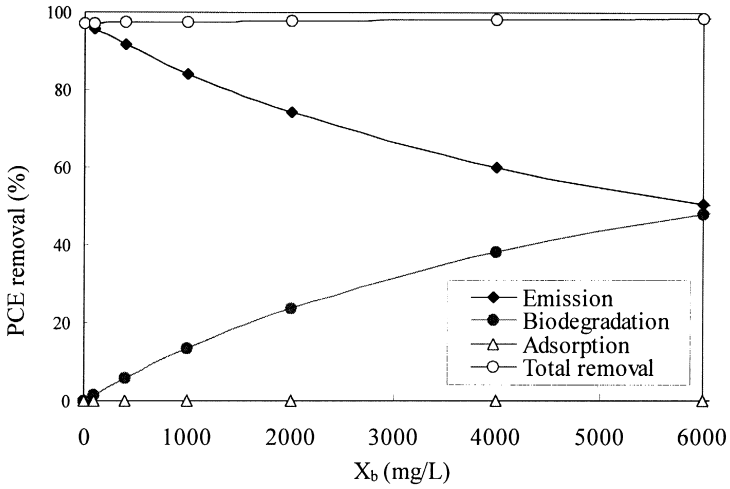


Fig. 1. Effect of X_b on perchloroethylene (PCE) removal.

adsorption. Data in Table 3 and Figs. 1–3 indicate that the $k_{b,CP}$ and CB values decrease with the decreasing Henry’s law constant. Namkung and Rittmann [3] suggested that total VOC removal reached a maximum level when the k_b value was above $0.1 \text{ m}^3/\text{g VSS-d}$. Since the k_b values for these 10 selected compounds were far below $0.1 \text{ m}^3/\text{g VSS-d}$ (Table 1), the stripping for both chlorinated and nonchlorinated compounds is expected to play an important role. Clearly, the stripping removal depends on not only chemical structure, but also biological rate constant which affects the competing mechanism.

The significance of competing mechanism is illustrated by comparing $k_{b,CP}$ and k_b values shown in Fig. 4. VOC removal was dominated by the biodegradation mechanism

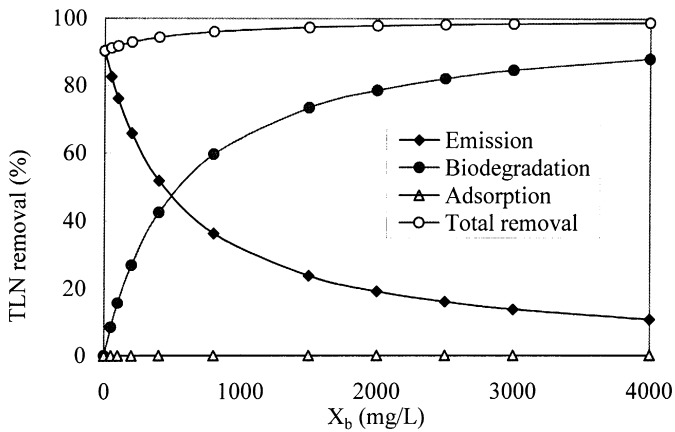


Fig. 2. Effect of X_b on toluene (TLN) removal.

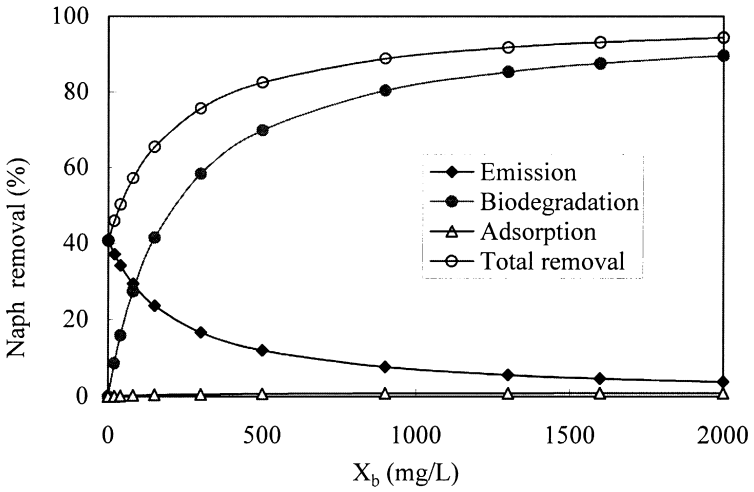


Fig. 3. Effect of X_b on naphthalene (Naph) removal.

for those VOCs (such as MEK, Naph, 12DCA, MC, CLF, TLN) with k_b values higher than $k_{b,CP}$, whereas VOCs (PCE and 111TCA) with higher $k_{b,CP}$ values result in higher stripping removal. TCE was equally removed by stripping (46%) and biodegradation (51%) due to very close values of $k_{b,CP}$ and k_b .

The distribution between biodegradation and stripping can also be expressed by the CB data. For example, when the required CB values of PCE (6300 mg/l) and 111TCA (3933 mg/l) are higher than X_b (2040 mg/l), the major removal of PCE and 111TCA is stripping. For the remaining eight VOCs, the CB values are below 2040 mg/l; thus,

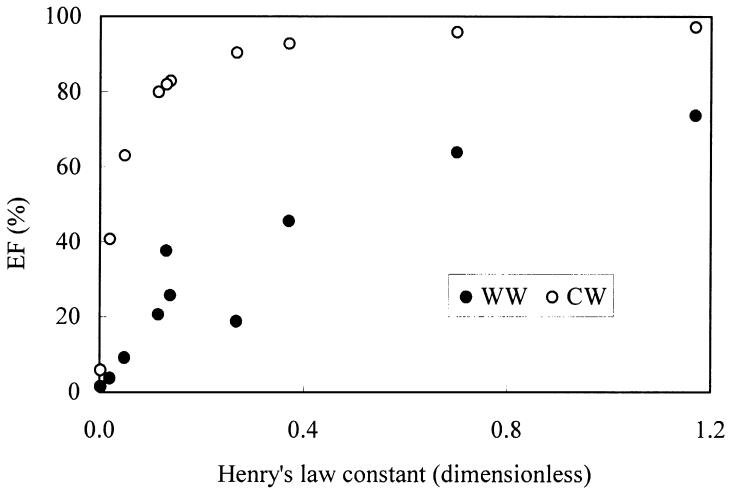


Fig. 4. Comparison of biological rate constants at competing point.

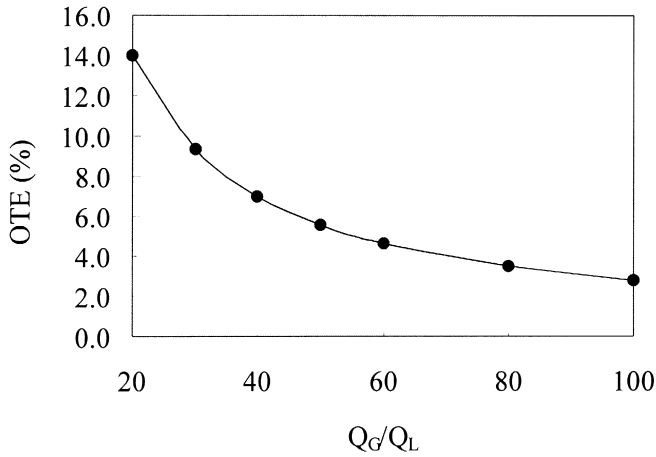


Fig. 5. Relationship between air-to-water ratio and oxygen transfer efficiency.

biodegradation is the major removal mechanism. The total removal of PCE was not affected much by changing the X_b values, whereas the total removal of SVOC, such as Naph and MEK, were significantly influenced by increasing the X_b values. As a result, stripping removal can be practically reduced by increasing X_b above the CB value.

3.2. Effect of air-to-water ratio

The required air flow rate depends on oxygen requirement (R_{O_2}) and OTE. Fig. 5 shows the relationship between Q_G/Q_L and OTE. The product of Q_G/Q_L and OTE is 2.8, which should be constant at a given operating condition. The CB of four VOCs including PCE, styrene, TLN and Naph under various Q_G/Q_L ratios are shown in Fig. 6. Obviously, data in Fig. 6 illustrate that VOCs with higher volatility and under high

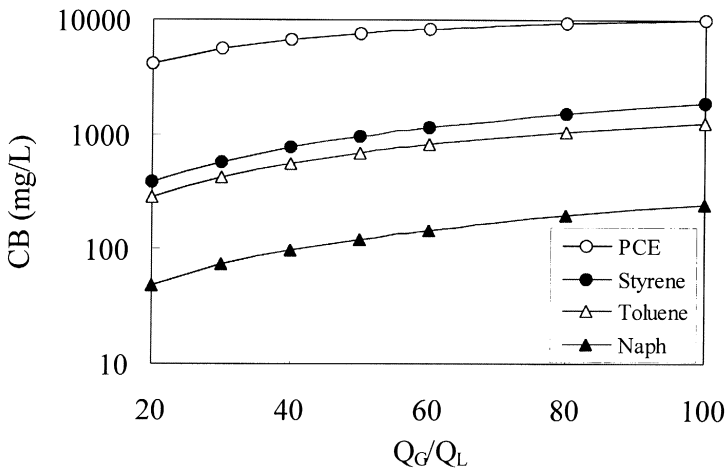


Fig. 6. CB values under different Q_G/Q_L ratio.

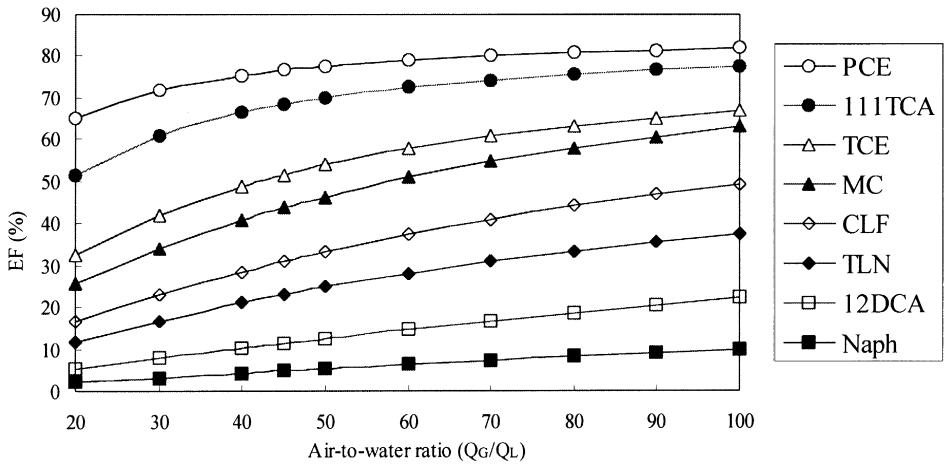


Fig. 7. Effect of air-to-water ratio on emission factor.

Q_G/Q_L require higher X_b to abate the stripping removal. For the same chemical volatility, an ASP with higher Q_G/Q_L requires higher X_b to produce sufficient biodegradation to compete with the stripping removal. On the other hand, using fine diffusers to provide higher OTE can reduce stripping.

The effect of different Q_G/Q_L on stripping removal is illustrated in Fig. 7. It is apparent that the stripping removal increases with Hc and Q_G/Q_L . However, this relationship is not linear for higher volatility compounds such as PCE and 111TCA. As the airflow rate increases, the extent of stripping increases at a declining rate for higher volatility compounds. The results of Fig. 7 essentially confirm the previous study conducted by Parker et al. [4]. Fig. 8 shows the relative EF between different Q_G/Q_L values and those of Q_G/Q_L at 20. The trend of these plots suggests that the stripping removal of high volatility VOC is less sensitive to Q_G/Q_L , while the EF of low volatility compounds increases significantly with increasing Q_G/Q_L .

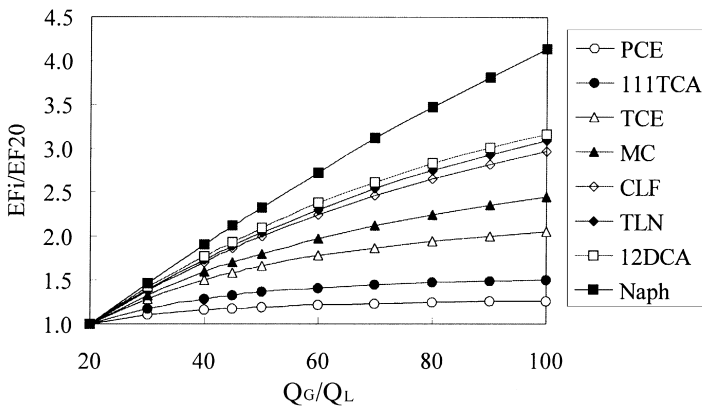


Fig. 8. Effect of air-to-water ratio on relative stripping fraction.

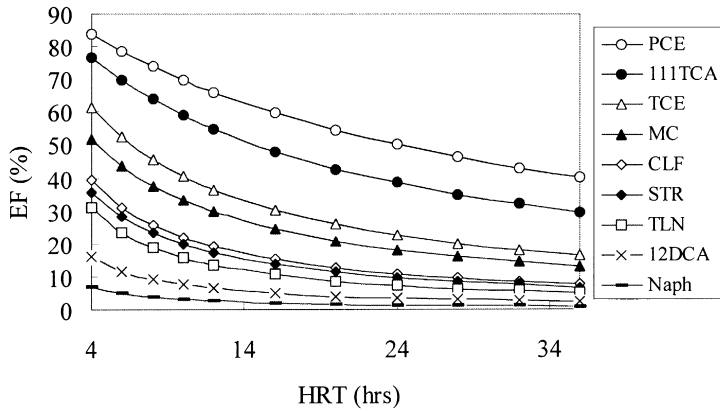


Fig. 9. Effect of hydraulic retention time on stripping fraction.

3.3. Effect of hydraulic retention time (HRT)

The effect of HRT upon stripping removal is shown in Fig. 9. Longer HRT can reduce stripping removal significantly if other variables such as the oxygen requirement and OTE are constant. As shown in Eq. (6), the product of the $K_L a$ and V is constant and is equal to the oxygen required per unit time divided by the driving force ($C_{LO_2}^* - C_{LO_2}$). Longer HRT requires a larger aeration basin volume, which increases the biodegradation rate (Eq. 7) but reduces the oxygen transfer coefficient requirement. Consequently, VOC mass transfer decreases with a decreasing oxygen transfer coefficient. From the point of view of biodegradation, longer HRT also provides sufficient biological reaction time that enhances the overall biodegradation removal. Thus, increasing HRT reduces stripping removal under a constant oxygen requirement.

3.4. VOC saturation in exit bubbles

VOC saturation in exit bubbles (S_d) of PCE, 111TCA, TCE and TLN with OTE from 2.8% to 13.0% is shown in Fig. 10. The compound PCE ($Hc = 1.17$) is the most volatile one evaluated in this study, with S_d from 47% to 96%. The S_d of the next volatile compounds, 111TCA ($Hc = 0.7$) and TCE ($Hc = 0.37$), ranged from 65% to 99% and from 83% to 100%, respectively. For VOC with Hc below 0.2, the VOC saturation exceeded 98% in all ranges of OTE. According to Eq. (2), the VOC stripping removal depends on the air-to-water ratio, Henry's law constant, and VOC saturation in exit bubbles. For a given low volatility compound, VOC in the exit bubbles is nearly saturated and can be assumed to be constant. Thus, the stripping removal is directly proportional to the air-to-water ratio, when the oxygen required per unit time and OTE are held constant. However, the air-to-water ratio is conversely proportional to the OTE at a constant oxygen requirement. Reducing the OTE increases the air-to-water ratio that provides higher carrier capacity for transferring VOC into the atmosphere.

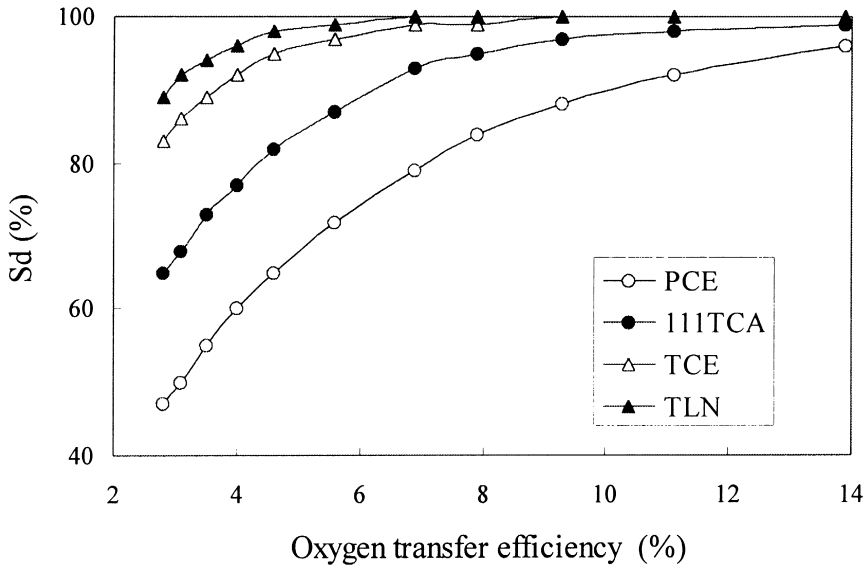


Fig. 10. Dependence of S_d on oxygen transfer efficiency.

3.5. Comparison of predicted results with WATER8 and available data

Predictions from this study are compared with the results of EPA's model and two field tests. The Wastewater Treatment Compound Property Processor and Air Emissions Estimator Program, or WATER8 [16], consists of analytical expressions for estimating air emissions of individual waste constituents in wastewater treatment. Two published field data include those from Parker et al. [4] and Bell et al. [5]. Parker et al. [4] investigated the fate of VOCs in a pilot-plant using ASP, with a daily average flow of 218,000 m³/d of which 22% is contributed by industrial sources. The aeration basin was operated at an HRT of 7.1 h with fine pore dome diffusers at 4.4 m³ air/m³. Off-gas was sampled by drawing a known volume of gas from the vent stack of the covered aeration basin. Bell et al. [5] presented the data collected at the full-scale Skyway plant in Burlington. The Skyway plant receives approximately 17% industrial wastewater operating in an HRT of 6.1 h and employing coarse bubble diffusers at an aeration rate of 16 m³ air/m³. Off-gas samples from the Skyway full-scale aeration basin were collected from 1.49 m² floating chambers.

The results of the stripping predictions and actual measurements are summarized in Table 4. The blanks in Table 4 represent no available data for comparison. The comparison shows that the predictions of this study agree well with the WATER8 for every compound. The major difference between WATER8 and this model is the approach used to estimate mass transfer coefficient. WATER8 uses Springer's correlation [17] for the liquid-phase mass transfer coefficient ($k_L a$) incorporated with two-film theory to estimate air emission rate. The liquid-phase mass transfer coefficient ($k_L a$) has been confirmed as a function of the constituent's diffusivity in water, windspeed, and

Table 4
Comparison of two model predictions and two field measurements

VOCs	Condition 1 ^a		Condition 2 ^b		Condition 3 ^c	
	This study	WATER8 [16]	This Study	Plant 1 [5]	This study	Plant 2 [4]
MEK	2	2				
Naph	4	4				
12DCA	9	10				
STR	58	59				
MC	38	38			44	34
CLF	26	26	17	73	32	33
TLN	19	19			23	15
TCE	46	46	33	29	52	48
111TCA	64	66	52	79	67	31
PCE	74	77	65	40	74	71

^aConditions: model predictions based on the parameters as shown in Table 2.

^bConditions: based on the parameters conducted at Skyway plant in Burlington [5].

^cConditions: based on the parameters conducted at the Highland Creek wastewater treatment plant in Toronto, Ontario [4].

liquid depth [17]. Whereas, this study applies oxygen transfer coefficient corrected for liquid resistance to estimate VOC emission rate. The proportional relationship of the mass transfer coefficients between VOCs and oxygen has been validated in several studies [7–13]. Additionally, the model presented in this study can be applied to estimate the VOC emission rate for intermediate and low volatility compounds. Basically, the model developed in this study is simple and useful for engineering application. Although the approach used in two models is different, they yield similar results and confirm each other.

The correlation between predictions and results for Condition 2 (Plant 1) does not match well, but it still within an acceptable range. Whereas, the correlation between predictions and results for Condition 3 (Plant 2) is good except for the compound 111TCA. A poor 111TCA prediction results from a lack of accurate biodegradation rate constant. As mentioned above, the results of the Plant 1 were collected from a floating flux chamber which covered only a portion of surface and hence may not reflect the actual dynamic conditions of aeration basin resulting in some uncertainties. The Plant 2 was operating in the pilot-plant with a well-controlled system; hence better results. In short, the model in general and many factors affecting stripping presented in this study in particular appear validated.

4. Conclusions

This study presents factors affecting VOC removal mechanisms in an ASP using the mass balance and general fate models. As expected, the stripping removal increases with increases in VOC Henry's law constant. The stripping rate can be reduced by increasing X_b , OTE, and HRT. As X_b increases, total VOC removal and biodegradation increase.

Increasing OTE decreases the air-to-water ratio requirement, which abates the gas-phase conveying capacity to transfer VOC into the atmosphere. Most of the VOCs in the exit bubbles were nearly saturated and can be assumed to be constant in this study. Thus, the stripping removal is proportional to the air-to-water ratio for a given compound, when the oxygen requirement and OTE are constant. Using a higher efficiency diffuser to provide higher OTE can reduce emissions. Longer HRT is also a good selection for controlling VOC emissions. The stripping predictions of this study and WATER8 for all compounds are closely matched, due to the same input parameters used. In comparison with two field data, the model appears validated.

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References

- [1] WEF, *Toxic Air Emissions from Wastewater Treatment Facilities*, Water Environment Federation, Alexandria, VA, 1995.
- [2] S.K. Bhattacharya, R.L. Madura, R.A. Dobbs, R.V.R. Angara, H. Tabak, *Water Environ. Res.* 68 (1996) 260.
- [3] E. Namkung, B.E. Rittmann, *J. Water Pollut. Contr. Fed.* 59 (1987) 670.
- [4] W.J. Parker, D.J. Thompson, J.P. Bell, H. Melcer, *Water Environ. Res.* 65 (1993) 58.
- [5] J. Bell, H. Melcer, H. Monteith, I. Osinga, P. Steel, *Water Environ. Res.* 65 (1993) 708.
- [6] H. Melcer, W.K. Bedford, *Water Environ. Res.* 66 (1994) 887.
- [7] C. Matter-Mueller, W. Gujer, W. Giger, *Water Res.* 15 (1981) 1271.
- [8] P.V. Roberts, C. Munz, *J. Water Pollut. Contr. Fed.* 56 (1984) 157.
- [9] J.H. Smith, *Environ. Sci. Technol.* 14 (1980) 1332.
- [10] P.V. Roberts, P.G. Dandliker, *Environ. Sci. Technol.* 17 (1983) 484.
- [11] R.E. Rathbun, D.Y. Tai, *Volatilization of Chlorinated Hydrocarbons from Water, Gas Transfer at Water Surfaces*, Reidel Publishing, 1983, pp. 27–34.
- [12] C.C. Hsieh, K.S. Ro, M.K. Stenstrom, *J. Environ. Eng. ASCE* 119 (1993) 1077.
- [13] C.C. Hsieh, R.W. Babcock, M.K. Stenstrom, *J. Environ. Eng. ASCE* 119 (1993) 1099.
- [14] S.W. Karickhoff, D.S. Brown, T.A. Scott, *Water Res.* 13 (1979) 241.
- [15] EPA, *Workshop — Organic Air Emissions from Waste Management Facilities*, US Environmental Protection Agency, 1990, CER190-124d.
- [16] EPA, *Air Emissions Models for Waste and Wastewater*, U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, NC, 1994, Oct.
- [17] C. Springer, P.D. Lunney, and K.T. Valsaraj, *US Environmental Protection Agency, Solid and Hazard Waste Research Division*, Cincinnati, OH. 808162-02, Dec. 1984.