Modeling VOC Emissions in the High-Purity Oxygen Activated Sludge Process

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Abstract: Mass balances for volatile organic compounds (VOCs) were added to a structured mathematical model of the high-purity oxygen activated sludge (HPO-AS) process. The model was sized to correspond to two large existing HPO-AS treatment plants. The stripping of ten different VOCs was modeled and compared to stripping from conventional air activated sludge process. The results show that the covered aeration tanks can reduce stripping by more than 90%, depending on the specific VOC. If biodegradation is considered, the HPO-AS process degrades more than the conventional process due to the higher liquid-phase concentrations that result because of reduced stripping. The increase in biodegradation depends on the VOCs degradability but should increase to nearly 100% for highly volatile but biodegradable VOCs.

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Introduction

Volatile organic compound (VOC) emissions from wastewater treatment plants are being specifically regulated in California. It has been reported that nearly half of the emissions occur in secondary treatment processes (Mills and Haith 1985; McDonald et al. 1991). The specific regulation application will depend on the location and the existing air quality (Tata et al. 2003). A potential advantage of the high-purity oxygen activated sludge (HPO-AS) process is reduced emissions from covered aeration tanks with shorter hydraulic retention times [only 1–3 h for HPO-AS as compared to 4–8 h for conventional (Metcalf and Eddy, Inc. 2003)], as compared to a conventional, uncovered air activated sludge (AS) process.

In the HPO-AS process, the gas-phase may become saturated for any specific VOC. The saturation reduces the stripping driving force, further reducing VOC emissions. In an air AS process, the gas above the tanks is rarely saturated. Surface aeration systems in an air AS process tend to operate at maximum driving force, which maximizes stripping. Subsurface aeration systems tend to reduce stripping since the air bubbles may be partially or fully saturated; however, the gas flow rate is always greater than in a HPO-AS process. The combination of gas saturation and low gas flow rate throughout reduces VOC emissions in a HPO-AS process compared to air AS process.

In order to explore these potential advantages, a model developed and calibrated with pilot plant data previously was modified by adding material balances and gas transfer kinetics for 10 VOCs. The model was then used to explore stripping rates in comparable treatment processes. Comparisons were initially made assuming no biodegradation. Biodegradation was next added to show how the impact of reduced stripping increases the mass of VOCs degraded.

Model Development

The previously developed model (Tzeng 1992; Tzeng et al. 2003) for the HPO-AS process was modified by adding material balances for VOCs. This is a structured model and includes mass balances for soluble and particulate substrates as well as stored, active, and inert biomass. The model was built upon the earlier work of Busby and Andrews (1975), Stenstrom and Andrews (1979), and Clifft (1980) and is similar to the International Water Association (IWA) AS Model 3 (Gujer et al. 1999) for carbonaceous substrate removal. The differences between the IWA Model 3 and Tzeng's model do not involve the gas transfer mass balances (Yuan et al. 1993).

The stripping rate of VOCs from clean water into the atmosphere has been well studied and the mass transfer kinetics of VOC stripping is known to be a first-order process. Material balance equations were added as follows for the gas phase and liquid phase, respectively,

$$\frac{dC_L}{dt} = \frac{Q_L}{V_L}(C_{L_o} - C_L) - K_L a_{\mathrm{VOC}}(C_L - C_L^*) \tag{1}$$

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$$\frac{dC_G}{dt} = \frac{Q_{G_o}C_{G_o} - Q_G C_G}{V_G} + K_L a_{\mathrm{VOC}}(C_L - C_L^*)\frac{V_L}{V_G} \tag{2}$$

where C_G^*=gas-phase VOC equilibrium concentration (ML^{-3}); C_L^*=liquid-phase VOC equilibrium concentration (ML^{-3}); C_L =real-time liquid-phase VOC concentration (ML^{-3}); C_G=real-time gas-phase VOC concentration (ML^{-3}); C_{L_o} =influent liquid-phase VOC concentration (ML^{-3}); K_L=overall VOC liquid-phase mass transfer coefficient (T^{-1}); K_G=overall VOC gas-phase mass transfer coefficient (T^{-1}); a=specific volumetric area=area/volume; Q_{G_o}=inlet gas flow rate ($\mathrm{L}^3\, T^{-1}$); C_{G_o}=feed gas VOC concentration (ML^{-3}); Q_G=outlet gas flow rate ($\mathrm{L}^3\, T^{-1}$); Q_L=wastewater flow rate ($\mathrm{L}^3\, T^{-1}$); V_G=gas-phase volume (L^3); V_L=liquid-phase volume (L^3); and VOC=as subscript indicates VOC mass transfer rates.

The following development uses the two-resistance theory for describing the stripping rate. The two-resistance theory differs from the two-film theory in that the mass transfer coefficient, $K_L a$, is assumed proportional to the liquid diffusivity (D) in two-film theory while in two-resistance theory, $K_L a$ is proportional to a D^n, where n is usually in the range between 0.5 and 0.6. Also, the resistances of both gas and liquid films are included. The difference is important when predicting transfer of compounds with molecular diffusivities different from oxygen, and the gas-film resistance becomes significant when considering semivolatiles, such as naphthalene, with subsurface aeration systems. The ratio of liquid-phase to gas-phase resistance can be expressed as

$$\frac{R_L}{R_G} = H_c\left(\frac{k_G}{k_L}\right) \tag{3}$$

where R_L=liquid-film resistance (dimensionless); R_G=gas-film resistance (dimensionless); H_c=Henry's law coefficient (dimensionless); k_G=gas-film mass transfer coefficient (T^{-1}); and k_L =liquid-film mass transfer coefficient (T^{-1}).

For VOCs, Henry's law coefficient can be related to the ratio between the liquid-phase and gas-phase transfer coefficients or the ratio between the gas-phase and liquid-phase equilibrium concentrations

$$H_c = \frac{K_L}{K_G} = \frac{C_G^*}{C_L^*} \tag{4}$$

The total mass does not change in a closed system. This yields the following mass balance equation between a steady-state condition and a nonequilibrium status:

$$C_G^* V_G + C_L^* V_L = C_G V_G + C_L V_L \tag{5}$$

From Eq. (4), C_G^* equals the product of C_L^* and H_c, and Eq. (5) can be rearranged as

$$C_L^* = \frac{C_G V_G + C_L V_L}{H_c V_G + V_L} \tag{6}$$

Using Eq. (6) and appropriate $K_L a_{\mathrm{VOC}}$ values, Eqs. (1) and (2) can be used to dynamically estimate the concentration change in both gas phase and liquid phase. The $K_L a_{\mathrm{VOC}}$ values are usually determined by correlating the VOC stripping rates with a factor to the oxygen transfer rate, and the symbol ψ is used to denote this factor, when considering only the diffusivities. The improved approach including both film resistances, called modified ψ concept, uses the symbol ψ_M, which estimates the VOC stripping rate more accurately.

Modified ψ Concept

The ψ_M was presented by Hsieh et al. (1993a,b) for the estimation of VOC mass transfer rates. According to the two-resistance theory, ψ_M is mathematically expressed as the ratio between the VOC and oxygen diffusivities, to some power, multiplied by the ratio of liquid-film resistance to overall resistance (the sum of gas-film and liquid-film resistances). Therefore, the following two equations are derived:

$$\psi_M = \left(\frac{D_{L\mathrm{VOC}}}{D_{L\mathrm{O}_2}}\right)^n \times \frac{R_L}{R_T} \tag{7}$$

and

$$K_L a_{\mathrm{VOC}} = K_L a_{\mathrm{O}_2} \times \psi_M \tag{8}$$

where $D_{L\mathrm{VOC}}$=VOC liquid diffusivity; $D_{L\mathrm{O}_2}$=oxygen liquid diffusivity; n=exponential coefficient, 0.5–0.6 for most VOCs; and R_T=overall resistance$=1/[(1/R_L)+(1/R_G)]$. The Wilke-Chang correlation was used for liquid diffusivities and the values are shown in Table 2.

Wind speed has been long recognized as a parameter which affects volatilization rates from an open tank (Mackay and Yeun 1983). In the case of HPO-AS simulations, the wind speed is not a factor for the overall mass transfer rate because the wind velocity approaches zero in the covered aeration tanks. In the VOC estimation for air AS process, the wind speed is a state variable and is subject to change at different treatment plants with different climates. To simplify the procedure, values of $\psi_M\, K_L a_{\mathrm{O}_2}$ from Eq. (8) [the ψ_M and $K_L a_{\mathrm{O}_2}$ experiments conducted by Hsieh et al. (1993a,b), considering the wind speed] were used for estimating the VOC emission rates.

Pilot-scale experiments conducted by Mueller and Di Toro (1991) have verified the constant saturation concentration for a single VOC in multicomponent adsorption of VOCs from air stripper off-gas using granular activated carbon. This study assumed the equilibrium concentration and stripping rate for a specific VOC is not disturbed by the existence of any other compounds in the AS processes.

VOC Emissions Estimation

The above equations were combined with the structured AS process model (Tzeng et al. 2003) and converted into FORTRAN codes. The dimensions and arrangement of two treatment plants were selected to demonstrate the structured model used to simulate the performance of surface aeration and subsurface diffusion aeration on VOC emissions.

West Point Treatment Plant

The model was first used to estimate emissions from a hypothetical plant, identical in design to the West Point Treatment Plant (WPTP) in Seattle, Wash. Table 1 gives the design parameters for the WPTP. Ten VOCs were chosen for the simulation. Table 2 presents the properties of selected VOC species. The upper part of Table 3 shows hypothetical but realistic primary effluent VOC concentrations used in the simulations [see, for example, Parker et al. (1993) for actual values]. The concentrations were assumed constant over time for easier comparison, but flow and other pollutant concentrations varied diurnally (Tzeng et al. 2003). The simulations were computed for 240 h to achieve "periodic steady state," meaning that the concentrations in 24 h between 192 and

Table 1. HPO-AS Operational Parameters

Parameter	WPTP	SRWTP
Influent flow rate	607,066–986,000 $\mathrm{m^3/day}$ diurnal variation	1,442,267 $\mathrm{m^3/day}$ annual average
Primary effluent BOD_5	91 mg/L	175 mg/L
Liquid-phase volume	2,220 $\mathrm{m^3/stage}$ 4 stages X 6 trains	1,957 $\mathrm{m^3/stage}$ 4 stages X 16 trains
Headspace volume	355 $\mathrm{m^3/stage}$ 4 stages X 6 trains	258 $\mathrm{m^3/stage}$ 4 stages X 16 trains
Aeration type	Surface aeration with draft tubes	Submerged turbine/surface aeration
Surface stage $\alpha K_L a$'s	4.20, 4.24, 3.74, and 4.20 $\mathrm{h^{-1}}$ at average	12.9, 9.81, 4.60, and 4.51 $\mathrm{h^{-1}}$ at average
Turbine stage $\alpha K_L a$'s	—	6.98, 3.00, 2.88, and 2.98 $\mathrm{h^{-1}}$ at average
Turbine effective depths	—	1.38, 1.32, 1.32, and 1.32 for stages

Table 2. Properties of Selected VOC Compounds

Compound	Symbol	H_c [a]	D_L [b] (cm/s 10^{-5})
Carbon tetrachloride	CCl_4	1.122	0.92×10^5
Perchloroethylene	PCE	0.565	0.89×10^5
1,1,1-Trichloroethane	1,1,1-TCA	0.525	0.90×10^5
Trichloroethylene	TCE	0.252	0.96×10^5
Chloroform	CLF	0.160	1.01×10^5
Chlorobenzene	CBZ	0.146	0.86×10^5
1,3-Dichlorobenzene	1,3-DCB	0.124	0.78×10^5
1,4-Dichlorobenzene	1,4-DCB	0.110	0.76×10^5
1,2-Dichlorobenzene	1,2-DCB	0.087	0.78×10^5
Naphthalene	NAPH	0.038	0.72×10^5

[a] Henry's Law coefficient, dimensionless, adopted from Hsieh (1991).

[b] Diffusivity, (oxygen $= 2.11 \times 10^5$ cm/s).

216 h were identical to the concentrations between 216 and 240 h. The ψ_M values were taken from the experimental results of Hsieh et al. (1993a,b) corresponding to the design $\alpha K_L a$ values. The parameter $\alpha K_L a$ is the product of the clean water $K_L a$ and the α factor, which accounts for the reduction in transfer due to contaminants such as surfactants (Stenstrom and Gilbert 1981; ASCE 2006). The values of the α factor for the two aeration systems are different: 0.8–0.95 for surface aeration (Tzeng et al. 2003) and 0.4–0.5 for submerged turbines (Stenstrom et al. 1989). The value of α for oxygen and the VOCs are assumed to be the same, although they may differ depending on the specific VOC, its Henry's coefficient, and the power input per unit volume. Libra (1991) found the α factor for a turbine aeration system varied from 0.6 to 0.8 for oxygen, and from 0.75 to 1.1 for toluene, and from 0.5 to 0.7, over a range of power densities from 20 to 350 W/m^3, respectively. These VOC stripping rates were initially simulated by ignoring biodegradation and adsorption. The power densities for the plants simulated range from 0.057 to 0.030 $\mathrm{kW/m^3}$ (2.17–1.16 $\mathrm{hp/1,000\ ft^3}$); for Sacramento it is

Table 3. Comparison of VOC Emissions from the WPTP as an HPO Plant with a Hypothetical Surface Aeration Plant

	Compound	ψ_M [a]	Influent[b] conc.	Effluent[c] conc. Min	Effluent[c] conc. Max	%Stripped[d]
HPO-AS process	CCl_4	0.463	10	9.67	9.81	2.35
	PCE	0.393	10	9.83	9.90	1.20
	1,1,1-TCA	0.414	10	9.84	9.91	1.12
	TCE	0.413	10	9.92	9.96	0.54
	CLF	0.363	10	9.95	9.97	0.34
	CBZ	0.382	10	9.96	9.97	0.31
	1,3-DCB	0.337	10	9.96	9.98	0.27
	1,4-DCB	0.336	10	9.97	9.98	0.24
	1,2-DCB	0.321	10	9.97	9.98	0.19
	NAPH	0.229	10	9.99	9.99	0.08
Surface aeration air AS process	CCl_4	0.658	10	0.56	0.86	92.28
	PCE	0.553	10	0.65	1.01	90.95
	1,1,1-TCA	0.564	10	0.64	0.99	91.15
	TCE	0.576	10	0.63	0.98	91.28
	CLF	0.515	10	0.70	1.08	90.35
	CBZ	0.535	10	0.68	1.04	90.68
	1,3-DCB	0.484	10	0.74	1.14	89.80
	1,4-DCB	0.484	10	0.74	1.14	89.80
	1,2-DCB	0.463	10	0.77	1.19	89.39
	NAPH	0.336	10	1.04	1.56	85.95

[a] Adopted from Hsieh's (1991) experiment number S24 for HPO-AS process, S29 for air AS process.

[b] In units of $\mu g/L$.

[c] The lowest and highest effluent VOC concentrations within 1 day, $\mu g/L$.

[d] Percent VOC stripped.

Table 4. Comparison of the Fates of VOCs in the WPTP as an HPO Plant with a Hypothetical Surface Aeration Plant

	Compound	Inf. conc.	%Bio[a]	%Strip[b]	%Re[c]	Strp/Re[d]
HPO-AS process	CCl_4	10	18.4	1.9	79.7	0.024
	PCE	10	18.8	1.0	80.2	0.012
	1,1,1-TCA	10	18.8	0.9	80.3	0.011
	TCE	10	19.0	0.4	80.5	0.005
	CLF	10	19.1	0.3	80.6	0.003
	CBZ	10	19.1	0.3	80.6	0.003
	1,3-DCB	10	19.1	0.2	80.7	0.003
	1,4-DCB	10	19.1	0.2	80.7	0.002
	1,2-DCB	10	19.1	0.2	80.7	0.002
	NAPH	10	19.2	0.1	80.8	0.001
Surface aeration air AS process	CCl_4	10	5.8	87.0	7.3	12.0
	PCE	10	6.7	84.9	8.4	10.1
	1,1,1-TCA	10	6.6	85.1	8.3	10.3
	TCE	10	6.5	85.4	8.2	10.5
	CLF	10	7.1	83.9	9.0	9.4
	CBZ	10	6.9	84.4	8.7	9.7
	1,3-DCB	10	7.5	83.1	9.4	8.8
	1,4-DCB	10	7.5	86.1	9.4	9.1
	1,2-DCB	10	7.8	82.4	9.8	8.4
	NAPH	10	10.0	77.3	12.6	6.1

[a] Percent VOC biodegraded.

[b] Percent VOC stripped.

[c] Percent VOC remaining in the liquid phase.

[d] %stripped//%remaining.

0.042–0.025 (1.60–0.96 hp/1,000 ft^3). For simplicity, we have assumed the same α factors for oxygen and the VOCs.

By removing the tank covers and stage baffles, doubling the hydraulic retention time, and modifying the volumetric oxygen mass transfer coefficient, $\alpha K_L a$, the process is equivalent to an air AS process. The $\alpha K_L a$ values were modified by assuming both processes transfer an equal quantity of oxygen. Given the same influent VOC species and concentrations, the air process produces effluent concentrations as shown in the lower part of Table 3. A quick comparison between the upper and lower parts of Tables 3 shows that HPO-AS reduces 85–90% of VOC emissions compared to air AS. Three kinetic removal mechanisms, volatilization, adsorption, and biodegradation, occur in the AS process and have been well-recognized (e.g., Barton 1987; Blackburn 1987; Namkung and Rittmann 1987).

The adsorption of VOCs onto solids, which is a physical process and does not eliminate the VOCs, plays a minor role in AS processes because of high VOC fugacities (e.g., Barton 1987 has found $CHCl_3$ does not adsorb appreciably in either surface or subsurface aeration systems). Since VOCs usually exist in water in trace levels, biodegradation rates can be simulated using the substrate-limited Monod kinetic equation. We used a typical value of mass yield [0.4 mg mass/mg COD removed (Metcalf and Eddy, Inc. 2003)] and applied different values of maximum growth rates (μ_m, 0.000 1–0.01 h^{-1}), half-saturation coefficients (K_s, 1.0–30.0 mg/L), and influent concentrations (1 μg/L–1 mg/L) for all VOC species. Using these values, we estimated the percent removed through biodegradation, emissions to the atmosphere, and residual remaining in treated water (includes adsorption onto wasted sludge), and the results are listed in Table 4 (results from $\mu_m = 0.0001\ h^{-1}$ and $K_s = 1.0$ mg/L) for HPO-AS and air AS.

Despite the shorter hydraulic retention time employed with HPO-AS (typically half of that in air AS), all biodegradation is greater in HPO-AS than in air AS. This is due to the high VOC concentrations maintained in the liquid phase, which lead to higher degradation rates $[\mu_m S/(K_s + S)]$.

The ratio between mass stripped and mass remaining in the water phase (Strp/Re) was relatively constant for each single compound in the air AS process, no matter how large the removal due to biodegradation (from 0 to 99% biodegradation). Table 5 presents the fate of chloroform through an air AS process at different biodegradation levels by varying the maximum specific growth rate (μ_m and Monod half-saturation coefficient $K_{s\text{VOC}}$) as an example. This suggests that in an air AS treatment plant, the emission of a single VOC can be estimated from its effluent concentration if the Strp/Re ratio has been calibrated. The Strp/Re ratio was constant in the simulation because of high mass transfer rates and Henry's law, which indicates a constant ratio between equilibrium concentrations in gas phase and liquid phase.

The Strp/Re ratio increased in HPO at higher biodegradation rates. This phenomenon can be explained as follows: less VOC in the liquid means less VOC concentration in the gas-phase, and thus, a higher driving force. As a result, the VOC escapes faster. However, the percentage stripped is still low. At 99% biodegradation, Strp/Re is close to double of that without biodegradation, which gives a ratio of less than 0.05 for all the 10 compounds simulated in this study.

Sacramento Regional Wastewater Treatment Plant

The Sacramento Regional Wastewater Treatment Plant (SRWTP) is an HPO-AS treatment plant using a submerged turbine aeration system. The simulation considered both surface and submerged aeration systems. The results for eight surface aeration trains and

Table 5. Fate of Chloroform through a Surface Aeration Air AS Process

$\mu_{m_{\text{VOC}}}$[a]	$K_{S_{\text{VOC}}}$[b]	%Bio	%Strp	%Re	Strp/Re
0	N.A.	0.0	90.4	9.6	9.4
0.0001	1,000	7.1	83.9	9.0	9.4
0.001	1,000	43.4	51.1	5.5	9.4
0.01	1,000	88.5	10.4	1.1	9.3
0.0001	5,000	1.5	89.0	9.5	9.4
0.001	5,000	13.3	78.3	8.4	9.4
0.01	5,000	60.5	35.7	3.8	9.4
0.0001	15,000	0.5	89.9	9.6	9.4
0.001	15,000	4.9	86.0	9.2	9.4
0.01	15,000	33.8	59.8	6.4	9.4
0.0001	30,000	0.3	90.1	9.6	9.4
0.001	30,000	2.5	88.1	9.4	9.4
0.01	30,000	20.4	72.0	7.7	9.4

[a] Maximum growth rate on VOC, h^{-1}.

[b] Half-saturation coefficient for Monod kinetics, $\mu g/L$.

eight submerged turbine trains will be discussed separately. Alpha factors used for existing subsurface aeration were not from expansion designs; instead, we used the values calibrated in Tzeng's (1992) early study. Table 1 shows the operational parameters for completed SRWTP HPO process.

The volatilization rates of VOCs in diffused aeration have been previously researched (Doyle et al. 1983; Roberts et al. 1984; Gurol and Nekovinaini 1985) but important questions still require resolution. Most of the estimation equations proposed for stripping do not consider a covered tank condition, such as an HPO-AS process. The VOC saturation in rising bubbles has been frequently ignored (e.g., Namkung and Rittmann 1987). The ψ_M concept and the saturation parameter (Hsieh et al. 1993a,b) were used to predict the VOC emissions in submerged aeration.

Four different preassigned influent flow rates (wet weather, average dry weather, seasonal dry weather, and maximum month) were simulated and each provided similar results. For better illustration, an average annual flow, the average of the four mentioned flow rates (16 $m^3\ s^{-1}$), was simulated and assumed to be constant to estimate an overall annual average volatilization rate.

Following the same procedure we used for analyzing the VOC emissions in WPTP, we estimated the volatilization in SRWTP. Tables 6 and 7 show the simulation results of SRWTP and an equivalent air AS process with small biodegradation rates ($\mu_m = 0.0001\ h^{-1}$ and $K_s = 1.0\ mg/L$). Comparing Fig. 2 and Tables 6 and 7 shows that with the same biodegradation parameters, a HPO-AS degrades much more VOCs than an air AS process in both surface and subsurface aeration systems. Furthermore, different values of biodegradation parameters have been tested and the ratio of Strp/Re in the air AS process was found to be constant. Table 8 gives an example of constant Strp/Re ratios using PCE passing through both subsurface and surface aerations.

Table 6. Estimated VOC Fate through SRWTP HPO-AS Process

	Compound	Inf. conc.	%Bio	%Strip	%Re	Strp/Re
Submerged turbine HPO-AS process	CCl_4	10	31.9	4.3	63.7	0.07
	PCE	10	32.8	2.3	64.9	0.04
	1,1,1-TCA	10	32.9	2.1	65.0	0.03
	TCE	10	33.3	1.0	65.6	0.02
	CLF	10	33.5	0.7	65.9	0.01
	CBZ	10	33.5	0.6	65.9	0.01
	1,3-DCB	10	33.6	0.5	66.0	0.01
	1,4-DCB	10	33.6	0.4	66.0	0.01
	1,2-DCB	10	33.6	0.3	66.1	0.01
	NAPH	10	33.7	0.1	66.2	0.0
Surface aeration HPO-AS process	CCl_4	10	31.5	5.9	62.6	0.1
	PCE	10	32.6	3.1	64.3	0.05
	1,1,1-TCA	10	32.6	2.9	64.5	0.05
	TCE	10	33.2	1.4	65.4	0.02
	CLF	10	33.4	0.9	65.7	0.01
	CBZ	10	33.4	0.8	65.8	0.01
	1,3-DCB	10	33.4	0.7	65.9	0.01
	1,4-DCB	10	33.5	0.6	65.9	0.01
	1,2-DCB	10	33.5	0.5	66.0	0.01
	NAPH	10	33.6	0.2	66.2	0.0

Table 7. Estimated VOC Fate through SRWTP Air AS Process

	Compound	Inf. conc.	%Bio	%Strip	%Re	Strp/Re
Submerged turbine air AS process	CCl_4	10	4.1	86.3	9.6	9.0
	PCE	10	5.2	82.4	12.4	6.6
	1,1,1-TCA	10	5.3	82.0	12.7	6.5
	TCE	10	7.3	75.3	17.4	4.3
	CLF	10	9.2	69.1	21.7	3.2
	CBZ	10	10.2	65.5	24.3	2.7
	1,3-DCB	10	11.3	62.0	26.8	2.3
	1,4-DCB	10	12.3	58.6	29.1	2.0
	1,2-DCB	10	13.3	54.9	31.7	1.7
	NAPH	10	19.2	35.0	45.8	0.8
Surface aeration air AS process	CCl_4	10	2.6	92.2	5.2	17.8
	PCE	10	3.0	90.9	6.0	15.1
	1,1,1-TCA	10	2.9	91.4	5.7	15.9
	TCE	10	2.9	91.3	5.8	15.8
	CLF	10	3.3	90.3	6.5	13.9
	CBZ	10	3.1	90.7	6.2	14.7
	1,3-DCB	10	3.5	89.6	6.9	12.9
	1,4-DCB	10	3.6	89.1	7.2	12.3
	1,2-DCB	10	3.5	89.6	6.9	12.9
	NAPH	10	4.9	85.4	9.7	8.8

Discussion and Conclusions

These results suggest that covered aeration tanks (e.g., HPO-AS) can be one of the most effective solutions to reduce VOC emissions from wastewater treatment plants. If the VOC species is biodegradable, a larger portion of the VOCs may be degraded before being stripped or discharged in an HPO process as compared to the air AS, especially when a subsurface aeration system (e.g., turbines or fine pore diffusers) is used. If the VOCs are not degradable, they will likely be stripped in downstream processes

Table 8. Fate of PCE through SRWTP Air AS Process

	$\mu_{m_{\mathrm{VOC}}}$	$K_{S_{\mathrm{VOC}}}$	%Bio	%Strp	%Re	Strp/Re
Submerged turbine air AS process	0	N.A.	0.0	86.9	13.1	6.6
	0.0001	1,000	5.2	82.4	12.4	6.6
	0.001	1,000	35.6	56.0	8.4	6.6
	0.01	1,000	84.6	13.3	2.0	6.6
	0.0001	5,000	1.1	86.0	12.9	6.6
	0.001	5,000	9.9	78.2	11.8	6.6
	0.01	5,000	52.5	41.3	6.2	6.6
	0.0001	15,000	0.4	86.6	13.0	6.6
	0.001	15,000	3.5	83.8	12.6	6.6
	0.01	15,000	26.9	63.5	9.6	6.6
	0.0001	30,000	0.2	86.8	13.1	6.6
	0.001	30,000	1.8	85.3	12.8	6.6
	0.01	30,000	15.5	73.4	11.0	6.6
Surface aeration air AS process	0	N.A.	0.0	93.8	6.2	15.1
	0.0001	1,000	3.0	90.9	6.0	15.1
	0.001	1,000	23.8	71.5	4.8	15.0
	0.01	1,000	75.8	22.7	1.5	15.1
	0.0001	5,000	0.6	93.2	6.2	15.1
	0.001	5,000	5.9	88.3	5.8	15.1
	0.01	5,000	38.5	57.7	3.8	15.1
	0.0001	15,000	0.2	93.6	6.2	15.1
	0.001	15,000	2.0	91.9	6.1	15.1
	0.01	15,000	17.2	77.6	5.1	15.1
	0.0001	30,000	0.1	93.7	6.2	15.1
	0.001	30,000	1.0	92.8	6.2	15.1
	0.01	30,000	9.4	84.9	5.6	15.1

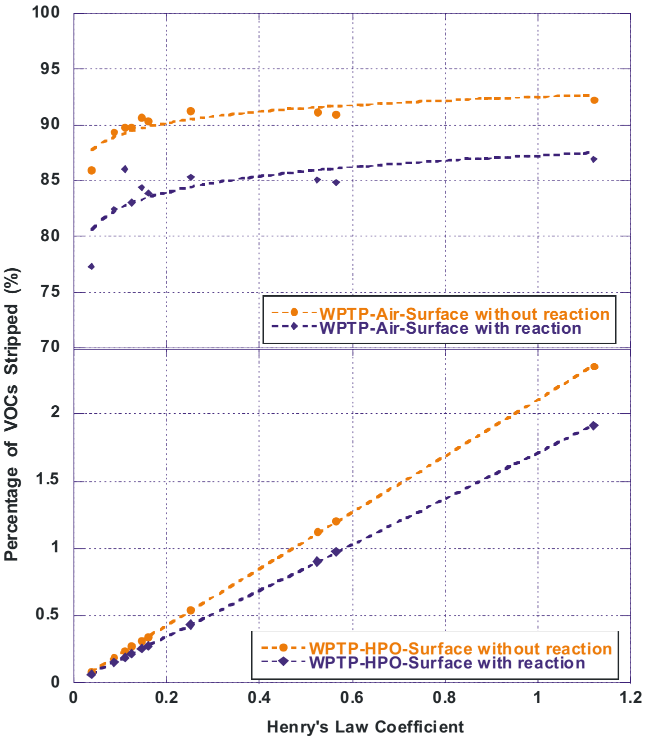

Fig. 1. Simulated results of VOC emissions for WTWP with and without reaction comparison

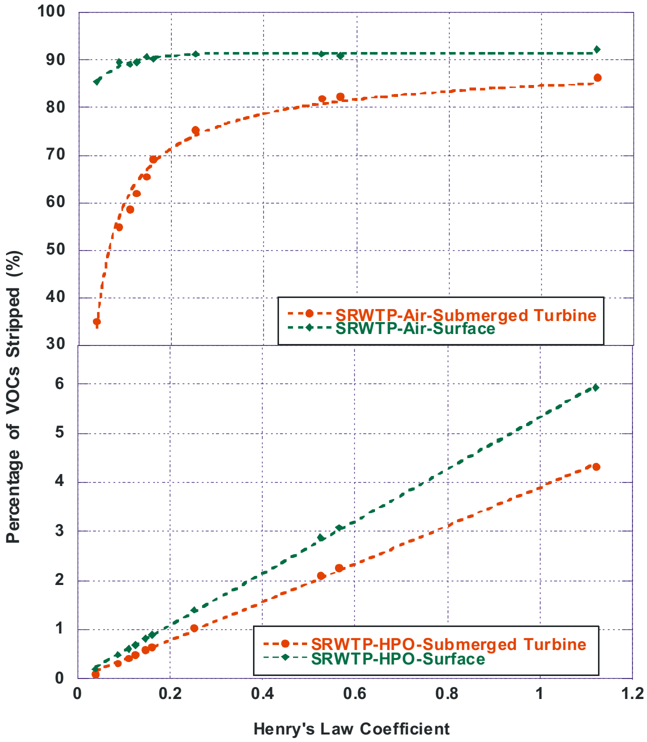

Fig. 2. Simulated results of VOC emissions from SRWTP surface and submerged turbine comparison

(secondary clarifiers, etc.) or be discharged to receiving waters.

A comparison of corresponding tables between SRWTP HPO subsurface and surface aeration systems (Fig. 2 bottom and Table 6) reveals that surface aeration emits slightly greater amounts of high volatility organic compounds (e.g., carbon tetrachloride). The phenomenon might result from the fully saturated headspace and gas bubbles which reduce the emissions in subsurface systems.

The emissions of low volatility organic compounds (e.g., naphthalene) are much lower from a subsurface system than those from a surface aeration in an air AS process (compare Table 3 lower part and Fig. 2). This is because low VOCs reach their saturation conditions early and mass transfer rates slow down as bubbles rise toward the water surface. The result indicates submerged turbines may be a solution for emissions control of organic compounds with low volatilities. These results suggest that subsurface aerations might be better techniques than surface aerations in control of VOC emissions for both HPO and conventional AS processes.

The total emissions from WPTP were predicted by the model to be between 0 and 3% of the influent for 10 different VOCs simulated, while the emissions for SRWTP were 0 to 8%. The difference was due to higher mass transfer rates employed in SRWTP. For a hypothetical surface aeration air AS process, the emissions were predicted to be approximately 85% (with reaction) to approximately 90% (without reaction) of total influent VOCs as shown in Fig. 1. For a hypothetical submerged turbine air AS process the emissions were predicted to be 42–90% of the influent. This indicates that for an air AS process, the emission rates of low volatility VOCs can be better controlled using a submerged turbine aeration system.

The ratio between percent stripped and percent remaining in the discharged water for a specific VOC was found to be a constant under a given hydrodynamic condition in both surface and subsurface uncovered aeration systems and is probably useful for the estimation of total VOC emissions from measured VOC concentrations remaining in effluent from uncovered AS treatment plants. Additionally, the biodegradation rates of VOCs could be approximated given corresponding influent and effluent VOC concentrations.

This was explained by the correlation between the stripping driving force and the liquid-phase VOC concentration in open systems. The constant ratio is useful to predict the total VOC emissions and biodegradation in an air AS process without measuring the off-gas which is difficult and expensive, especially for a surface aeration system.

The HPO-AS process is now almost 45 years old and many communities are considering upgrading to other technologies, especially if nitrification is required. An important consideration before abandoning the HPO-AS process is the impact on stripping of organics. For comparison, the mass stripped from an air AS process are shown in Table 7. The turbine system modeled in this table has high oxygen transfer efficiency (OTE) and is nearly the same as might be expected from a fine pore diffuser system (6%/m or 1.8%/ft). This air system strips from 35 (naphthalene) to 86% (carbon tetrachloride) of the VOCs which is much greater than either HPO option (0.2–5.9% maximum). This paper provides quantitative evidence of reduced air emissions with HPO-AS as compared to other AS processes and aeration systems.

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