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Gas Transfer Parameter Estimation:

Applications and Implications of Classical Assumptions

A dissertation submitted in partial satisfaction of the  
requirements for the degree Doctor of Philosophy

in Civil Engineering

by

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## ABSTRACT OF THE DISSERTATION

Gas Transfer Parameter Estimation:  
Applications and Implications of Classical Assumptions

by

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Gas transfer is a key process in a wide range of water and wastewater treatment operations. It provides aeration in biological treatment processes such as the activated sludge process, transfers disinfectants during gas chlorination and ozonation, and strips volatile compounds in both water and wastewater treatment. This dissertation extends our understanding of three aspects of gas transfer in environmental processes. The first relates to the way aeration is quantified in a defensible way and describes the ASCE Standard for the Measurement of Oxygen Transfer in Clean Water and the ASCE Standard Guidelines for In-Process Oxygen Transfer Testing. Both have found

widespread application and have reduced design variability and allowed operators and engineers to better evaluate process operation of existing treatment plants. The reasons for the Standard's success were described as well as the pitfalls of earlier approaches. Key new areas of the revised clean water Standard are highlighted and an analysis is presented that shows how the numerical treatment of the transfer data minimizes the impacts of gas-side oxygen depletion.

The second relates to mass-transfer characteristics and reaction kinetics of ozone in reclaimed water. Five columns were operated in series at an advanced reclamation plant, treating effluent from a trickling filter process. A mathematical model was developed to describe transfer rate and steady state ozone concentrations. Ozone decay was modeled accurately as a pseudo first-order reaction between ozone and ozone-demanding materials. A methodology is proposed and the observed decrease in oxygen transfer rate caused by contaminants in reclaimed water was only 10% to 15% compared to tap water.

The final area relates to the stripping of volatile organic compounds (VOCs) in wastewater treatment. Previous work, using oxygen as a tracer and combining the impacts of both liquid and gas films was extended to the high purity oxygen activated sludge process (HPO-AS). The model was sized to correspond to two large existing HPO-AS treatment plants. The psi factors, which are the ratio of volumetric

mass-transfer coefficients of ozone/ VOCs to oxygen, were determined in each study for different types of aeration systems. 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.

# 1. INTRODUCTION

## 1.1 DISSERTATION ORGANIZATION

This dissertation addresses issues associated with gas transfer in water and wastewater treatment processes. Gas transfer is a key process in a wide range of water and wastewater treatment operations. It provides aeration in biological treatment processes such as the activated sludge process, transfers disinfectants during gas chlorination and ozonation, and strips volatile compounds in both water and wastewater treatment. This dissertation is a compilation of research thrusts summarized in three papers published or submitted during the course of the dissertation research. Chapter 2 includes the paper submitted in April 2010, and now is under review. Chapter 3 contains the paper published in 2008 and Chapter 4 contains a paper that was accepted in March 2010, and is expected to be published in late 2010. Chapter 5 summarizes the results of all three chapters and discusses how they relate to each other. The appendix includes a conference paper that presents some of the material associated with Chapter 2 as well as different materials on process water testing.

## 1.2 TREATMENT PROCESSES

The activated sludge process is currently the most popular method of biological wastewater treatment. Reliable operation of this process is dependent upon an aeration system to supply dissolved oxygen to the mixed liquor. Aeration is the most important

and the most energy-intensive aspect of wastewater treatment, which usually represents up to sixty percent of the total energy requirements in a modern wastewater treatment plant (Houck and Boon, 1981; Reardon 1995). Therefore, designers and operators can substantially reduce overall plant energy costs by using accurate oxygen transfer information to make the aeration system as energy efficient as possible. The most commonly used indicator of the aeration systems performance is the Standard Oxygen Transfer Rate (SOTR), a hypothetical mass of oxygen transferred per unit of time at zero dissolved oxygen concentration, water temperature of 20°C, and barometric pressure of 1.00 atm (101.3kPa) under specified gas rate and power conditions. A clean water test, standardized by ASCE (1984, 1997; 2006) is typically used to estimate the SOTR.

The ASCE standard precisely defines testing techniques and methods for the analysis and interpretation of experimental data, which enables meaningful comparison of the oxygen transfer efficiency for different types of aeration systems, and ensures that all use the same procedures (Stenstrom and Gilbert, 1981; Hwang and Stenstrom, 1985).

Several major improvements in estimating oxygen transfer rates were incorporated into the Standard. The first was the methodology of estimating  $K_La$  from non-steady state reaeration data (Stenstrom et al., 1981). Prior to the Standard, the log deficit method was used which required a priori knowledge of  $C_\infty^*$ , the equilibrium oxygen

concentration. The equilibrium concentration differs from handbook saturation dissolved oxygen concentration because it includes the effect of hydrostatic pressure. Previously, several methods for calculating  $C_{\infty}^*$  from hydrostatic pressure existed, but all had pitfalls, allowing the introduction of errors that could easily bias the overall transfer rate by  $\pm 15$  to 20% (Boyle, *et al.*, 1974). The Standard uses a non-linear regression technique which avoids the use of a priori methods and eliminates the possibility of bias. A number of other improvements in testing procedures were realized, including the geometry of DO sampling locations, method for adding sodium sulfite, the impact of cobalt interference in the Winkler dissolved oxygen (DO) measurement procedure, the impact of DO probe lag on estimates of  $K_La$  (Philichi and Stenstrom, 1989), and more precise ways of defining power and its measurement.

The goal of the first paper was to describe the key concepts used in developing the Clean Water Standard and to illustrate why they are still important. The error introduced using previous methods, such as assumptions for  $C_{\infty}^*$ , are quantitatively described. A second goal was to show why bubble oxygen depletion during diffused aeration does not create a bias between clean water testing and process water conditions.

Ozone-based advanced oxidation processes are gaining popularity as a method to remove pharmaceuticals, personal care products (PPCPs), and endocrine-disrupting

chemicals from wastewaters (Nakada et al., 2007). This method effectively disinfects treated wastewater effluents before discharge or reuse and works well in special applications, such as laundry wastewaters from nuclear energy facilities (Mezzanotte et al., 2007; Vilve et al., 2007). The higher oxidation potential of ozone makes it a better disinfection agent than chlorine for many pathogens, and a better oxidant, especially for unsaturated compounds. Therefore, ozonation can be used to increase the biodegradability of biologically refractory compounds. Even small doses of ozone can change the structure of compounds, making them easier to break down (Brambilla et al., 1993; Ikehata and El-Din, 2004). Ozone enhances the efficiency of the biological activated carbon process in a physical-chemical water treatment plant (Chang and Chian, 1981; Khan et al., 1998a, 1998b). The increased concern over PPCPs may stimulate greater use of ozone in water and wastewater treatment.

Commercially available ozone generators are only capable of producing ozone concentrations of approximately 10%, which limits the available driving force for mass transfer. Therefore, prediction and optimization of mass transfer are important for the proper design of ozonation systems (Grasso, 1987). The highly reactive nature of ozone, however, makes it difficult to directly measure its mass-transfer coefficient. An oxygen surrogate has been used to estimate stripping rates of volatile organic compounds (VOCs) (Hsieh et al., 1993a, 1993b). The oxygen mass-transfer coefficient, which is much easier to measure, may be a more effective way to predict ozone mass-transfer

rates.

The limited mass-transfer data for ozone contactors that exists is often system-specific, applying to small scales or drinking water applications only (Smith and El-Din, 2002). There also is limited information available regarding full- or pilot-scale application of ozone in reclaimed wastewater. In the second paper, results from ozone contactors in a pilot-scale reclaimed wastewater investigation were used to determine mass-transfer characteristics and reaction kinetics, and to evaluate use of oxygen as a surrogate for quantifying ozone transfer.

Overall transfer efficiency alone is not sufficient to evaluate the effectiveness of an ozone contactor. It is also necessary to know the concentration profile of ozone throughout the height of the contactor column (Laplanche et al., 1991; LeSauze et al., 1993). The performance of ozone disinfection is determined by both the ozone concentration in the water and the contact time in the bubble column. The U.S. Environmental Protection Agency has adopted this “contact-time” concept to define the degree of disinfection (Zhou, 1995). In the second paper, the ozone decay rate and mass-transfer coefficients were determined, and the ozone concentration profile along the column was modeled. The affects of higher oxygen and ozone demands of the reclaimed waters also were studied. All model simulations were compared to measured results.



Oxygen has also been used as a surrogate to determine the mass transfer coefficients of volatile organic compounds. The ratios of the molecular diffusivities and film coefficients, described as a  $\psi$  or  $\psi_m$  factor, have been used by Hsieh et al (1993a, 1993b). The  $\psi_m$  factor can be applied to the study of mass transfer of VOCs. 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 (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. The process also uses shorter hydraulic retention times that typically needed for air activated sludge (only 1 to 3 hrs for HPO-AS as compared to 4 to 8 hrs for conventional; Metcalf and Eddy, 2003). 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 an HPO-AS process. The combination of gas saturation and low gas flow rate throughout reduces VOC emissions in an 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 volatile organic compounds (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.

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2. OXYGEN TRANSFER PARAMETER ESTIMATION:  
IMPACT OF METHODOLOGY

**Pan Jiang, and Michael K. Stenstrom, F. ASCE**

**ABSTRACT:** Oxygen transfer is an important part of wastewater treatment and accounts for as much as 50% of the energy consumption for the activated sludge process. Prior to 1984, no standard method for quantifying oxygen transfer existed, which created problems in the design and warranties for treatment plants. The ASCE Standard for the Measurement of Oxygen Transfer in Clean Water and the ASCE Standard Guidelines for In-Process Oxygen Transfer Testing have found widespread application and have reduced design variability and allowed operators and engineers to better evaluate process operation of existing treatment plants. This paper illustrates the key concepts of the Standard and shows why they are important and how they reduce the variability of oxygen transfer testing. The reasons for the Standard's success are described as well as the pitfalls of earlier approaches. The paper also highlights key new areas of the revised clean water Standard, which includes an optional correction for test water total dissolved solids concentration, and applications to loop (ditch) activated sludge process and the high purity oxygen activated sludge process. Finally an analysis is presented that shows how the numerical treatment of the transfer data minimizes the impacts of gas-side oxygen depletion.

**KEYWORDS:** Activated sludge; aeration; ASCE; off-gas; oxygen transfer; Standard.

## 2.1 INTRODUCTION

In 1977, under the sponsorship of the US EPA, a Committee organized by ASCE began the study of methods to quantify oxygen transfer rates in wastewater treatment. The Committee met as a group in Asilomar, California in 1978 (US EPA, 1979) and proposed consensus methods for establishing uniform and repeatable test conditions, estimating clean water parameters (mass transfer coefficient or  $K_La$ , and equilibrium oxygen concentration or  $C_\infty^*$ ) from reaeration data, and translating clean water rates to process conditions. The resulting methods were evaluated over next several years by the committee members, consultants and manufactures and refined through the collective experience of the group. The final result was the 1984 version of the *ASCE Standard for the Measurement of Oxygen Transfer in Clean Water*. The Standard was subsequently improved, updated and republished in 1991 and in 2006. The Standard also provides standard procedures for calculating process water rates from clean water rates, by adjusting for standard conditions, such as barometric pressure, temperature and the effects of the contaminants in the process water ( $\alpha$  and  $\beta$  factors for  $K_La$  and  $C_\infty^*$ , respectively). Based on the success of the clean water standard, the US EPA and ASCE funded a new effort to develop process water testing methods, which were published by the US EPA in 1989 and later adopted into a standard guideline (ASCE, 1997).

Several major improvements in estimating oxygen transfer rates were incorporated



into the Standard. The first was the methodology of estimating  $K_La$  from non-steady state reaeration data (Stenstrom, et al., 1981). Prior to the Standard, the log deficit method was used which required a priori knowledge of  $C_\infty^*$ , the equilibrium oxygen concentration. The equilibrium concentration differs from handbook saturation dissolved oxygen concentration because it includes the effect of hydrostatic pressure. Previously, several methods for calculating  $C_\infty^*$  from hydrostatic pressure existed, but all had pitfalls, allowing the introduction of errors that could easily bias the overall transfer rate by  $\pm 15$  to 20% (Boyle, *et al.*, 1974). The Standard uses a non-linear regression technique which avoids the use of a priori methods and eliminates the possibility of bias.

A number of other improvement in testing procedures were realized, including the geometry of DO sampling locations, method for adding sodium sulfite, the impact of cobalt interference in the Winkler dissolved oxygen (DO) measurement procedure, the impact of DO probe lag on estimates of  $K_La$  (Philichi and Stenstrom, 1989), and more precise ways of defining power and its measurement

The improved precision and reduced error associated with clean water testing created a need for improved process water testing, which lead to the development of the process water testing guidelines. Process water testing is not the subject of this paper, but it is worth citing several significant improvements. The most significant is off-gas

testing developed (Redmon, et al., 1983). This method, in the ten years following its development, became the method of choice for measuring oxygen transfer in subsurface aeration systems for conventional processes as well as occasional use in novel process such as biological aerated filters (Stenstrom, et al. 2008), and in column testing to estimate  $\alpha$  factors (Hwang and Stenstrom, 1985; Redmon 2000).

A second major change was the realization that  $\alpha$  factors, which prior to 1980 had almost always been routinely specified as 0.8, were dependent not only on just the wastewater type, but also on the aeration devices (i.e., fine pore diffusers have lower  $\alpha$  factors than surface aerators, Stenstrom and Gilbert, 1981). Additionally  $\alpha$  factors depend on the conditions of the activated sludge mixed liquor: processes operating with longer mean cell retention times (SRT) have higher  $\alpha$  factors than processes operating at low SRT (Rosso, et al, 2005).

The goal of this paper is to describe the key concepts used in developing the Clean Water Standard and to illustrate why they are still important. The error introduced using previous methods, such as assumptions for  $C_{\infty}^*$ , are quantitatively described, A second goal is to show why bubble oxygen depletion during diffused aeration does not create a bias between clean water testing and process water conditions.

## 2.2 ASCE STANDARD MODEL AND PREEXISTING MODELS FOR $C_{\infty}^*$

Data are collected for the Standard method in the form of dissolved oxygen concentration versus time from a non-steady state reaeration test. This allows the use of a dynamic model to describe oxygen transfer rate in clean water and a best-fit parameter estimation method based on nonlinear regression.

The mathematical model for non-steady state test is:

$$\frac{dC_L}{dt} = K_L a (C_{\infty}^* - C) \quad (2.1)$$

where:

$C$  = liquid-phase oxygen concentration,

$C_{\infty}^*$  = equilibrium liquid-phase oxygen concentration, and

$K_L a$  = overall volumetric liquid-side mass transfer coefficient.

If  $K_L a$  and  $C_{\infty}^*$  are considered as constants through the non-steady state testing period, and the integrated form can be used to estimate  $C$  as a function of time:

$$C = C_{\infty}^* - (C_{\infty}^* - C_0) \exp(-K_L a t) \quad (2.2)$$

where  $C_0$  = liquid-phase oxygen concentration at  $t=0$ .

To describe the transfer rate, three parameters:  $C_0$ ,  $C_{\infty}^*$  and  $K_L a$  need to be estimated.

Boyle et al. (1974) discussed three ways of estimating the parameter and concluded

that a non-linear method estimating all three simultaneously was best. This was a major departure from the common way of estimating  $K_La$  using the logarithmic form of Equation 2.2, as follows:

$$\ln(C_{st}^* - C) = \ln(C_{st}^* - C_0) - K_L a t \quad (2.3)$$

where  $C_{st}^*$  is the a priori estimate of  $C_\infty^*$ .

Equation 2.3 can be plotted on semi-log paper to estimate  $K_La$  if  $C_\infty^*$  and  $C_0$  are known. The accuracy of the estimate for  $K_La$  depends on a good estimate for  $C_\infty^*$ . The value of  $C_0$  has less impact on  $K_La$  estimation. This log-deficit approach requires a priori knowledge of  $C_\infty^*$ . There were quite a few models for estimating  $C_\infty^*$  which all involve the use of the saturation values of dissolved oxygen  $C_s$  (handbook values), and water depth. The value of  $C_s$  is determined from published tables as a function of barometric pressure and temperature. The choice of  $C_\infty^*$  affects the estimate of  $K_La$  in a predictable way (as shown later), which means that aeration equipment suppliers preferred the method of estimating  $C_\infty^*$  that provided the highest transfer rate for their equipment. The two most common methods for predicting  $C_\infty^*$  are shown in Equations 2.4 and 2.5.

i) Surface saturation model:

$$C_\infty^* = C_s \quad (2.4)$$

ii) Mid-depth model:

$$C_{\infty}^* = C_s (1 + \gamma h / 2P) \quad (2.5)$$

where:

$C_s$  = the dissolved oxygen saturation concentration at surface,

$\gamma$  = weight density of water, f/L<sup>3</sup>,

P = Barometric pressure, f/L<sup>2</sup>, and

h = Diffuser submergence, L.

Table 2.1 summarizes the methods including their impacts on transfer estimation. All of these models above in the effort of getting  $C_{\infty}^*$  are arbitrary to some extent but work much better than just using surface saturation concentration as the a priori estimate of  $C_{\infty}^*$ .

**Table 2.1** Summary of Models for priori  $C_{st}^*$

Model for $C_{st}^*$	Equation	Comments
Surface Saturation Model	$C_{st}^* = C_s$	Assumes no increase due to hydrostatic pressure; good for surface aerators
Mid-depth Model	$C_{st}^* = C_{sm} = C_{st} \left[ \frac{P_0 + \gamma \left( \frac{H}{2} \right)}{P_0} \right]$	Assumes average hydrostatic pressure equals one-half diffuser submergence
Mid-depth corrected Model	$C_{st}^* = C_s (1 + \gamma H / 2P + O_r / 2O_i)$	Improvement over the Mid-depth model <sup>+</sup>
Log-Mean Model	$\ln C_{st}^* = \frac{1}{2} [\ln(C_s + C_s \gamma H / 2P) + \ln(C_s O_r / O_i)]$	-
Bottom Saturation Model	$C_{st}^* = C_{sb} = C_{st} \left[ \frac{P_0 + \gamma(H)}{P_0} \right]$	Assumes average hydrostatic pressure equals diffuser submergence; rarely provides a good fit for any aeration conditions

+ Campbell et al., 1976

$O_i$  =inlet oxygen content in air by volume (20.95%),

$O_r$  = oxygen content in the air leaving the aeration tank (%),

$$O_r = O_i(1 - E) \times 100 / [(1 - O_i) + O_i(1 - E)],$$

where  $E$  = Fractional oxygen transfer efficiency.

$H$  = Henry's law coefficient,

$Y$  = mole fraction of oxygen in gas phase,

$r$  = weight density of water,

$P_0$  = atmospheric pressure at the surface (psi), and

0.433 = conversion factor from feet to PSI

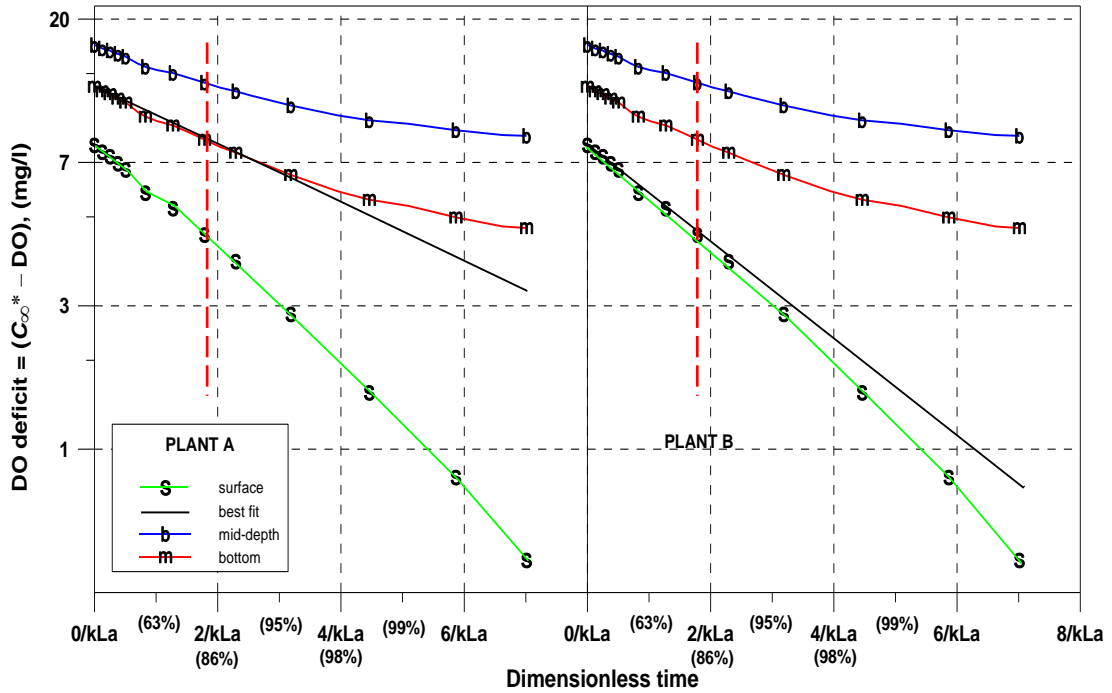
A complicating factor when translating clean water transfer efficiencies to process water conditions relates to oxygen depletion in the bubbles associated with diffused aeration. In a clean water test the transfer rate is very high in the early part of the test, but tends to zero in the later part of the test. Under process conditions, there is always transfer and always some amount of oxygen depletion in the bubbles. This difference has lead some investigators to speculate that the value of  $C_\infty^*$  obtained in a clean water reaeration test should be reduced for steady-state operation under process conditions, to account for bubble oxygen depletion. Later it will be shown that the parameter estimation procedure produces paired estimates for  $K_La$  and  $C_\infty^*$  that are different than the "true" values, and include the effects of bubble gas depletion.

## 2.3 COMPARISON OF METHODS

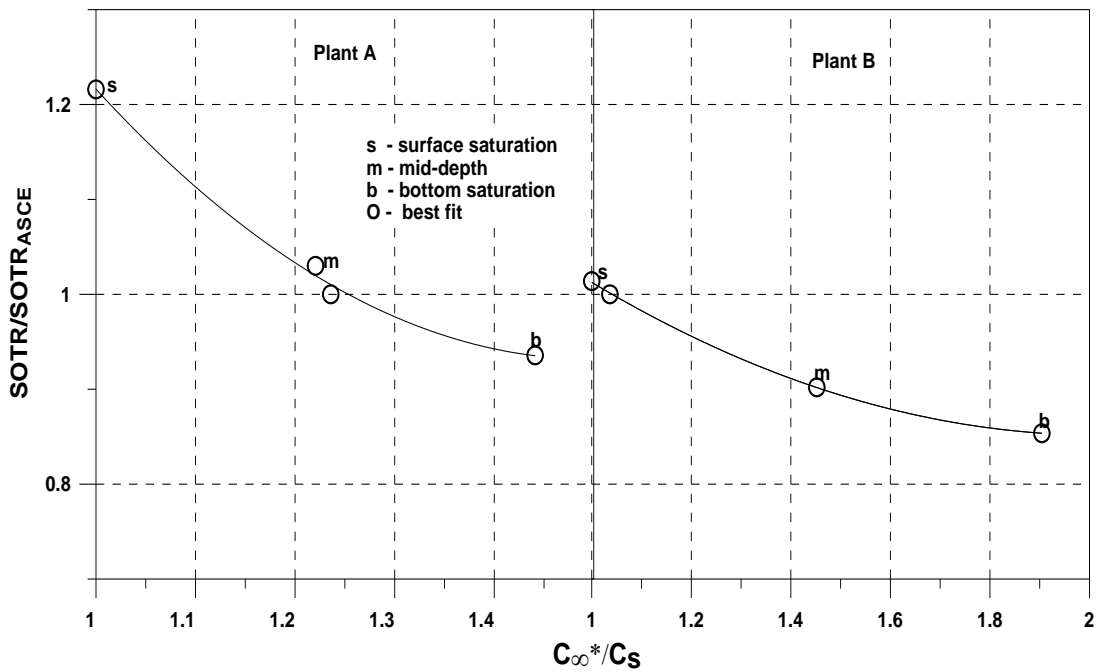
This section shows the differences among the various methods and how they impact the overall estimate of transfer efficiency. Example data sets were selected, from surface and diffused aeration tests operating over a range of air fluxes (air flow per unit area of tank bottom). The log deficit method with a priori estimates as well as the non-linear regression method were used to analyze the datasets.

Figure 2.1 shows the reaeration data, plotted to conform to Equation 2.3. The left panel represents the subsurface aeration system and the right panel shows the surface aerator. The curved lines are indicative of poor fit. For the diffused aeration system on the left panel, both bottom saturation and surface saturation models show curvature beginning at about 80% of saturation, marked by the vertical dashed line. If the data are truncated at 80% of saturation, the error associated with incorrect value of  $C_{\infty}^*$  is not observable – all three regressions appear straight and to fit the data well. The mid-depth model is close to but not equal to the best fit model (ASCE Standard Method). The right panel shows similar curvature but for mid-depth and bottom saturation, while the surface model and the best fit model provide similar results.





**Fig. 2.1** Reaeration data plotted to conform to the Log Deficit Method of parameter estimation and ASCE method.



**Fig. 2.2** Changes in predicted SOTR as a function of equilibrium DO concentration.

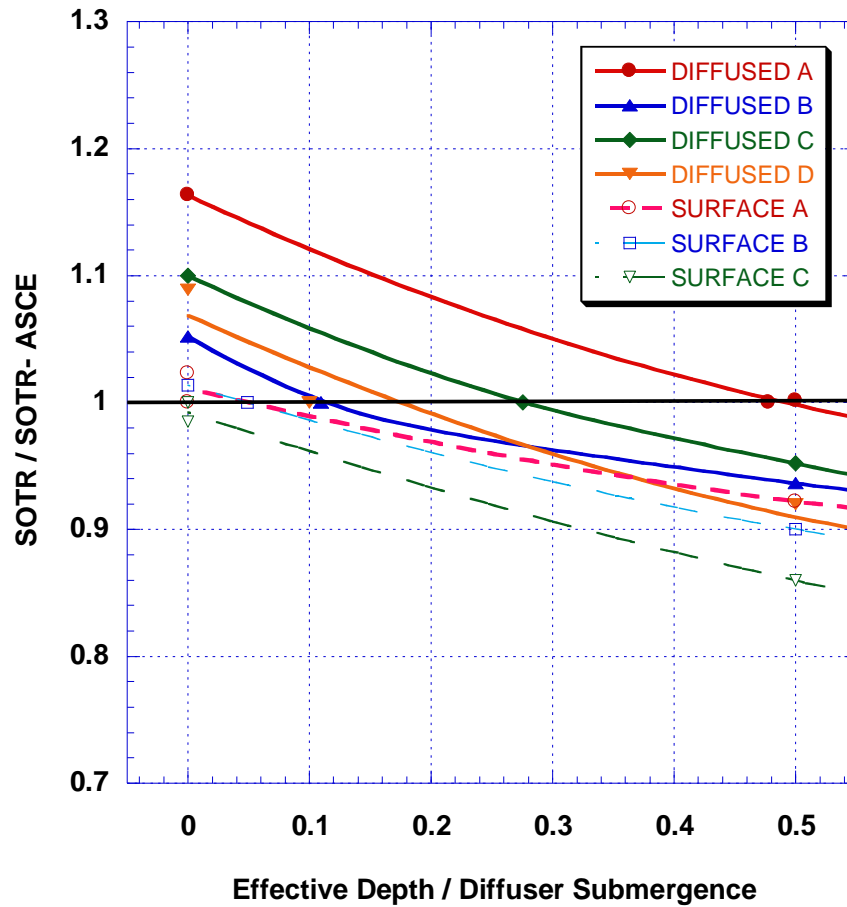
Figure 2.2 shows the results of these errors on the overall mass transfer rate, called the

Standard Oxygen Transfer Rate (SOTR), when specified at standard conditions. The left vertical axis shows the ratio of the transfer rate or SOTR obtained using the a priori models to the best fit model. In the case of the subsurface system shown in the left panel, a 20% bias of greater transfer (defined as positive) is obtained if a surface saturation model is used, and a 5% negative bias is obtained if the bottom saturation model is used. For the surface aerator, as in the right panel, there is 10 to 12 % negative bias when the mid-depth model is used and up to 22% bias when the bottom saturation model is used. The best fit model and the most correct a priori models (mid depth model for subsurface aerator, surface model for surface aerator) differ by approximately 2 to 5%. Bottom saturation never provides a good fit for any aeration device, at least in the experience of the authors. The best fit model selects the correct value of  $C_{\infty}^*$  solely based upon the reaeration data, which means that there is no need to speculate about the choice of  $C_{\infty}^*$ .

Figure 2.3 shows the SOTR calculated from both Log Deficit Method and ASCE Standard Method for seven aeration systems. Four of them used subsurface aeration devices shown as Diffused A, B, C and D, while the other three, Surface A, B, C applied to surface aerators. The results reinforce the conclusions from Figures 2.1 and 2.2, but also show a range of saturation depths. The mid-depth model works well for high efficiency diffused aeration systems, but is clearly incorrect for less efficient systems. The recent European (German) standard using a fixed value  $C_{\infty}^*$  equal to the

mid-depth saturation, would clearly be in error for many of the subsurface systems.

Bottom saturation is not shown since it never provides a good fit.



**Fig. 2.3** Relationship between SOTR's from Log Deficit Method, ASCE Method and the depth measured.

The extreme limits of the bias (+22% and -12%) are large by today's methods for

specifying aerators. Bids are won and lost by as little as 2% differences in transfer rates. The most troublesome part of the results shown in the above Figures 2.1-2.3 is the inability to detect a bias if the analysis shown in Figure 2.1 and 2.2 is conducted to only 80% of saturation (vertical lines at  $1.61/ K_L a$ ). The curvature of the line is not obvious until the test is conducted to 90% ( $2.3/ K_L a$ ) or more of saturation. Therefore it was possible to use the wrong a priori model, bias the final results and not know that an error had been made.

To prevent this type of error it is necessary to continue the reaeration test until the DO approaches saturation, typically greater than 96% of saturation. Unfortunately, this can have an unexpected negative impact on test accuracy and precision if the log deficit method (Eq. 2.3) is used. This occurs because of error transformation. When using the log deficit method, the residuals are not actual errors in DO concentration, but errors in the log of DO concentration. Taking the logarithm of the error transforms it: small values of error are made larger while large errors are reduced in size. Therefore, minimizing the log of the residuals does not minimize the difference in the actual residuals. All log deficit methods minimize the log of the error while the ASCE Standard Method minimizes the actual error.

A simple example is useful. Suppose the value of  $C_\infty^*$  is 10 mg/L and the error in DO measurement is  $\pm 0.1$  mg/L. At 1.0 mg/L DO concentration, the error in log deficit

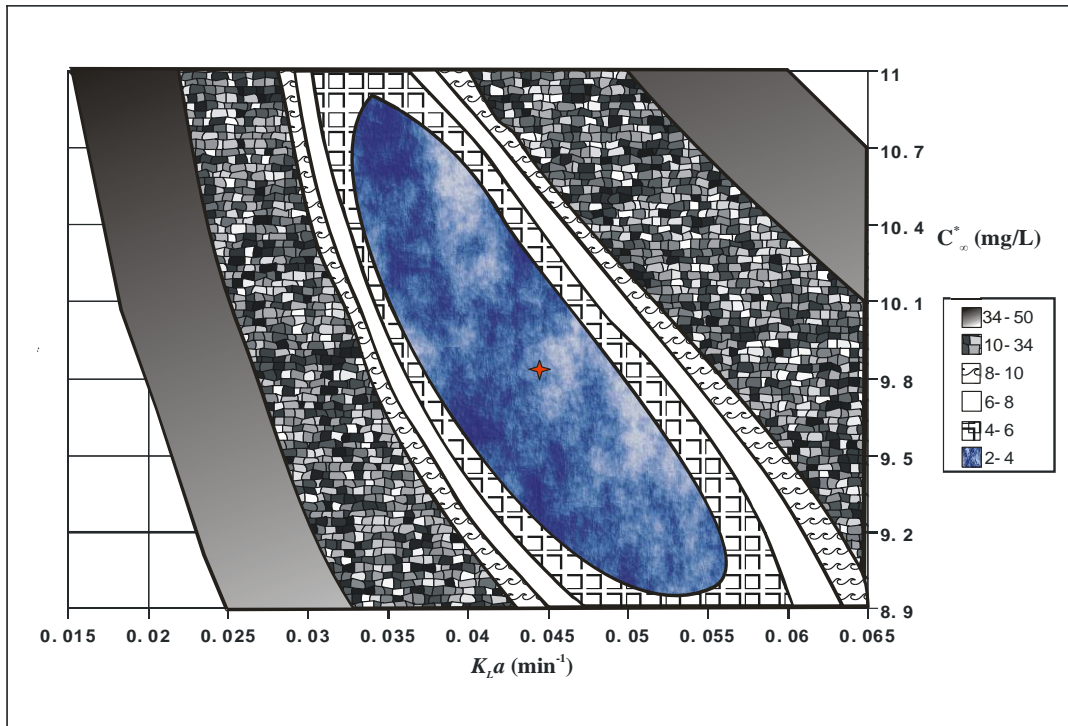
will be difference between  $\log |10-1.1|$  or  $\log |10-0.9|$  and  $\log |10-1.0|$ , which is  $\pm 0.004$ . At 96% of  $C_{\infty}^*$ , near the end of a reaeration test, the error will be the difference in  $\log |10-9.7|$  or  $\log |10-9.5|$  and  $\log |10-9.6|$ , which is 0.09 or -0.12. The relative contribution of a 0.1 mg/L error in DO measurement is 24 to 31 times greater at the end of the test than at the beginning of the test. The transformed error structure weighs measurements at the conclusion of the test more heavily than at the beginning. Also, if the DO measurement error is higher, it may be possible near saturation to have undefined error due to a negative deficit.

The error transformation is one possible reason for the former practice of terminating reaeration tests early (Boyle, *et al.*, 1974). The two types of errors, non-uniform residuals and bias due to the incorrect value of  $C_{\infty}^*$ , require mutually exclusive modifications (continuing the test to 96% of saturation to insure accuracy in  $C_{\infty}^*$  or terminating the test early to avoid transforming the error) to the data analysis methodology. The best fit method has neither problem. The error structure is not transformed and it is possible to conduct the test arbitrarily close to  $C_{\infty}^*$ .

Another difference between methods is the correlation of random errors. In fitting Equation 2.3 to experimental data, small, random errors in DO measurement create inversely correlated errors in the parameters estimates for  $K_L a$  and  $C_{\infty}^*$  (an error in DO measurement is compensated by a small increase in the estimate of  $C_{\infty}^*$  and a small

decrease in the estimate of  $K_{La}$ , or vice-versa). Figure 2.4 shows a contour of error associated with estimates of  $C_{\infty}^*$ . This figure was created using data from an actual reaeration test and calculating the sum of squared error over the range of  $K_{La}$  and  $C_{\infty}^*$  in steps of 0.005/min for  $K_{La}$  and 0.2 mg/L for  $C_{\infty}^*$ . Best fit occurs with  $K_{La} = 0.045$  /min and of and  $C_{\infty}^* = 9.851$  mg/L and is shown by the cross in the center. Note that overestimates in  $K_{La}$  are compensated by lower estimates in  $C_{\infty}^*$ , and vice versa.

When the SOTR is calculated, the estimates of  $K_{La}$  and  $C_{\infty}^*$  are multiplied, which partially cancels the net error in SOTR. For this reason, the Standard requires that the estimates of  $K_{La}$  and  $C_{\infty}^*$  from each measuring point or probe be multiplied to obtain the SOTR first and then the SOTR from each measuring point be averaged to obtain the overall SOTR. This improvement due to negative correlation in the errors associated with parameters does not occur in the log deficit procedures.



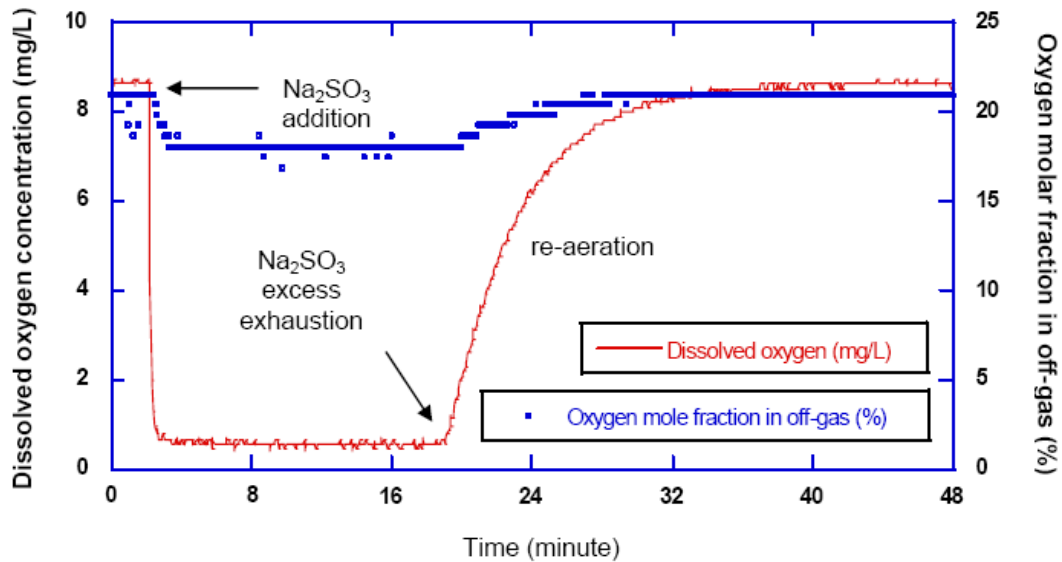
**Fig. 2.4** Contour of the sum of squared differences with the center mark for point (0.0457, 9.851)

## 2.4 GAS PHASE OXYGEN DEPLETION DISCUSSION

A criticism of the non-steady state reaeration test (regardless of data analysis methods) is the effect of oxygen depletion in the rising bubbles. As the bubbles rise, oxygen is absorbed by the liquid, reducing the oxygen mole fraction in the bubbles. Also, nitrogen and carbon dioxide can be stripped from the liquid which further reduces the oxygen partial pressure. The loss of oxygen is greatest in the early part of the reaeration test, where the deficit, and therefore transfer rate, is greatest.

Figure 2.5 shows this phenomenon for a typical reaeration test. The test was performed according to the ASCE Standard, except that the off-gas from the surface

of the tank was collected in a hood and analyzed for oxygen with a fuel cell oxygen analyzer (Model 320, Teledyne, City of Industry, CA).



**Fig. 2.5** DO concentration and oxygen mole fraction in the off-gas during a clean water re-aeration test.

The oxygen in the off-gas is depleted in the early part of the test and then returns to 0.2095 mole fraction at the end of the test. The effect of this deficit on parameter estimation and subsequent use of the data for steady-state design calculations was examined by Baillod (1979) and Brown and Baillod (1982). They noted that the effect of gas side depletion on parameter estimation was to reduce the estimate of  $K_La$  and increase the estimate of  $C_\infty^*$ . They formulated a conversion equation between “observed”  $K_La$  and  $C_\infty^*$  and “true”  $K_La$  and  $C_\infty^*$  by modeling oxygen transfer in a column, and concluded that the errors in observed and true  $K_La$  and  $C_\infty^*$  canceled for depths below approximately 10 m, depending on oxygen transfer rate. For this reason



it was decided not to introduce the concept of true and apparent  $K_{La}$  into the ASCE Standard since the effect was negligible and unnecessarily complicated analysis. The authors adopted the calculation method in Brown and Bailod (1982) and expanded the database from one coarse bubble, clean water data set, (e.g. low SOTE's), to several data sets, including turbines and fine pore diffusers to cover a whole range of SOTE's from medium (3% SOTE/m) to high (8% SOTE/m) scenarios. The results show that in all situations, the differences between products of true and apparent  $K_{La}$  and  $C_{\infty}^*$  were not significant or even measurable in most cases. For this reason, it is not necessary to adjust the value of  $C_{\infty}^*$  for process conditions due to gas phase bubble depletion. In rare cases, such as fermentation systems, or systems using fine pore aeration with pure oxygen, it may be necessary to compensate for gas phase oxygen depletion.

## **2.5 ADDITIONAL IMPROVEMENTS IN THE STANDARD**

The 2006 release of the Standard contains several important additions, in addition to many small improvements. The major improves are summarized below:

1. The Standard provides specific recommendations for loop reactors (i.e, oxidation ditches) and cites case studies showing how the Standard has been successfully applied to full scale, field clean water tests (Boyle, *et al.*, 1989).

2. The Standard provides a method for estimating oxygen transfer rates for the high purity oxygen activated sludge (HPO-AS) process, using clean water test results in air and the gas phase purities observed or designed for the HPO-AS process.

3. A correction factor to total dissolved solids (TDS) is also recommended but is not mandatory. The Standard still requires the TDS of the tap water to be less than 2,000 mg/L, but now provides an empirical correlation to adjust the results to 1,000 mg/L. TDS. This is a recommendation in the new Standard, and if supported by a consensus of the users, can become mandatory in the next version of the Standard.

4. The requirement for adding sodium sulfite in dissolved form has been relaxed and can be added as a powder for specific circumstances.

5. A pure oxygen method, which avoids deaeration using nitrogen gas or sodium sulfite, is offered as a trial method. The Committee hopes that those using the pure oxygen method can report their results in order to formalize the method for future releases of the Standard.

## **2.6 CONCLUSIONS**

The ASCE Oxygen Transfer Standard is more than 25 years old. Its use has eliminated many of the experimental and analysis errors previously encountered in

clean water testing. The Standard has created standard terms for transfer rate, such as SOTR (lbO<sub>2</sub>/hr or kg O<sub>2</sub>/hr), and efficiencies, such as Standard Oxygen Transfer Efficiency (SOTE, %), and Standard Aeration Efficiency (SAE, lbO<sub>2</sub>/hp-hr or kg O<sub>2</sub>/kW-hr), and provided conversion methodology for translating from clean water to process water conditions. One of its most important contributions is the avoidance of systemic errors by eliminating the need for a priori estimates of  $C_{\infty}^*$ . The original objections to the Standard, that it was difficult to understand and that a computer was required, are no longer valid.

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3. MODELING OZONE MASS TRANSFER IN RECLAIMED  
WASTEWATER

**Pan Jiang, Hsiao-Ting Chen, Roger W. Babcock, Jr. ,  
and Michael K. Stenstrom**

**ABSTRACT:** Ozone mass transfer in reclaimed water was evaluated at pilot scale to determine mass-transfer characteristics and reaction kinetics and to assess the use of oxygen as a surrogate to measure this process. Tests were conducted in a 40-L/min pilot plant over a 3-year period. Nonsteady-state mass-transfer analyses for both oxygen and ozone were performed for superficial gas flow rates ranging from 0.13m/min to 0.40m/min. The psi factor, which is the ratio of volumetric mass-transfer coefficients of ozone to oxygen, was determined. The decrease in oxygen transfer rate caused by contaminants in reclaimed water was only 10% to 15% compared to tap water. A simple mathematical model was developed to describe transfer rate and steady state ozone concentration. Ozone decay was modeled accurately as a pseudo first-order reaction between ozone and ozone-demanding materials.

**KEYWORDS:** Aeration; ozone; mass transfer; water reclamation.

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### **3.1 INTRODUCTION**

Ozone-based advanced oxidation processes are gaining popularity as a method to remove pharmaceuticals, personal care products (PPCPs), and endocrine-disrupting chemicals from wastewaters (Nakada et al., 2007). This method effectively disinfects treated wastewater effluents before discharge or reuse and works well in special

applications, such as laundry wastewaters from nuclear energy facilities (Mezzanotte et al., 2007; Vilve et al., 2007). The higher oxidation potential of ozone makes it a better disinfection agent than chlorine for many pathogens, especially for unsaturated compounds. Therefore, ozonation can be used to increase the biodegradability of biologically refractory compounds. Even small doses of ozone can change the structure of compounds, making them easier to break down (Brambilla et al., 1993; Ikehata and El-Din, 2004). Ozone enhances the efficiency of the biological activated carbon process in a physical-chemical water treatment plant (Chang and Chian, 1981; Khan et al., 1998a, 1998b).

Commercially available ozone generators are only capable of producing ozone concentrations of approximately 10%, which limits the available driving force for mass transfer. Therefore, prediction and optimization of mass transfer are important for the proper design of ozonation systems (Grasso, 1987). The highly reactive nature of ozone, however, makes it difficult to directly measure its mass-transfer coefficient. An oxygen surrogate, however, has been used to estimate stripping rates of volatile organic compounds (Hsieh et al., 1993). The oxygen mass-transfer coefficient, which is much easier to measure, may be a more effective way to predict ozone mass-transfer rates.

The limited mass-transfer data for ozone contactors that exists is often system-specific,



applying to small scales or drinking water applications only (Smith and El-Din, 2002). There also is limited information available regarding full- or pilot-scale application of ozone in reclaimed wastewater. In this study, researchers performed experiments using a pilot-scale ozone contactor in reclaimed wastewater to determine mass-transfer characteristics and reaction kinetics and to evaluate use of oxygen as a surrogate for quantifying ozone transfer.

This study used the commonly found bubble-column contactor, the most popular mass-transfer method in both the United States and Europe (El-Din and Smith, 2003). Of the 40 drinking water ozone treatment facilities in the United States, 34 were equipped with fine-bubble columns (Robson and Rice, 1991). In addition to bubble columns, there are several other types of ozone contactors, including packed towers, deep U-tubes, submerged turbines, and pipeline injectors.

Mixing in the reactor is obtained from the sparging action of the gas alone for the bubble columns. The significant advantage of bubble columns is simplicity of design, which allows for easy operation and reduced maintenance because of the absence of moving parts (Deckwer et al., 1974; Marinas, et al., 1993). In addition, bubble columns typically achieve high ozone transfer efficiencies. Ozone contactors treating drinking water with a depth of 5 to 6 m can achieve transfer efficiency of more than 90% (AWWA Research Foundation, 1991). For reclaimed water and wastewaters,

contaminants, particularly surface active agents, can affect mass transfer. Bubbles released by the diffuser may decrease in diameter with increasing surfactant concentration, but coalescence typically will increase. The film coefficient will decrease, resulting in an overall negative effect on transfer (Stenstrom and Gilbert, 1981; Rosso and Stenstrom, 2006).

Overall transfer efficiency alone is not sufficient to evaluate the effectiveness of an ozone contactor. It is also necessary to know the concentration profile of ozone throughout the height of the contactor column (Laplanche et al. 1991; LeSauze et al. 1993). The performance of ozone disinfection is determined by both the ozone concentration and the contact time in the bubble column. The U.S. Environmental Protection Agency has adopted this “contact-time” concept to define the degree of disinfection (Zhou, 1995). In this chapter, the ozone decay rate and mass-transfer coefficients were determined, and the ozone concentration profile along the column was modeled. The affects of higher oxygen and ozone demands of the reclaimed waters also were studied. All model simulations were compared to measured results.

## **3.2 METHODOLOGY**

### ***3.2.1 Experimental Setup***

Experiments were conducted in a countercurrent bubble column, constructed from Schedule 80 PVC (polyvinyl chloride). Gas was introduced at the bottom of the

column through a single, 20-cm-diameter, fine-pore ceramic dome designed for commercial ozone service (Aercor, Brown Deer, Wisconsin). Liquid was introduced at the top of the column. The column was 650 cm tall with 29 cm internal diameter and a water depth of 615 cm. These columns originally were used in a 40-L/min pilot water reclamation facility operated for 3 years at Lake Arrowhead, California (Madireddi et al., 1997). Five ozone contactor columns were operated in series. Two different water types were used for mass-transfer experiments. The first water was reverse-osmosis product water from the pilot plant, which was secondary wastewater effluent that had been denitrified, alum coagulated, settled, sand-filtered, ozonated, filtered with activated carbon, and then passed through nanofiltration and reverse osmosis membranes (Madireddi et al., 1997). This water had purity similar to or better than drinking water and was denoted as “tap water.” The second type of water came from the same source, but only received denitrification, alum coagulation, sedimentation, and sand-filtration pretreatment. This water was denoted “reclaimed wastewater” and was of sufficient quality to be used for nonpotable applications in California. The main characteristics of tap water and reclaimed wastewater are summarized in Table 3.1.

**Table 3.1** Primary characteristics of tap water and reclaimed wastewater (TOC = total organic carbon).

Characteristics	Tap water	Reclaimed wastewater
TOC, mg/L	0.36	12.5
UV absorbance at 254 nm, $\text{cm}^{-1}$	0.004	0.17
pH	6	7
Temperature, $^{\circ}\text{C}$	16-23	13-21
Alkalinity, mg/L as $\text{CaCO}_3$	3.5	67

High-purity oxygen was used for oxygen transfer experiments as well as for ozone generation for the ozone mass-transfer experiments. When using tap water, the maximum ozone dosage was limited to 24 to 25 mg/L by adjusting the power input to the ozone generator. When using reclaimed wastewater, the maximum ozone dosage was set to 7 to 8 mg/L. The higher concentrations used with tap water facilitated experiments, but would not be practical with reclaimed wastewater because the high dosage would not be typical of expected operation.

### **3.2.2 Analytical Methods**

The indigo method was used to analyze ozone concentrations in both gas and liquid phases (Bader and Hoigne, 1982). Absorbance was measured on a spectrophotometer (Spectronic 20, Milton Roy Co., Ivyland, Pennsylvania) at 600 nm with a path length of 1 cm. Ozone concentration was calculated based on the absorbance coefficient of  $4.2 \text{ mm}^{-1}$  per mg/L. The spectrophotometer also was used to measure UV absorbance

at 254 nm (UV254). This method is sensitive at low ozone concentrations, with a detection limit of 0.002 mg/L and is subject to little interference. The dissolved oxygen concentrations were measured with dissolved oxygen meters and membrane probes (YSI Models 57 and 58, Yellow Springs Instruments, Columbus, Ohio), which were routinely calibrated by the Winkler method [American Public Health Association (APHA), 2005]. Gas-phase oxygen concentrations were measured by gas-phase oxygen meter with a micro-fuel cell (Teledyne Model 320B, City of Industry, California). Alkalinity was determined according to the Method 2320B (APHA, 2005).

A Dohrmann DC-80 Carbon Analyzer was used to determine total organic carbon (TOC) with a detection limit of 0.05 mg/L. The TOC analyzer was calibrated with a 10-mg/L potassium hydrogen phthalate solution. Inorganic carbon was eliminated by bubbling helium gas into the sample after acidification with phosphoric acid. The TOC values reported here are the averages of three replicate measurements. Because both waters were free of suspended solids, there was no need to filter the samples.

Ozone/oxygen gas samples were taken at the inlet tubing to the bubble diffuser with a glass syringe containing a valve. The valve on the syringe was locked after sampling the ozone/oxygen gas to ensure that the pressure in the syringe was the same as the pressure in the diffuser inlet. The gas was then injected into a glass bottle sealed with

a septum and containing indigo reagent, phosphate buffer, and distilled water. Once the ozone/oxygen gas was injected, the bottle was shaken well for 20 to 30 s. Absorbance at 600 nm was then measured as in the indigo method procedure for liquid samples.

### ***3.2.3 Oxygen Transfer Test Protocols***

Non-steady state tests were conducted for oxygen mass transfer. At the end of each test, three water samples were taken at each dissolved oxygen probe position and analyzed by the Winkler method to verify the accuracy of the membrane DO probes (Standard Methods, 2005). The non-steady state method was used to obtain the volumetric mass-transfer coefficients for oxygen to compare with the ozone experimental results. The bubble column was first filled with either tap water or reclaimed wastewater. Three dissolved oxygen probes were placed 0.6 m from the top, mid-depth, and 0.6 m from the bottom of the column. The probes were inverted (membrane up) and equipped with a stirrer to prevent trapping of individual bubbles on the membrane. Before aeration, readings from all three probes were recorded and samples were taken from the middle of the column for alkalinity, TOC, UV254, and pH analysis. Aeration with pure oxygen was then started. Liquid samples were obtained every 5 min and dissolved oxygen readings were taken every minute. The experiments ended when the dissolved oxygen reached 96% of the expected final value.

In a batch reactor, the oxygen mass balance is given by Equation 3.1:

$$\frac{dC}{dt} = K_L a(C^* - C) - r \quad (3.1)$$

where,

$C$  = liquid-phase oxygen concentration (mg/L),

$t$  = time (min),

$K_L a$  = volumetric mass-transfer coefficient ( $\text{min}^{-1}$ ),

$C^*$  = steady-state saturated liquid phase oxygen concentration (mg/L), and

$r$  = rate of oxygen reaction (mg/L-min).

At steady state, Equation 3.1 can be simplified as follows:

$$r = K_L a(C^* - C_{ss}) \quad (3.2)$$

where,

$C_{ss}$  = steady state liquid phase oxygen concentration (mg/L).

The value of steady-state saturated liquid phase oxygen concentration can be estimated from the experimental data or calculated from the gas-phase oxygen concentration using Henry's Law:

$$C^* = H C_g$$

where,

$H$  = Henry's law coefficient and

$C_g$  = gas-phase oxygen concentration.

### ***3.2.4 Ozone Transfer Test Protocols***

The ozone test protocols were similar to the oxygen tests except that the feed gas was ozone and ozone concentrations rather than oxygen were measured. Nonsteady-state tests were conducted for both ozone mass transfer and decomposition kinetics studies. Four gas flow rates of 2.8, 4.7, 6.6, and 8.5 L/min (6, 10, 14, and 18 ft<sup>3</sup>/h) were reported at standard conditions of 20°C and 1 atm pressure. The bubble column was first filled with tap water or reclaimed wastewater. Before aerating the water, samples were obtained from the middle of the column for analysis of alkalinity, TOC, UV254, and pH. Samples also were obtained from both the top and bottom of the column for liquid-phase ozone concentration measurements. Next, the output of the ozone generator was fed continuously into the column through the ceramic dome diffuser. The ozone concentration in the gas phase was measured in each run by the indigo method. During ozonation, liquid samples were taken every 5 min from the top, middle, and bottom of the column. At the same time, dissolved oxygen was measured in the middle of the column. When steady-state oxygen and ozone concentrations in the liquid phase were observed, the gas stream was shut off, and liquid-phase samples were collected every 3 min and analyzed using the indigo method. The same Equations 3.1 and 3.2 apply to ozone mass transfer.

Because some physical properties are dependent on temperature—such as viscosity,



density, surface tension, and molecular diffusivity—all volumetric mass transfer coefficient values obtained at different temperatures were corrected to 20°C to allow for comparison. The conversion is as follows:

$$K_{La}(20^{\circ}C) = K_{La}(T^{\circ}C) \times 1.024^{(20-T)} \quad (3.3)$$

For convenience, the temperature subscript (20°C) will not be used in this paper, unless reference is made to volumetric mass transfer coefficient values at temperatures other than 20°C.

### ***3.2.5 Ozone Concentration Profile Model***

To evaluate the effectiveness of an ozone reactor, it is necessary to understand the concentrations of ozone over the entire height of the reactor. A mathematical model is used here to calculate the ozone concentration profile. There are several assumptions for the simulation:

- The reactor operates at steady state.
- The flow rate, interfacial area, temperature, and overall mass-transfer coefficient are constant during each experiment.
- Both gas and liquid phases behave as plug flow.
- The hydrostatic head or pressure varies linearly with water depth.
- There is no short-circuiting or dead zones.
- For a small unit of height in the reactor, the ozone concentrations in both gas and liquid phases are constant.

- Equilibrium holds at the gas-liquid interface and is described by Henry's Law.
- The ozone decay rate is pseudo first-order in the liquid phase and negligible in the gas phase.

The mass balance of ozone during mass transfer between the heights (h) and (h + dh)

in the liquid phase and gas phase are:

$$C_h = C_{h+dh} + \frac{K_L a (C_h^* - C_h) h_L A dh}{Q_L} - \frac{k C_h h_L A dh}{Q_L} \quad (3.4)$$

$$C_{gh} = C_{g(h+dh)} + \frac{K_L a (C_h^* - C_h) h_L A dh}{Q_g} \quad (3.5)$$

where,

$C_h, C_{h+dh}$  = liquid phase ozone concentration at height h, h+dh,

$C_{gh}, C_{g(h+dh)}$  = gas phase ozone concentration at height h, h+dh,

$K_L a (C_h^* - C_h) h_L A dh$  = amount of ozone transferred from the gas phase to

the liquid phase,

$k C_h A h_L dh$  = amount of ozone consumed because of reaction,

$k = k_1$  = first-order rate constant for ozone decomposition reaction

( $\text{min}^{-1}$ ), for tap water,

$k = w$  = reaction rate constant ( $\text{min}^{-1}$ ), for reclaimed wastewater,

$h_L$  = liquid hold-up, i.e. liquid volume/system volume,

$Q_L$  = liquid flow rate (L/min),

$Q_g$  = gas flow rate (L/min),

H = 0 at the bottom of the column = 615 cm at the top of the column.

Taking limit as  $dh \rightarrow 0$ , Equations 3.4 and 3.5 can be rewritten as:

$$\frac{dC}{dh} = - \frac{(K_L a h_L + k_1 h_L) C - K_L a h_L C^*}{u_g} \quad (3.6)$$

$$\frac{dh}{dC_g} = - \frac{K_L a h_L (C^* - C) u_L}{u_g} \quad (3.7)$$

where,

$$u_L = \frac{Q_L}{A} ; u_g = \frac{Q_g}{A} = \text{liquid flow and gas flow superficial velocity}$$

respectively, and  $C^*$  = the saturation concentration of ozone in the liquid phase.

$$\text{Let } M = \frac{K_L a h_L}{u_L} \quad N = \frac{K_L a h_L + k_1 h_L}{u_L},$$

Equations 3.6 and 3.7 can be integrated along the height of column reactor as

$$\int_0^H d(e^{Nh} \cdot C) = \int_0^H e^{Nh} \cdot M \cdot C^* \cdot dh \Rightarrow e^{NH} C_t - C_b = M \int_0^H e^{NH} C^* \Delta h \quad (3.8)$$

$$C_{gt} = C_{gt}^* - (C_{gb}^* - C_{gb}) \exp\left(-\frac{K_L a h_L H}{u_g}\right) \quad (3.9)$$

where,

h = the height of liquid in column reactor, with the range from 0 to the maximum H = 615cm, and  $\Delta h = 5\text{cm}$ ,

$C_b, C_t$  and  $C_{gb}, C_{gt}$  = liquid phase and gas phase ozone concentration at the top and bottom of reactor.

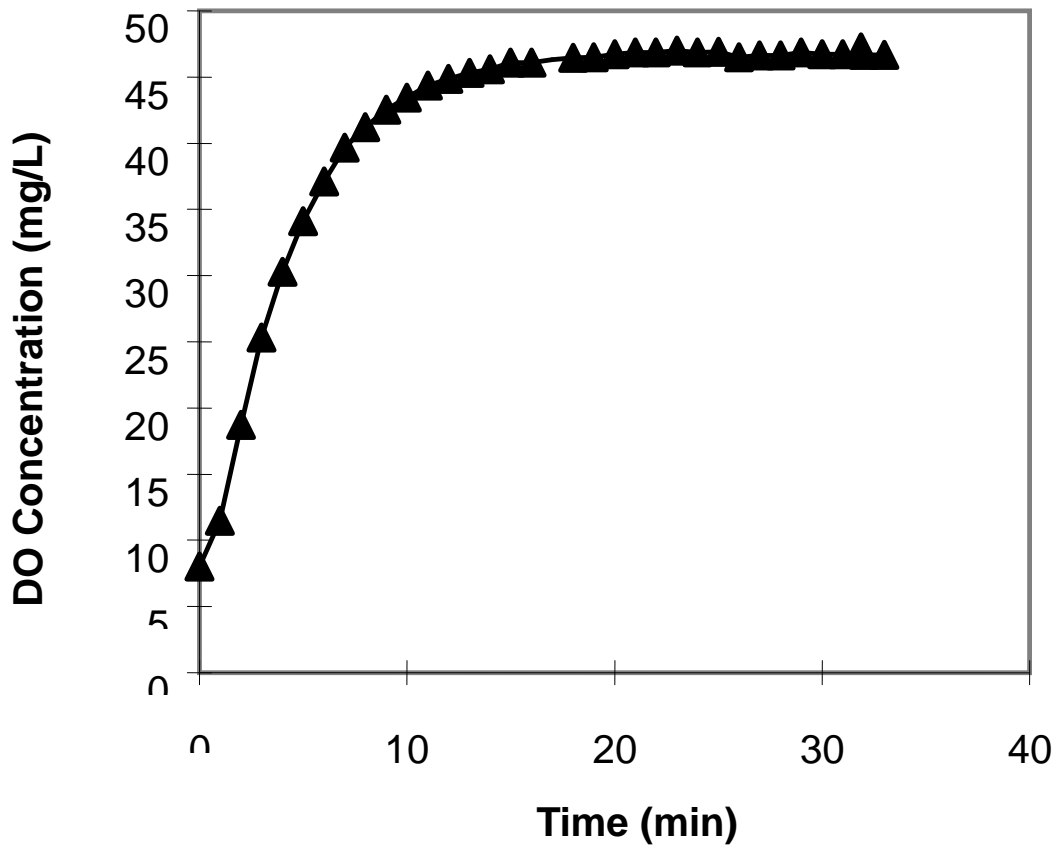
Ozone concentrations in both the water and the gaseous phase along the column were calculated using an iterative solution of Equations 3.8 and 3.9. The calculation started

from the top of the column, where the liquid-phase ozone concentration was known. An arbitrary value was taken for an initial guess of gas-phase ozone concentration ( $C_{gt}$ ) and both gas- and liquid-phase ozone concentration profiles were calculated with all the other known parameters. The gas-phase ozone concentration in the influent ( $C_{gb}$ ) also was calculated and compared with the measured value. The iterative procedure was continued with new estimates of  $C_{gt}$  continued until the value of the difference between measured and simulated gas-phase ozone concentrations in the influent converged close to zero.

### **3.3 RESULTS AND DISCUSSION**

#### ***3.3.1 Oxygen Mass Transfer: Nonsteady-State Method***

Figure 3.1 shows the oxygen concentrations as a function of time for a re-aeration test, at the gas flow rate of 6.6 L/min. Experiments at other gas flow rates gave similar trends. Table 3.2 shows volumetric mass transfer coefficient values for tap water and reclaimed wastewater, along with the ratios of volumetric mass transfer coefficient values of reclaimed wastewater to tap water (alpha factor).



**Fig. 3.1** Liquid-phase oxygen concentration versus time (gas flow: 6.6 L/min, T: 17.5°C).

**Table 3.2** Volumetric mass-transfer coefficient ( $K_{La}$ ) values for oxygen transfer in tap water and reclaimed wastewater at different depths within the column at gas flow rates of 2.8, 4.7, 6.6, and 8.5 L/min ( $K_{La,t} = K_{La}$  for tap water;  $K_{La,r} = K_{La}$  for reclaimed wastewater).

Gas Flow (L/min)	Tap Water $K_{La,t}$ ( $\text{min}^{-1}$ )				Reclaimed Water $K_{La,r}$ ( $\text{min}^{-1}$ )				Average alpha
	Top	Middle	Bottom	Average	Top	Middle	Bottom	Average	
2.8	0.146	0.143	0.153	0.147	0.096	0.102	0.115	0.104	0.709
4.7	0.164	0.182	0.186	0.178	0.150	0.149	0.185	0.162	0.910
6.6	0.207	0.228	0.245	0.227	0.188	0.206	0.241	0.212	0.933
8.5	0.240	0.250	0.260	0.250	0.204	0.218	0.290	0.237	0.949

The mass-transfer rates vary with positions in the column because of the plug-flow characteristics of both liquid and gas phases. As bubbles ascend the column, their diameter increases because of decreasing water pressure. Bubble coalescence further increases diameter, which decreases the specific interfacial area. Therefore, the volumetric mass-transfer coefficient may be larger at the bottom than at the top of the column. In full-scale reactors with lower height-to-diameter ratios, vertical mixing will be greater, deviating from plug flow and reducing this tendency. In Table 3.2, as expected, volumetric mass transfer coefficient increases with increasing gas flow rate because of the resulting greater specific surface area. It is often assumed that the relationship between volumetric mass transfer coefficient and superficial gas velocity takes the form of a power law as follows (Bello et al., 1985):

$$K_L a = a U_g^b \quad (3.10)$$

where,

$$K_L a = 1/\text{min},$$

$$U_g = \text{superficial gas velocity (m/h), and}$$

$$a \text{ and } b = \text{constants to be determined.}$$

The relationship was developed from a linear regression between the logarithms of volumetric mass transfer coefficient and superficial gas velocity. The relationship was determined for tap water:

$$K_L a = 0.076 U_g^{0.569} \quad (r^2 = 0.98) \quad (3.11)$$

And for reclaimed wastewater:

$$K_L a = 0.040 U_g^{0.8692} \quad (r^2 = 0.98) \quad (3.12)$$

where,

$$K_L a = 1/\text{min, and}$$

$$U_g = \text{superficial gas velocity} = Qg/A = (\text{m/h}).$$

### ***3.3.2 Alpha Factor***

The main difference between reclaimed wastewater and tap water in this study is that the reclaimed wastewater contains more organic matter (Table 3.1). Organic matter and surface-active compounds can affect mass transfer in two ways: (1) by changing the mass-transfer coefficient; or (2) changing the interfacial area. Surface-active compounds tend to adsorb to the liquid/gas interface, which reduces the surface renewal of gas molecules and depresses the hydrodynamic activity. Accordingly, surface-active compounds typically reduce the mass-transfer coefficient. When the surface-active compounds adsorb to the liquid/gas interface, they tend to lower the surface tension of water, which reduces the energy required to make smaller bubbles. The overall effect of surface-active compounds is to reduce bubble size, which increases the interfacial area, while reducing the mass-transfer coefficient. Typically, the decline in mass-transfer coefficient is not compensated by the increase in area, and there is a net reduction in volumetric mass transfer coefficient.

To quantify the effects of water quality on the mass-transfer coefficient, the alpha factor was calculated as the ratio of the volumetric mass-transfer coefficient for reclaimed wastewater to volumetric mass-transfer coefficient for tap water. Table 3.2 shows the values for the alpha factor that were obtained in this study.

A variety of conditions affect the alpha factor. Different aeration methods are affected differently with surfactants. Fine-pore diffusers (bubbles 3 mm or smaller) are more negatively affected than coarse-bubble diffusers and mechanical surface aerators (Stenstrom and Gilbert, 1981). The degree of treatment also affects alpha factors, because treatment tends to remove the surfactants through oxidation or by adsorption to biosolids. Recently, Rosso and Stenstrom (2005) have shown that alpha factors are associated with sludge age or mean cell retention time (MCRT). Higher MCRT systems remove more surface active agents, and hence improve mass-transfer rates.

Table 3.2 also shows that the alpha factors are always less than 1.0, but increase with increasing gas flow rate. This phenomenon is caused by increasing turbulence as gas flow rate increases (Rosso et al., 2006). Organic compounds can affect the behavior of the bubbles and typically increase coalescence. Organic compounds that decrease coalescence may be more important at higher flow rates because more bubbles are present that might collide and cause more coalescence. Also surfactants, depending upon the characteristics, require a finite amount of time to adsorb to the bubble



surfaces. At higher gas flow rates, the bubble surface renewal is greater, providing less opportunity for surfactants to build up. Hwang and Stenstrom (1985) have shown that alpha factors increased with increasing power input per unit volume. Eckenfelder and Ford (1968) and Gurol and Nekouinaini (1985) also noted similar effects.

### 3.4 OZONE MASS TRANSFER

#### 3.4.1 Ozone Self-Decomposition in Tap Water

In organic matter-free tap water, the ozone self-decomposition reaction is the only possible reaction. When the pH is lower than 4, decomposition is negligible, but tap water (approximately 6 to 7 pH) ozone self-decomposition can be significant (Gurol and Singer, 1982). The rate of self-decomposition is required to determine the volumetric mass transfer coefficient. For clean water, it is assumed that ozone decomposition can be approximated as a first-order process (Zhou, 1995; Roustan et al., 1996):

$$\frac{dC}{dt} = -k_1 C \quad (3.13)$$

where,

$k_1$  = first-order rate constant for ozone decomposition reaction ( $\text{min}^{-1}$ ), and

$C$  = ozone concentration in the liquid phase (mg/L).

The integrated form of Equation 3.13 is:  $\ln(C) = \ln(C_0) - k_1t$  with  $C_0$  as the initial ozone concentration in the liquid phase.

The first-order assumption can be checked by plotting  $\ln(C)$  versus time. If the relationship is linear, then the slope of the straight line is the decomposition rate constant. Four tests were conducted to determine the decomposition rate constant using least squares linear regression. A straight line was obtained for each of the decomposition experiments with a coefficient of determination greater than 0.95. Thus, a first-order decomposition reaction was observed for tap water in this study. Other researchers, such as Roth and Sullivan (1981), Hoigne and Bader (1983), and Zhou (1995), also found first-order decomposition in their experiments. Because the experiments were performed in pilot plant treating water at ambient conditions, it was not possible to conduct all four experiments at the same temperature. To adjust the value of the first-order rate constant for ozone decomposition reaction to 20 °C, a relationship to temperature was used (Roth and Sullivan, 1983):

$$k_{1,(20^\circ C)} = 4 \times 10^{-9} k_{1,(T^\circ C)} \exp(5606/T) \quad (3.14)$$

Table 3.3 shows rate constants for ozone decomposition. The value of the first-order rate constant for ozone decomposition reaction was  $0.029 \text{ min}^{-1}$  at pH 6 and 20 °C, which is much lower than the values observed by Yurteri and Gurol (1987) for ozonation of natural waters. This difference indicates that a much slower ozone decay

process occurred in the tap water used in this study. Yurteri and Gurol (1987) also developed an equation for the prediction of the first-order rate constant for ozone decomposition reaction:

$$k_1 = -3.98 + 0.66pH + 0.61\log( TOC ) - 0.42\log( ALK / 10 ) \quad (3.15)$$

where,

*TOC* = total organic carbon (mg/L), and

*ALK* = alkalinity (mg/L as CaCO<sub>3</sub>).

**Table 3.3** Summary of ozone decomposition rate constants at experiment conditions and 20°C (SD = standard deviation; T = time).

T, °C	16.2	18.6	19.4	19.5	Average ± SD
$k_{1, (T^{\circ}C)}, \text{min}^{-1}$	0.0193	0.0254	0.0313	0.0309	
$k_{1, (20^{\circ}C)}, \text{min}^{-1}$	0.0248	0.0278	0.0326	0.0319	0.0293±0.00366

The first-order rate constant for ozone decomposition reaction value calculated using Equation 3.15 is 0.013 min<sup>-1</sup>, which is less than half of the observed value. The difference can be expected because Yurteri's test conditions were different from this study. They validated their equation for pH from 7 to 9, and alkalinity from 25 to 550 mg/L (as CaCO<sub>3</sub>). Both the alkalinity and pH were lower in this study. The rate constant obtained here agreed more closely with Zhou's (1995) observed rate for

deionized water, which was  $0.028 \text{ min}^{-1}$ .

### 3.4.2 Nonsteady-State Method

In nonsteady-state reaeration testing, the liquid-phase concentration increases to an equilibrium concentration, which is a function of gas solubility and hydrostatic pressure. If a reaction is present, then the equilibrium concentration is reduced in proportion to the reaction rate (Roth et al., 1981; Sotelo et al., 1989). In a batch reactor, the ozone mass balance is given by a modified form of Equation 3.1:

$$\frac{dC}{dt} = K_L a(C^* - C) - r_1 \quad (3.16)$$

where,

$r_1$  = ozone decomposition rate ( $r_1 = k_1 C^n$ ),

$n, k_1$  = empirically determined reaction coefficients,

$C$  = liquid-phase ozone concentration, and

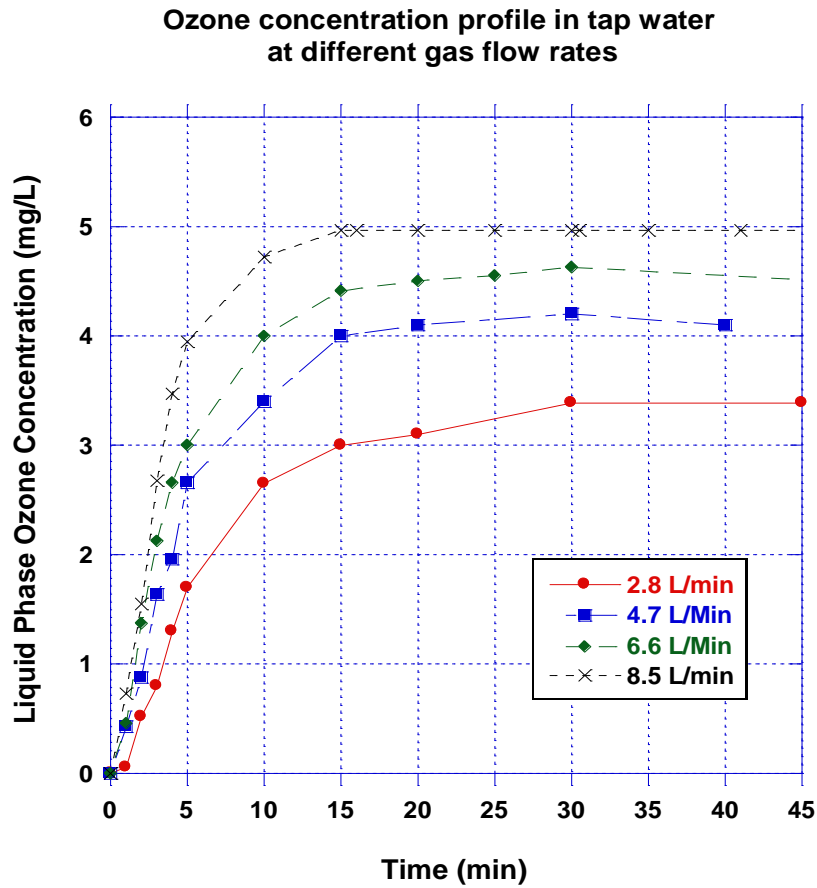
$C^*$  = liquid-phase ozone concentration in equilibrium.

The liquid-phase ozone equilibrium concentrations increase with gas flow rate or volumetric mass transfer coefficient as shown in Figure 3.2. To use Equation 3.16 to estimate the reaction coefficients, the liquid-phase ozone concentration was plotted for a range of concentrations and the reaction decomposition coefficients were found ( $n = 1, k_1 = 0.029 \text{ min}^{-1}$  at pH 6 and  $20^\circ \text{C}$  in tap water). The ozone decomposition rate constant was then adjusted for different temperatures using Equation 3.14. The ozone mass-transfer coefficients were then obtained from Equation 3.16 by rearranging:

$$dC/dt + r_l = K_L a (C^* - C)$$

And then plotting the left hand side ( $dC/dt + r_l$ ) versus the ozone residual. The corresponding slope is the value of the volumetric mass transfer coefficient. This procedure has been used before by Sotelo et al. (1989) and Roth and Sullivan (1981), and is also recognized by the American Society of Civil Engineers (ASCE) Standard Guidelines for Process Water Testing (1997). Using this method, the volumetric ozone mass-transfer coefficients were determined at four different gas flow rates. Table 3.4 shows the column average volumetric mass-transfer coefficients adjusted to 20°C using parameter theta value of 1.024 (ASCE, 2006) together with the alpha values. The value of 1.024 is typically accepted for aeration and its use for ozone has been recommended by others (El-Din and Smith, 2003). The relationship between gas flow rate and ozone volumetric mass transfer coefficient was determined as before for oxygen.

$$K_L a = 0.0636U_g^{0.586} \quad (r^2 = 0.97) \quad (3.17)$$



**Fig. 3.2** Gas flow rate influence on absorbed ozone concentration in tap water.

**Table 3.4** Volumetric mass-transfer coefficient ( $K_{L,a}$ ) values at 20°C for ozone mass transfer at different points in the column at gas flow rates of 2.8, 4.7, 6.6, and 8.5 L/min ( $K_{L,a,t} = K_{L,a}$  for tap water;  $K_{L,a,r} = K_{L,a}$  for reclaimed wastewater).

Gas Flow (L/min)	Tap Water $K_{L,a,t}$ ( $\text{min}^{-1}$ )	Reclaimed Water $K_{L,a,r}$ ( $\text{min}^{-1}$ )	alpha
2.8	0.127	0.102	0.801
4.7	0.150	0.136	0.909
6.6	0.194	0.181	0.933
8.5	0.220	0.198	0.899

For gas-liquid systems with rapid reactions in the liquid phase, such as ozonation reaction, it is possible that the mass-transfer coefficient is enhanced by the reaction in the liquid film surrounding the gas bubbles. The enhancement factor is defined as the ratio of the ozone concentration gradient at the outer surface of the liquid film to that at the inner bound of the liquid film. A necessary condition to ensure that no reaction is occurring in the film for an irreversible first order reaction is:

$$Ha = (D_L w)^{0.5} / K_L < 0.3 \quad (3.18)$$

where,

$Ha$  = Hatta number,

$D_L$  = diffusivity of the dissolved species, ozone ( $\text{m}^2\text{s}^{-1}$ ),

$w$  = reaction rate constant, either self decomposition for tap water or reaction with ozone demand for reclaimed water ( $\text{s}^{-1}$ ), and

$K_L$  = ozone mass-transfer coefficient ( $\text{ms}^{-1}$ ).

The value of the ozone mass-transfer coefficient is estimated to be approximately  $2.5 \times 10^{-4} \text{ ms}^{-1}$  (Laplanche et al., 1991). The diffusivity of the dissolved species is approximately  $1.74 \times 10^{-9} \text{ m}^2\text{s}^{-1}$  at  $20^\circ\text{C}$  (Guroi, 1983). Thus, the maximum possible reaction rate constant to ensure no reaction in the liquid film is  $194 \text{ min}^{-1}$ , which is much larger than the reaction rate constant obtained in this study. This means enhanced mass transfer can be neglected. Several studies have shown similar results demonstrating that there is only minor enhancement of mass transfer even at high pH

values where ozone decomposition is fast (Yurteri, 1988; Chang and Chian, 1981). In many chemical processes, it would be unusual for a gases being transferred to react only in the bulk liquid (Levenspiel, 1972). This situation is likely for most organic pollutants in water because the concentrations are low and noncatalytic reactions are typically slow at ambient temperatures (Chang and Chian, 1981).

### ***3.4.3 Ratio of Volumetric Mass-Transfer Coefficients of Ozone to Oxygen (Psi)***

The ratios of experimentally determined volumetric mass-transfer coefficient for ozone to oxygen (Roberts et al., 1984) at various gas flow rates in both tap water and reclaimed wastewater are listed in Table 3.5. As expected, the ratio remains constant for all gas flow rates because the liquid film resistance dominates for both ozone and oxygen transfer. The average value of Psi ( $\Psi$ ) was 0.86 for tap water and 0.88 for reclaimed water. According to the two-film theory, the ratio of mass-transfer coefficients is the ratio of diffusion coefficients for ozone and oxygen to the first power. The diffusion coefficients are  $1.74 \times 10^{-9} \text{ m}^2\text{s}^{-1}$  and  $2.09 \times 10^{-9} \text{ m}^2\text{s}^{-1}$  at 20 °C, respectively using the Wilke-Chang correlation. Thus, theoretical ratio of the volumetric mass transfer coefficient of ozone to oxygen is calculated to be around 0.83, which is only slightly different from what was found in this study (0.86 to 0.88). Penetration and surface renewal theories predict the mass-transfer coefficient to be proportion to the square root of the ratio of the diffusion coefficients, which equals 0.91. The experimental results fit well within the theoretical predictions based on gas



transfer theories. Also, differences may arise from the method used to estimate diffusion coefficients, because the Wilke-Chang correlation is only considered valid within  $\pm 15\%$ . This means that the possible range is 0.70 to 1.10. The ratio found in this study, 0.86 to 0.88, falls within the range.

**Table 3.5** Volumetric mass transfer coefficient for oxygen ( $K_{LaO_2}$ ) and for ozone ( $K_{LaO_3}$ ) and the ratio of mass transfer coefficient for ozone to oxygen ( $\Psi$ ) obtained by non-steady state method at various gas flow rates.

	Gas flow (L/min)	$K_{LaO_2}$ ( $\text{min}^{-1}$ )	$K_{LaO_3}$ ( $\text{min}^{-1}$ )	$\Psi$
Tap water	2.8	0.147	0.127	0.863
	4.7	0.178	0.150	0.845
	6.6	0.227	0.194	0.855
	8.5	0.250	0.220	0.880
Reclaimed wastewater	2.8	0.104	0.102	0.975
	4.7	0.162	0.136	0.844
	6.6	0.212	0.181	0.855
	8.5	0.237	0.198	0.834

In summary, the approximate relationships can be derived from the experimental results shown in Table 3.5, assuming two-film theory, as follows:

$$\Psi = \frac{D_{O_3}}{D_{O_2}} = \frac{K_{LaO_3,r}}{K_{LaO_2,r}} = \frac{K_{LaO_3,t}}{K_{LaO_2,t}} \quad (3.19)$$

$$\alpha = \frac{K_{LaO_3,r}}{K_{LaO_3,t}} = \frac{K_{LaO_2,r}}{K_{LaO_2,t}} \quad (3.20)$$

where,

$$K_{LaO_3,r} = K_{La} \text{ for ozone in reclaimed wastewater,}$$

$$K_{LaO_2,r} = K_{La} \text{ for oxygen in reclaimed wastewater,}$$

$K_{LaO_3,t} = K_{La}$  for ozone in tap water, and

$K_{LaO_2,t} = K_{La}$  for oxygen in tap water.

The most desired and most difficult to measure parameter, volumetric mass transfer coefficient for ozone in reclaimed water, can be estimated by the volumetric mass transfer coefficient for oxygen in tap water through the combination of Equations 3.19 and 3.20:

$$K_{LaO_3,r} = \alpha \times \psi \times K_{LaO_2,t} \quad (3.21)$$

The results suggest that ozone mass-transfer rate in reclaimed wastewater can be predicted by oxygen transfer rates in tap water. These rates can be obtained by a clean water test, which is much easier and more economical to perform.

#### ***3.4.4 Ozone Reaction Kinetics in Reclaimed Water***

In this study, it has been shown that ozone self-decomposition can be successfully described as a first-order process in tap water. Pollutants in natural waters and reclaimed wastewater can react with ozone. There are two pathways to oxidize solutes: (1) direct reactions of organic or inorganic solutes with ozone molecules; and (2) indirect reactions of solutes with the ozone decomposition products (Stahelin and Hoigne, 1985). The rate of these reactions can differ by more than several orders of magnitude, depending on the structure of pollutants (Hoigne and Bader, 1983; Zhou, 1995). It is assumed that ozone consumption is dominated by direct reactions and that

the rate of dissolved ozone consumption can be lumped into an overall expression that is first-order with respect to ozone concentration (Staehelin et al., 1985; Yuteri and Gurol, 1987; Watt et al., 1989; Roustan et al., 1996):

$$r = -wC \quad (3.22)$$

where,

$w$  = reaction rate constant.

Including the rate equation, the overall mass balance yields:

$$\frac{dC}{dt} = K_L a(C^* - C) - wC \quad (3.23)$$

At steady state, the accumulation term,  $dC/dt$ , goes to zero, leading to:

$$K_L a(C^* - C_{ss}) = wC_{ss}$$

where,

$C_{ss}$  = steady state liquid-phase ozone concentration.

By substituting into the overall mass balance equation:

$$dC/dt = K_L a((wC_{ss} / K_L a) + C_{ss} - C) - wC = K_L a(C_{ss} - C) + w(C_{ss} - C)$$

The new overall mass balance becomes:

$$\frac{dC}{dt} = (K_L a + w)(C_{ss} - C) \quad (3.24)$$

Assuming liquid-phase ozone concentration is zero at the start, Equation 3.24 can be integrated as:

$$C = C_{ss} \{1 - \exp[(-K_L a - w)(t - t_0)]\} \quad (3.25)$$

Steady-state liquid-phase ozone concentration can be determined experimentally by

sparging pure ozone-containing gas through the liquid in the column until the liquid-phase ozone concentration reaches its plateau level. Volumetric mass transfer coefficient for ozone is predicted from the equation for oxygen mass transfer by assuming that ozone mass transfer is not enhanced by reactions involved in reclaimed wastewater, and the ratio of mass transfer coefficient for ozone to oxygen of reclaimed water  $(K_L a_{O_3}/K_L a_{O_2})_{\text{reclaimed water}}$  is equal to the ratio of tap water  $(K_L a_{O_3}/K_L a_{O_2})_{\text{tap water}}$  from the former study of  $\Psi$  shown in Equation 3.19, 0.86 was adopted as the value of  $\Psi$  here. The value of volumetric mass transfer coefficient for oxygen in tap water was obtained earlier as  $0.04 U_g^{0.8692}$ , and therefore the coefficient for ozone can be given as:

$$K_L a_{O_3} = 0.86 \times 0.04 U_g^{0.8692} = 0.0344 U_g^{0.8692} \quad (3.26)$$

Thus, liquid-phase ozone concentrations as a function of time can be calculated by assigning a reaction rate constant to minimize the sum of squares of errors (SSE) between observed and modeled ozone concentrations. The reaction rate constant that minimized the SSE was determined using an interval search between 0.5 and 5. The average reaction rate constant for four sets of experiments is  $1.1 \text{ min}^{-1}$ , which was found comparable with the results of other researchers with similar water quality. Roustan et al. (1996) obtained the pseudo-first-order reaction rate constant to be  $0.4\text{-}1.1 \text{ min}^{-1}$  for water with TOC of 2 to 6 and pH of 7.8 to 8.1. Chang and Chian (1981) found the reaction rate constant to be  $1.0 \text{ min}^{-1}$  with a TOC value of 15 mg/L.

## 3.5 OZONE CONCENTRATION SIMULATION

### 3.5.1 Tap Water

Based on the previous experimental results for volumetric mass transfer coefficient for oxygen [ $K_{La} = 0.0636 U_g^{0.586} \text{ min}^{-1}$  ( $r^2 = 0.97$ )] and first-order rate constant for ozone decomposition reaction ( $0.029 \text{ min}^{-1}$ ), according to the method provided by Equations 3.8 and 3.9. Ozone concentrations in both liquid phase and gas phase along the column were simulated using an iterative procedure. The volumetric mass transfer coefficient in the above equation is at  $20^\circ\text{C}$  and need to be adjusted to tap water temperature. The value of liquid holdup  $h_L$  in Equations 3.4 and 3.5 was estimated by the relationship:

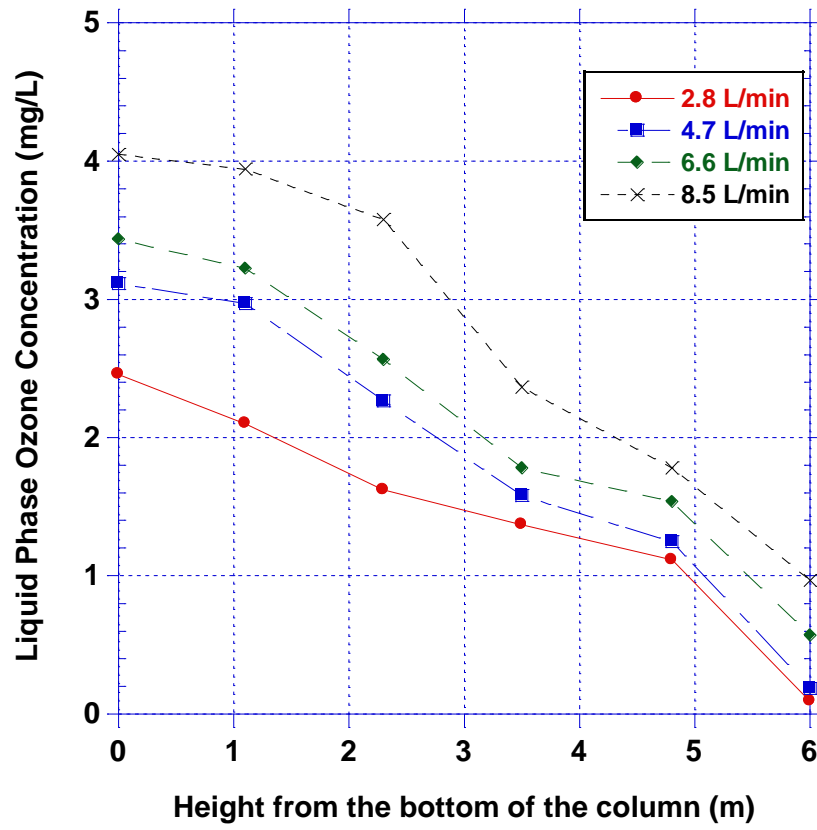
$$(1-h_L) = 1.3 \times 10^{-3} U_g$$

where,

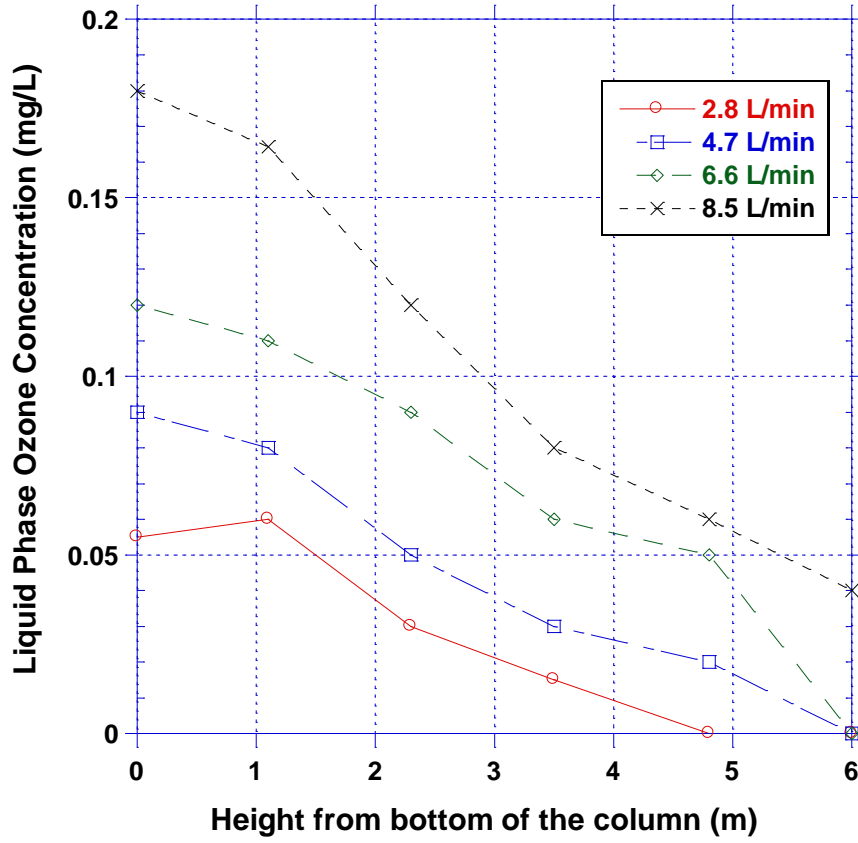
$$U_g = \text{superficial gas velocity (m/h) (Roustan et al., 1996).}$$

Experimentally, the ozone residual monotonically decreases along column height. The highest ozone concentration was detected at the bottom of the column where ozone/oxygen gas entered and water left the reactor. Figure 3.3 shows the measured liquid-phase ozone concentrations along the column at different gas flow rates in tap water. Figure 3.5 (upper two) shows the comparison between measured and simulated liquid-phase ozone concentrations at various gas flow rates along the column.

Comparisons of measured and simulated liquid-phase ozone concentrations in the effluent and ozone transfer efficiency are tabulated in Table 3.6. The trend of the simulated values matches that of the experimental data well. This suggests that the simulation approaches—including the plug-flow model, the ozone decomposition rate constant, and measured ozone volumetric mass-transfer coefficients—are reasonable. In general, the simulation values are pretty close to experimental results except for those at the bottom and top of the column, as seen in Figure 3.5 (upper two). The observed effects are probably caused by significant mixing at both ends of the column where gas and liquid enter and exit the column, whereas the simulations are based upon a plug-flow assumption. It is also observed that measured liquid-phase ozone concentrations are slightly higher than the simulated values. A possible explanation for the difference might be that micro-bubbles containing ozone were captured during sampling, despite the care taken.

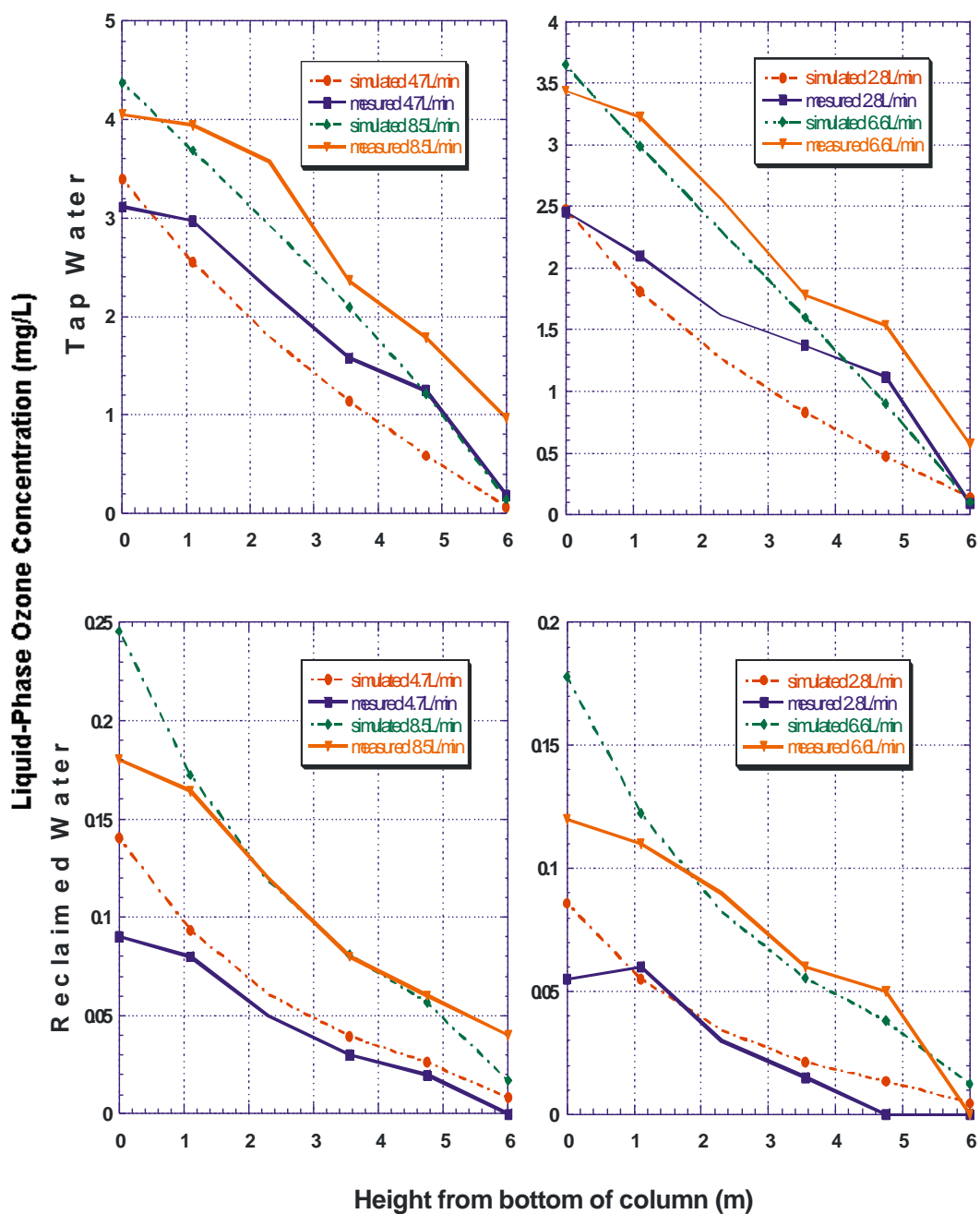


**Fig. 3.3** Measured liquid-phase ozone concentrations within the column in tap water.



**Fig. 3.4** Measured liquid-phase ozone concentration along the column at different gas flow rates in reclaimed wastewater.





**Fig. 3.5** Comparison of measured and simulated ozone concentration profiles along the column at four gas flow rates (2.8L/min, 4.7L/min, 6.6L/min and 8.5L/min) for both tap water (upper two) and reclaimed water (lower two).

**Table 3.6** Comparison of measured and simulated ozone transfer efficiency and liquid-phase effluent ozone concentrations in tap water ( $C_g$  = gas-phase oxygen concentration;  $C_b$  = liquid-phase oxygen concentration at the bottom of reactor.)

Gas flow rate (L/min)	8.5	6.6	4.7	2.8
$C_g$ influent, mg/L	23.81	23.39	24.83	24.93
$C_g$ effluent, mg/L				
Measured	6.72	6.22	4.82	4.5
Simulated	8.79	7.33	5.02	3.16
Simulation error, mg/L	2.07	1.11	0.20	1.34
Transfer efficiency ( $O_3TE$ ), %				
Measured	71.8	74.4	80.6	81.9
Simulated	63.1	68.7	79.8	87.3
Simulation error, %	8.7	5.7	0.8	5.4
$C_b$ effluent, mg/L				
Measured	4.05	3.44	3.12	2.46
Simulated	3.93	3.12	2.90	2.05
Simulation error, mg/L	0.12	0.32	0.22	0.41

### 3.5.2 Reclaimed Wastewater

Based on the previous experimental results for volumetric mass transfer coefficient for ozone ( $0.0344 U_g^{0.8692}$ ) as shown in Equation 3.26 and reaction rate constant ( $1.1 \text{ min}^{-1}$ ), according to the method given by Equations 3.8 and 3.9, ozone concentrations in both liquid phase and gas phase along the column were simulated using an iterative procedure. Other parameters are the same as in tap water part.

Figure 3.4 shows the measured liquid-phase ozone concentrations within the column at different gas flow rates in reclaimed wastewater. Figure 3.5 (lower two) shows the comparison between measured and simulated liquid-phase ozone concentrations at

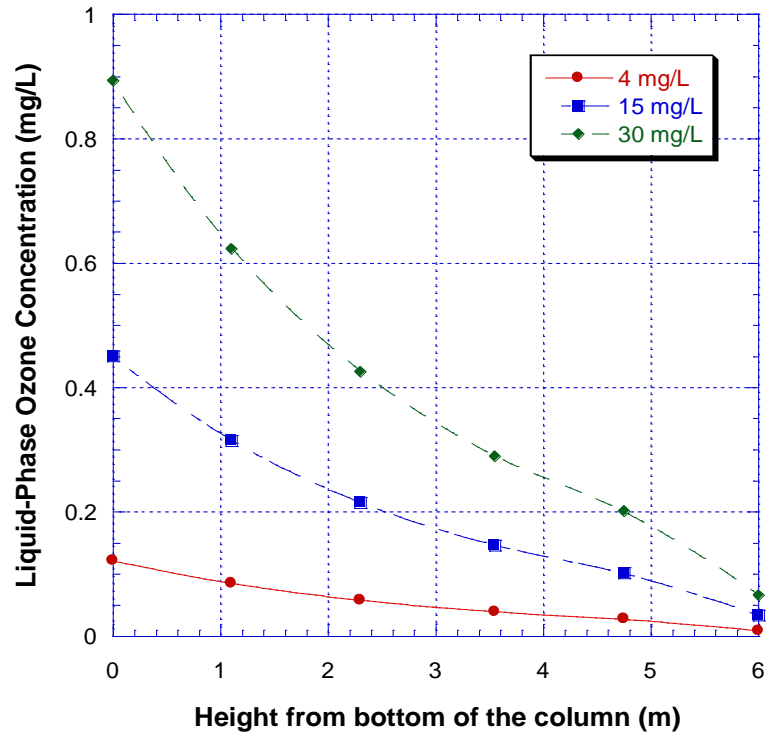
various gas flow rates along the column. The simulated and measured gas-phase ozone concentrations are listed in Table 3.7. The simulated transfer efficiencies are close to measured values with a difference of less than 10%. The comparison of liquid-phase ozone concentrations in the effluent between measured and simulated results are tabulated in Table 3.7. The absolute difference in liquid-phase ozone concentrations in the effluent is small, ranging from 0.035 to 0.07mg/L.

**Table 3.7** Comparison of measured and simulated ozone transfer efficiency and liquid-phase effluent ozone concentrations in reclaimed wastewater ( $C_g$  = gas-phase oxygen concentration;  $C_b$  = liquid-phase oxygen concentration at the bottom of reactor.)

Gas flow rate, L/min	8.5	6.6	4.7	2.8
$C_g$ influent, mg/L	7.25	7.18	7.68	7.45
$C_g$ effluent, mg/L				
Measured	0.59	0.56	0.48	0.28
Simulated	1.03	0.96	0.85	0.64
Simulation error, mg/L	0.44	0.40	0.37	0.36
Transfer efficiency ( $O_3TE$ ), %				
Measured	91.9	92.2	93.7	96.2
Simulated	85.8	86.6	88.9	91.4
Simulation error, %	6.1	5.6	4.8	4.8
$C_b$ effluent, mg/L				
Measured	0.18	0.12	0.091	0.055
Simulated	0.25	0.19	0.15	0.090
Simulation error, mg/L	0.07	0.07	0.059	0.035

Figure 3.6 indicates that applied ozone dose has to be greater than 1.2  $mgO_3/L$  water, to obtain a 0.1  $mg/L$  liquid-phase ozone concentration in the effluent. The real value

of applied ozone does should be greater than  $1.2\text{mgO}_3/\text{L}$  water because the plug-flow model does not describe the concentration at the bottom of the column well where the liquid exits. This result compares well with the observation of Roustan et al. (1987), who found a dose of  $1\text{ mgO}_3 /\text{L}$  water is required to obtain a liquid-phase ozone concentration of  $0.1\text{ mg/L}$ . The difference in the required ozone dose between these two studies is caused by the differences in water quality and temperature. Tap water used by Roustan et al. (1987) was cleaner than the reclaimed water used here, with TOC value of  $1.6\text{ mg/L}$ , and cooler, with a temperature of  $5^\circ\text{C}$ . Although the ozone reaction data was not provided by the author, there is no doubt that ozone decay is slower in their experiment.



**Fig. 3.6** Effect of variation of influent gas-phase ozone concentration on simulated liquid-phase concentration profile ( $T = 16\text{ }^{\circ}\text{C}$ ;  $Q_g = 8.5\text{ L/min}$ ;  $w = 1.1\text{ min}^{-1}$ ).

### 3.6 CONCLUSIONS

Ozone and oxygen mass-transfer rates were measured in tap water and reclaimed wastewater at different gas flow rates using the nonsteady-state method. The mass-transfer rates were found roughly proportional to gas flow rates. Through the studies of  $\psi$  and  $\alpha$ , the results suggest that ozone mass-transfer rates can be predicted by oxygen mass-transfer rates. The results also show that the contaminants in reclaimed wastewater do not appreciably reduce the mass-transfer rate.

A mathematical model was developed to describe transfer rates. The ozone decay reaction was included and accurately modeled as a pseudo first-order reaction between ozone and ozone demanding materials. The model and experimental results agreed well.

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4. MODELING VOC EMISSIONS IN THE HIGH PURITY OXYGEN  
ACTIVATED SLUDGE PROCESS

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and Michael K. Stenstrom, F. ASCE**

**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.

**KEYWORDS:** Activated sludge; aeration; high purity oxygen; mathematical modeling; oxygen transfer; volatile organic compounds; wastewater.

#### **4.1 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 (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 to 3 hrs for HPO-AS as compared to 4 to 8 hrs for conventional; Metcalf and Eddy, 2003), as compared to a conventional, uncovered air activated sludge 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 an HPO-AS process. The combination of gas saturation and low gas flow rate throughout reduces VOC emissions in an 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 volatile organic compounds (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.

## 4.2 MODEL DEVELOPMENT

The previously development 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), Clift (1980) and is similar to the IWA AS Model 3 (Gujer et al., 1999) for carbonaceous substrate removal. The differences between the IWA Model 3 and the Tzeng's model do not involve the gas transfer mass balances (Yuan et al., 1993).

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

$$\frac{dC_L}{dt} = \frac{Q_L}{V_L} (C_{L_0} - C_L) - K_L a_{VOC} (C_L - C_L^*) \quad (4.1)$$

$$\frac{dC_G}{dt} = \frac{Q_{G_0} C_{G_0} - Q_G C_G}{V_G} + K_L a_{VOC} (C_L - C_L^*) \frac{V_L}{V_G} \quad (4.2)$$

where

$$C_G^* = \text{gas-phase VOC equilibrium concentration, ML}^{-3}$$

$C_L^*$  = liquid-phase VOC equilibrium concentration,  $\text{ML}^{-3}$

$C_L$  = real-time liquid-phase VOC concentration,  $\text{ML}^{-3}$

$C_G$  = real-time gas-phase VOC concentration,  $\text{ML}^{-3}$

$C_{Lo}$  = influent liquid-phase VOC concentration,  $\text{ML}^{-3}$

$K_L$  = overall VOC liquid-phase mass transfer coefficient,  $\text{T}^{-1}$

$K_G$  = overall VOC gas-phase mass transfer coefficient,  $\text{T}^{-1}$

$a$  = specific volumetric area = area/volume

$Q_{Go}$  = inlet gas flow rate,  $\text{L}^3\text{T}^{-1}$

$C_{Go}$  = feed gas VOC concentration,  $\text{ML}^{-3}$

$Q_G$  = outlet gas flow rate,  $\text{L}^3\text{T}^{-1}$

$Q_L$  = wastewater flow rate,  $\text{L}^3\text{T}^{-1}$

$V_G$  = gas-phase volume,  $\text{L}^3$

$V_L$  = liquid-phase volume,  $\text{L}^3$

VOC = as subscript, indicates VOC mass transfer rates

The following development uses the Two-Resistance Theory for describing 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 an  $D^n$ , where  $n$  is usually in the range between 0.5-0.6. 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 semi-volatiles, such as naphthalene, with subsurface aeration systems. The ratio of liquid-phase to gas-phase resistance can be expressed as

$$\frac{R_L}{R_G} = H_c \frac{k_G}{k_L} \quad (4.3)$$

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,  $T^{-1}$

$k_L$  = liquid-film mass transfer coefficient,  $T^{-1}$

For VOCs, the 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:

$$H_c = \frac{K_L}{K_G} = \frac{C_G^*}{C_L^*} \quad (4.4)$$

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

$$C_G^* V_G + C_L^* V_L = C_G V_G + C_L V_L \quad (4.5)$$

From Equation 4.4,  $C_G^*$  equals the product of  $C_L^*$  and  $H_C$ , and Equation 4.5 can be rearranged as Equation 4.6.

$$C_L^* = \frac{C_G V_G + C_L V_L}{H_C V_G + V_L} \quad (4.6)$$

Using Equation 4.6 and appropriate  $K_L a_{\text{VOC}}$  values, Equations 4.1 and 4.2 can be used to dynamically estimate the concentration change in both gas- and liquid-phases. The  $K_L a_{\text{VOC}}$  values are usually determined by correlating the VOC stripping rates with a factor to the oxygen transfer rate, and the symbol  $\psi$  is used to denote this factor, when considering only the diffusivities. The improved approach including both film resistances, called Modified  $\psi$  Concept, uses the symbol  $\psi_M$ , which estimates the VOC stripping rate more accurately.

#### ***4.2.1 Modified $\Psi$ Concept***

The  $\psi_M$  was presented by Hsieh et al. (1993a, 1993b) for the estimation of VOC mass transfer rates. According to the Two-Resistance Theory,  $\psi_M$  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 resistance). Therefore, the following two equations are derived:

$$\psi_M = \left( \frac{D_{LVOC}}{D_{LO_2}} \right)^n \frac{R_L}{R_T} \quad (4.7)$$

and

$$K_L a_{VOC} = K_L a_{O_2} \cdot \psi_M \quad (4.8)$$

where

$D_{LVOC}$  = VOC liquid diffusivity;

$D_{LO_2}$  = oxygen liquid diffusivity;

$n$  = exponential coefficient, 0.5-0.6 for most VOCs;

$$R_T = \text{overall resistance} = \frac{1}{\frac{1}{R_L} + \frac{1}{R_G}}$$

The Wilke-Chang correlation was used for liquid diffusivities and the values are shown in Table 4.2.

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  $\psi_M$   $K_L a_{O_2}$  from Equation 4.8 (the  $\psi_M$  and  $K_L a_{O_2}$  experiments conducted by Hsieh et al. (1993a, 1993b), 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 activated sludge processes.

### **4.3 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 were used to simulate the performance of surface aeration and subsurface diffusion aeration on VOC emissions.

#### ***4.3.1 West Point Treatment Plant***

The model was first used to estimate emissions from a hypothetical plant, identical in design to the WPTP in Seattle, WA. Table 4.1 gives the design parameters for the WPTP. Ten VOCs were chosen for the simulation. Table 4.2 presents the properties of selected VOC species. Table 4.3 upper part 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 hours to achieve “periodic steady state,” meaning that the concentrations in 24 hours between 192 and 216 hours were identical to the concentrations between 216 and 240 hours. The  $\psi_M$  values were taken from Hsieh et al. (1993a, 1993b) experimental results 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  $\alpha$  factor, which accounts for the reduction in transfer due to contaminants such as surfactants (Stenstrom and Gilbert, 1981, ASCE 2006). The values of the alpha factor for the two aeration systems are different: 0.8 to 0.95 for surface aeration (Tzeng et al., 2003) and 0.4 to 0.5 for submerged turbines (Stenstrom et al., 1989). The value of alpha 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 alpha factor for a turbine aeration system varied from 0.6 to 0.8 for oxygen, and 0.75 to 1.1 for toluene, and 0.5 to 0.7, over a range of power densities from 20 to 350 W/m<sup>3</sup>, 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 kW/m<sup>3</sup> (2.17 to 1.16 hp/1000ft<sup>3</sup>), and for Sacramento it is 0.042 to 0.025 (1.60 to 0.96 hp/1000ft<sup>3</sup>). For simplicity, we have assumed the same alpha factors for oxygen and the VOCs.

**Table 4.1** HPO-AS Operational Parameters

Parameter	WPTP	SRWTP
Influent Flow Rate	607,066 to 986,000 m <sup>3</sup> /day diurnal variation	1,442,267 m <sup>3</sup> /day annual average
Primary Effluent BOD <sub>5</sub>	91 mg/L	175 mg/L
Liquid-Phase Volume	2,220m <sup>3</sup> /stage 4 stages X 6 trains	1,957 m <sup>3</sup> /stage 4 stages X 16 trains
Headspace Volume	355 m <sup>3</sup> /stage 4 stages X 6 trains	258 m <sup>3</sup> /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 hr <sup>-1</sup> at average	12.9, 9.81, 4.60 and 4.51 hr <sup>-1</sup> at average
Turbine Stage $\alpha K_L$ a's	-	6.98, 3.00, 2.88 and 2.98 hr <sup>-1</sup> at average
Turbine Effective Depths	-	1.38, 1.32, 1.32 and 1.32 for stages

**Table 4.2** Properties of Selected VOC Compounds

Compound	Symbol	$H_c$ <sup>1</sup>	$D_L$ <sup>2</sup> (cm/s $10^{-5}$ )
Carbon Tetrachloride	CCl <sub>4</sub>	1.122	0.92·10 <sup>5</sup>
Perchloroethylene	PCE	0.565	0.89·10 <sup>5</sup>
1,1,1-Trichloroethane	1,1,1-TCA	0.525	0.90·10 <sup>5</sup>
Trichloroethylene	TCE	0.252	0.96·10 <sup>5</sup>
Chloroform	CLF	0.160	1.01·10 <sup>5</sup>
Chlorobenzene	CBZ	0.146	0.86·10 <sup>5</sup>
1,3-Dichlorobenzene	1,3-DCB	0.124	0.78·10 <sup>5</sup>
1,4-Dichlorobenzene	1,4-DCB	0.110	0.76·10 <sup>5</sup>
1,2-Dichlorobenzene	1,2-DCB	0.087	0.78·10 <sup>5</sup>
Naphthalene	NAPH	0.038	0.72·10 <sup>5</sup>

<sup>1</sup> Henry's Law coefficient, dimensionless, adopted from Hsieh (1991)

<sup>2</sup> Diffusivity, (oxygen =  $2.11 \cdot 10^5$  cm/s)

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 4.3. A quick comparison between the upper and lower parts of Tables 4.3 shows that HPO-AS reduces 85% to 90% of VOC emissions compared to

air AS.

**Table 4.3** Comparison of VOC Emissions from the WPTP as an HPO Plant with a Hypothetical Surface Aeration Plant

Compound	$\Psi_M$ <sup>1</sup>	Influent <sup>2</sup> Conc.	Effluent <sup>3</sup>		%Stripped <sup>4</sup>	
			Conc.			
			Min	Max		
<b>HPO-AS Process</b>	CCl <sub>4</sub>	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
<b>Surface Aeration Air AS Process</b>	CCl <sub>4</sub>	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	

<sup>1</sup> adopted from Hsieh's (1991) experiment number S24 for HPO-AS Process, S29 for Air AS Process

<sup>2</sup> in units of µg/L

<sup>3</sup> the lowest and highest effluent VOC concentrations within one day, µg/L

<sup>4</sup> percent VOC stripped



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 has found  $\text{CHCl}_3$  does not adsorb appreciably in either surface or subsurface aeration systems, 1987). 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 & Eddy, 2002) and applied different values of maximum growth rates ( $\mu_m$ ,  $0.0001 \text{ hr}^{-1}$  to  $0.01 \text{ hr}^{-1}$ ), half saturation coefficients ( $K_s$ , 1.0 mg/L to 30.0 mg/L) and influent concentrations (1  $\mu\text{g/L}$  to 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 4.4 (results from  $\mu_m=0.0001 \text{ hr}^{-1}$  and  $K_s=1.0 \text{ mg/L}$ ) for HPO-AS and air AS.

**Table 4.4** Comparison of the Fates of VOCs in the WPTP as an HPO Plant with a Hypothetical Surface Aeration Plant

	Compound	Inf. Conc.	%Bio <sup>1</sup>	%Strip <sup>2</sup>	%Re <sup>3</sup>	Strp/Re <sup>4</sup>
<b>HPO-AS Process</b>	CCl <sub>4</sub>	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
<b>Surface Aeration Air AS Process</b>	CCl <sub>4</sub>	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

<sup>1</sup> percent VOC biodegraded      <sup>2</sup> percent VOC stripped

<sup>3</sup> percent VOC remaining in the liquid phase      <sup>4</sup> %stripped/%remaining

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 4.5 presents the fate of chloroform through an air AS process at different biodegradation levels by varying the maximum specific growth rate ( $\mu_m$  and Monod half-saturation coefficient  $K_{svoc}$ ) 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- and liquid-phases.

**Table 4.5** Fate of Chloroform through a Surface Aeration Air AS Process

$\mu_{\text{mVOC}}^1$	$K_{\text{SVOC}}^2$	%Bio	%Strp	%Re	Strp/Re
0	N.A.	0.0	90.4	9.6	9.4
0.0001	1000	7.1	83.9	9.0	9.4
0.001	1000	43.4	51.1	5.5	9.4
0.01	1000	88.5	10.4	1.1	9.3
0.0001	5000	1.5	89.0	9.5	9.4
0.001	5000	13.3	78.3	8.4	9.4
0.01	5000	60.5	35.7	3.8	9.4
0.0001	15000	0.5	89.9	9.6	9.4
0.001	15000	4.9	86.0	9.2	9.4
0.01	15000	33.8	59.8	6.4	9.4
0.0001	30000	0.3	90.1	9.6	9.4
0.001	30000	2.5	88.1	9.4	9.4
0.01	30000	20.4	72.0	7.7	9.4

<sup>1</sup> maximum growth rate on VOC, hr<sup>-1</sup>

<sup>2</sup> half saturation coefficient for Monod kinetics, µg/L

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, 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.

#### ***4.3.2 Sacramento Regional Wastewater Treatment Plant***

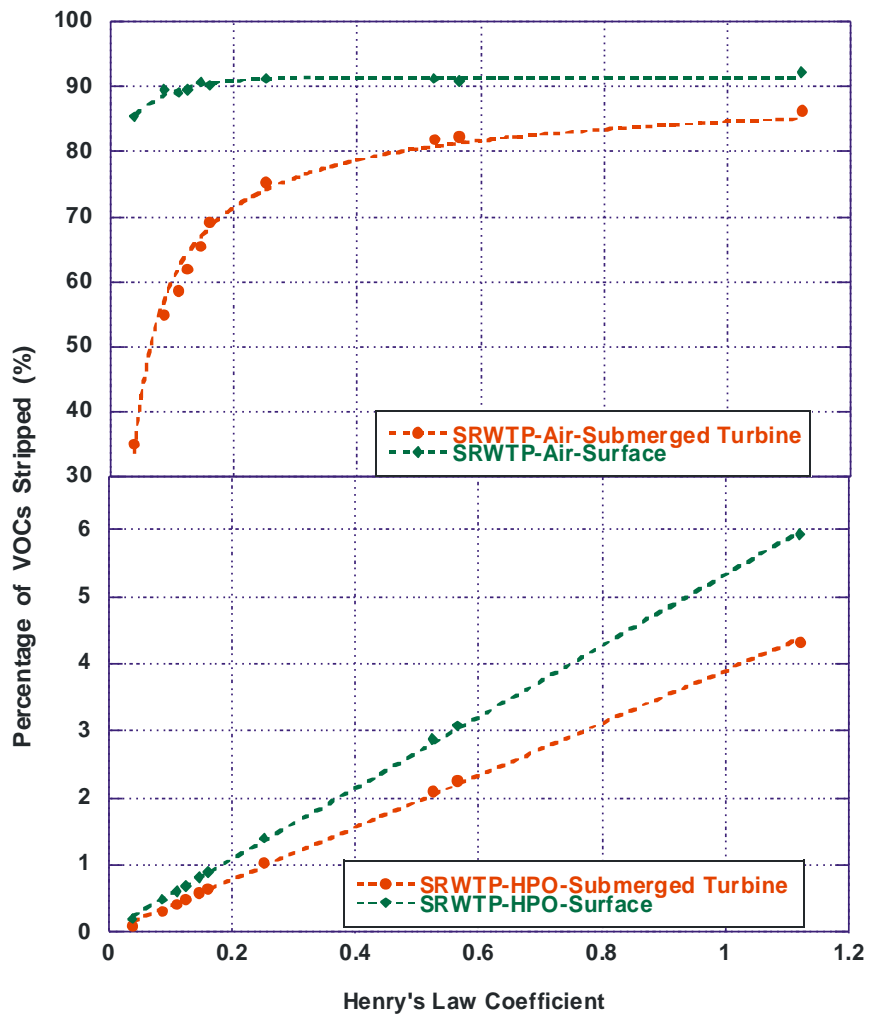
The SRWTP is an HPO-AS treatment plant utilizing a submerged turbine aeration system. The simulation considered both surface and submerged aeration systems. The results for 8 surface aeration trains and 8 submerged turbine trains will be discussed separately. Alpha factors used for existing subsurface aeration were not from expansion designs, instead, we used the values calibrated in Tzeng's early study (1992). Table 4.1 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 et al., 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  $\psi_M$  concept and the saturation parameter (Hsieh et al., 1993a, 1993b) 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 (373 MGD), 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 4.6 and 4.7 show the simulation results of SRWTP and an equivalent air AS process with small biodegradation rates, ( $\mu_m=0.0001 \text{ hr}^{-1}$  and  $K_s=1.0 \text{ mg/L}$ ). Comparing Figure 4.1, and Tables 4.6 and 4.7 shows that with the same biodegradation parameters, an 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 4.8 gives an example of constant  $Strp/Re$  ratios using PCE passing through both subsurface and surface aerations.



**Fig. 4.1** Simulated Results of VOC Emissions from SRWTP Surface and Submerged Turbine Comparison

**Table 4.6** Estimated VOC Fate through SRWTP HPO-AS Process

	<b>Compound</b>	<b>Inf. Conc.</b>	<b>%Bio</b>	<b>%Strip</b>	<b>%Re</b>	<b>Strp/Re</b>
<b>Submerged Turbine HPO-AS Process</b>	CCl <sub>4</sub>	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
<b>Surface Aeration HPO-AS Process</b>	CCl <sub>4</sub>	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 4.7** Estimated VOC Fate through SRWTP Air AS Process

	<b>Compound</b>	<b>Inf. Conc.</b>	<b>%Bio</b>	<b>%Strip</b>	<b>%Re</b>	<b>Strp/Re</b>
<b>Submerged Turbine Air AS Process</b>	CCl <sub>4</sub>	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
<b>Surface Aeration Air AS Process</b>	CCl <sub>4</sub>	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	

**Table 4.8** Fate of PCE through SRWTP Air AS Process

	$\mu_{mVOC}$	$K_{S_{VOC}}$	%Bio	%Strp	%Re	Strp/Re
<b>Submerged Turbine Air AS Process</b>	0	N.A.	0.0	86.9	13.1	6.6
	0.0001	1000	5.2	82.4	12.4	6.6
	0.001	1000	35.6	56.0	8.4	6.6
	0.01	1000	84.6	13.3	2.0	6.6
	0.0001	5000	1.1	86.0	12.9	6.6
	0.001	5000	9.9	78.2	11.8	6.6
	0.01	5000	52.5	41.3	6.2	6.6
	0.0001	15000	0.4	86.6	13.0	6.6
	0.001	15000	3.5	83.8	12.6	6.6
	0.01	15000	26.9	63.5	9.6	6.6
	0.0001	30000	0.2	86.8	13.1	6.6
	0.001	30000	1.8	85.3	12.8	6.6
	0.01	30000	15.5	73.4	11.0	6.6
<b>Surface Aeration Air AS Process</b>	0	N.A.	0.0	93.8	6.2	15.1
	0.0001	1000	3.0	90.9	6.0	15.1
	0.001	1000	23.8	71.5	4.8	15.0
	0.01	1000	75.8	22.7	1.5	15.1
	0.0001	5000	0.6	93.2	6.2	15.1
	0.001	5000	5.9	88.3	5.8	15.1
	0.01	5000	38.5	57.7	3.8	15.1
	0.0001	15000	0.2	93.6	6.2	15.1
	0.001	15000	2.0	91.9	6.1	15.1
	0.01	15000	17.2	77.6	5.1	15.1
	0.0001	30000	0.1	93.7	6.2	15.1
	0.001	30000	1.0	92.8	6.2	15.1
	0.01	30000	9.4	84.9	5.6	15.1

#### 4.4 DISCUSSION AND CONCLUSIONS

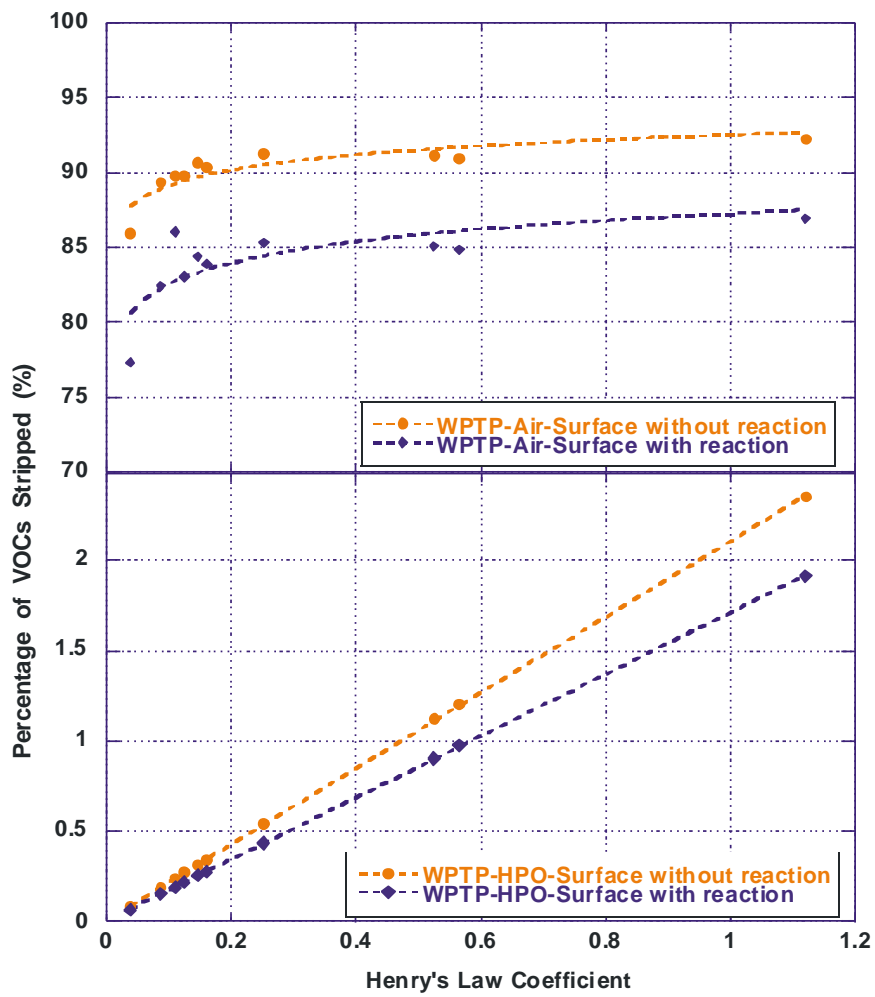
These results suggest that covered aeration tanks (e.g. HPO-AS) can be one of the most effective solutions to reduce VOC emissions from wastewater treatment plants. If the VOC species is biodegradable, a larger portion of the VOCs may be degraded before being stripped or discharged in an HPO process 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 (secondary clarifiers, etc) or be discharged to receiving waters.

A comparison of corresponding tables between SRWTP HPO subsurface and surface aeration systems (Figure 4.1 bottom and Table 4.6) 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 4.3 lower part, Figure 4.1). This is because low volatile organic compounds 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 Figure 4.2. For a hypothetical submerged turbine air AS process the emissions were predicted to be 42% to 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.



**Fig. 4.2** Simulated Results of VOC Emissions from WTP With and Without Reaction Comparison

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 activated sludge process are shown in Table 4.7. 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 to 5.9% maximum). This paper provides quantitative evidence of reduced air emissions with HPO-AS as compared to other activated sludge processes and aeration systems.

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## 5. CONCLUSIONS

This dissertation has examined three interrelated aspects of gas transfer in water and wastewater treatment. The first aspect is improved methodology for calculating oxygen mass transfer rates, through more controlled experimental conditions, but more importantly on the way the experimental data are analyzed. The improved methodology enables greater use of oxygen transfer rates to be used as tracers to predict other aspects of treatment plant performance and operation, such as ozone absorption and stripping of VOCs. The later two sections of the dissertations show how this can be done for ozonation of reclaimed waters and to quantify the differences in stripping rates between high purity oxygen and air activated sludge processes.

### 5.1 IMPROVED METHODOLOGY

The new methodology has eliminated many of the experimental and analysis errors previously encountered in clean water testing. The Standard has created standard nomenclature such as SOTR ( $\text{lbO}_2/\text{hr}$  or  $\text{kg O}_2/\text{hr}$ ), and efficiencies, such as Standard Oxygen Transfer Efficiency (SOTE, %), and Standard Aeration Efficiency (SAE,  $\text{lbO}_2/\text{hp-hr}$  or  $\text{kg O}_2/\text{kW-hr}$ ), and provided conversion methodology for translating to clean water to process water conditions. One of its most important contributions is the

avoidance of systemic errors by eliminating the need for a priori estimates of  $C_{\infty}^*$ . The original objections to the Standard, that it was difficult to understand and that a mainframe computer was required, are no longer valid.

This dissertation has shown how specific aspects of data handling, such as using the non-linear least squares, to calculate the product of  $K_La$  and  $C_{\infty}^*$  at each sampling location minimizes error because of the correlation of the two parameters. The parameter estimation method compensates for gas side (i.e., within bubbles) depletion because the value of  $K_La$  is biased low and  $C_{\infty}^*$  is biased high. Previous investigators (Brown and Baillod, 1982) showed this was true at low transfer rates, but this work was extended to the higher transfer rates typically used at treatment plants in the Chapter 2.

## **5.2 OZONE ABSORPTION**

Previous work, using the dependence of overall transfer rates on the combination of liquid and gas-side film resistances, along molecular diffusivities was used to predict VOC stripping rates. This technique has been extended to ozone mass-transfer rates in reclaimed wastewaters. Ozone and oxygen mass-transfer rates measured in tap water and reclaimed wastewater over a range of gas flow rates were analyzed using the nonsteady-state method. A mathematical model was developed to describe transfer rates and the ozone decay reaction was included and accurately modeled as a pseudo

first-order reaction between ozone and ozone demanding material. The mass-transfer rates were accurately estimated and adjusted using the molecular diffusivities. The average value of  $\Psi$  was 0.86 for tap water and 0.88 for reclaimed water. The rates were approximately proportional to gas flow rate, as expected. The depression of transfer rates due to the presence of contaminants in reclaimed wastewater did not substantially reduce the mass-transfer rate, as in wastewaters. The ratio of the transfer rates, commonly called the alpha factor, was 0.85.

### **5.3 VOC STRIPPING**

The modeling and analysis technique used in the ozone transfer analysis was also applied to VOC stripping in wastewater treatment plants. The 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 is used.

A comparison of corresponding tables between SRWTP HPO subsurface and surface aeration systems reveals that surface aeration emits slightly greater amounts of high volatility organic compounds. The phenomenon might result from the fully saturated headspace and gas bubbles which reduce the emissions in subsurface systems. The

emissions of less volatile organic compounds are much lower from a subsurface system than those from a surface aeration in an air AS process. This is because low volatility organic compounds quickly saturate the rising bubble column. The results indicate that submerged turbines are a better solution to reduce emissions of organic compounds with low volatilities.

A constant ratio between percent stripped and percent remaining in the discharged water for a specific VOC was found for a given hydrodynamic condition in both surface and subsurface uncovered aeration 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 can be difficult and expensive, especially for a surface aeration system. 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 rate driving force and the liquid-phase VOC concentration in open systems.

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 activated sludge process are shown in Table 4.7. 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 to 5.9% maximum). This dissertation provides quantitative evidence of reduced air emissions with HPO-AS as compared to other activated sludge processes and aeration systems.

## 6. APPENDIX

### WEFTEC® 2006

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#### **Theory to Practice: Oxygen Transfer and the New ASCE Standard**

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#### **ABSTRACT**

Oxygen transfer is an important part of wastewater treatment and accounts for as much as 60% of the energy consumption for the activated sludge process. Prior to 1984, no standard method for quantifying oxygen transfer existed, which created problems in the design and warranties for treatment plants. The ASCE Standard for the Measurement of Oxygen Transfer in Clean Water and the ASCE Standard Guidelines for In-Process Oxygen Transfer Testing have found widespread application and have reduced the variability in new designs and allowed operators and engineers to access the process operation of existing treatment plants. A new clean water standard is in press as of this writing and the in-process Guidelines are undergoing updating for reissue. This paper illustrates the key concepts of both the Standard and the Guidelines and shows why they are important and reduced the variability of testing. The paper also highlights key new areas of the revised clean water Standard, which includes an optional correction for test water total dissolved solids concentration, and applications to loop (ditch) activated sludge process and the high purity oxygen activated sludge process.

#### **KEYWORDS**

Activated sludge, aeration, ASCE, off-gas, oxygen transfer, standard

#### **INTRODUCTION**

In 1977, under the sponsorship of the US EPA, a Committee organized by ASCE began the study



of methods to quantify oxygen transfer rates in wastewater treatment. The Committee met as a group in Asilomar, California in 1978 (US EPA, 1979) and proposed consensus methods for establishing uniform and repeatable test conditions, estimating clean water parameters (mass transfer coefficient or  $K_LA$ , and equilibrium oxygen concentration  $C_\infty^*$ ) from reaeration data, and translating clean water rates to process conditions. The resulting methods were evaluated over next several years by the committee members, consultants and manufactures and refined through the collective experience of the group. The final result was the 1984 version of the *ASCE Standard for the Measurement of Oxygen Transfer in Clean Water*. The Standard was subsequently improved, updated and republished in 1991 and will be published again in 2006.

Following the development of the Clean Water Standard, it was realized that the next most important gap in knowledge was the characterization of process water transfer rates. The Standard provided ways of calculating expected process water rates from clean water rates, by adjusting for standard conditions, such as barometric pressure, temperature and the effects of the contaminants in the process water ( $\alpha$  and  $\beta$  factors for  $K_LA$  and  $C_\infty^*$ , respectively), but there were no consensus-based process water measurement procedures, and a lack of knowledge of the conditions that affect process water testing. The US EPA and ASCE funded a new effort to develop process water testing methods, which were published by the US EPA in 1989 and later adopted into a standard guideline (ASCE, 1997).

Several major changes and improvements were realized over the process of these projects. The first was in the methodology of estimating  $K_LA$  from the reaeration data. Prior to the Standard, the log deficit method was used which required *a priori* knowledge of  $C_\infty^*$ . Several methods for specifying  $C_\infty^*$  existed, but all had pitfalls, allowing the introduction of errors which might bias the overall transfer rate by  $\pm 15$  to 20% (Boyle, *et al.*, 1974). The Standard uses a non-linear regression technique which avoids the use of *a priori* methods and eliminates the possibility of bias. A second major change was the realization that  $\alpha$  factors, which prior to 1980 had almost always been routinely specified as 0.8, were dependent not only on just the wastewater type, but also on the aeration devices (i.e., fine pore diffusers have lower  $\alpha$  factors than surface aerators, Stenstrom and Gilbert, 1981) and on the conditions of the activated sludge mixed liquor (i.e., processes operating with longer mean cell retention times (MCRT) have higher  $\alpha$  factors than processes operating at low MCRT, Rosso, *et al.*, 2005). A series of other improvements were realized including the impact of cobalt as an interference in the Winkler dissolved oxygen (DO) measurement procedure, the impact of the lag in DO probes on estimates of  $K_LA$  (Philichi and Stenstrom, 1989). Finally, a new testing methodology, developed as part of the second project, called off-gas analysis was developed and perfected (Redmon, *et al.*, 1983), and this method, in the ten years following its development, has become the method of choice for measuring oxygen transfer in subsurface aeration systems for conventional processes as well as occasional use in

novel process such as biological aerated filters (Newman, *et al.*, 2005)

This paper describes some of the key concepts used in developing the Clean Water Standard and illustrates why they are still important. Several new aspects of the new Standard are described. Finally, in a similar fashion, several key concepts used in process water testing are also described.

## CLEAN WATER TESTING

The basic theory used in the Standard is the well-known “Two-film Theory” from Lewis and Whitman (1924), which states that transfer rate can be expressed in terms of an overall transfer coefficient and resistances on either side of the interface. With sparingly soluble gases such as oxygen, the resistance is primarily in the liquid film and the gas film can be ignored. This allows the transfer to be expressed as follows:

$$\frac{dC}{dt} = K_L a (C_\infty^* - C) \quad (1)$$

where  $K_L a$  = volumetric mass transfer coefficient (1/T),

$C_\infty^*$  = average DO concentration attained at infinite time (mg/L) and

$C$  = effective average DO concentration in the liquid phase.

The integrated form becomes:

$$\ln \frac{C_\infty^* - C_0}{C_\infty^* - C} = K_L a (t - t_0) \quad (2)$$

$$\text{or } C = C_\infty^* - (C_\infty^* - C_0) \cdot \exp[K_L a \cdot (t - t_0)] \quad (3)$$

where  $C_0$  = initial DO concentration at  $t = t_0$

Equation (2) is the log deficit form of the equation and equation (3) is the exponential form. The previous cited log deficit forms for parameter estimation use equation (2) while the non-linear regression forms associated with the Standard use equation (3).

Both approaches use a non-steady state clean water test to determine the oxygen transfer capacity of aeration equipment, which is widely applicable to a variety of aeration including both surface aerators and subsurface diffusers, such as coarse bubble tubes, perforated pipes, static tubes, fine pore diffusers (discs, domes, plates, strips and panels), submerged turbines and jet aerators. Data collection proceeds by taking DO measurements over time, after stripping the test water of DO. The final result of the test is expressed as the Standard Oxygen Transfer Rate (SOTR), a hypothetical mass of oxygen transferred per unit of time in tap water at zero dissolved oxygen concentration, water temperature of 20°C and barometric pressure of 1 atm under specified gas

rate and power conditions. Generally a test proceeds as follows:

1. The test tank (cleaned by washing with tap water) is filled with tap water to the desired volume.
2. The DO is reduced to zero by either stripping with nitrogen gas or oxidizing with sodium sulfite catalyzed with cobalt. The sodium sulfite is added in amounts usually equal to 125 or 175% of the stoichiometric requirement and cobalt chloride is added to produce a concentration of approximately 0.05 mg/L as cobaltous ion.
3. The aeration device is normally operating during the period of deaeration and reaeration. The DO concentration can be observed to plunge to zero and remain at zero for a few minutes depending on the specifics of the test. As DO returns to the liquid, the concentration is recorded or observed at appropriate intervals. The test is terminated when the DO equals to 98% of the expected value of  $C_{\infty}^*$ .

The test is relatively straightforward and the Standard describes both required and recommended conditions to create accurate and precise results. It should be consulted for the detailed procedure, but issues such as the way to add sodium sulfite, locate DO sampling points, methods for calculating flow rates and power etc. are all described.

The general form of the reaeration test was used prior to the Standard, and even though the theory of reaeration is unequivocal, the results of the test were affected by the techniques used to analyze the test data. Modeling and interpretation of the resulting data are critical for the characterization of the aeration system and, especially, for performance acceptance tests. The method for estimating the parameter used in equations (2) or (3) may influence the final results by  $\pm 15$  to 20%. In order to avoid bias, it is important for consultants and manufacturers to use the same procedure.

The ASCE Method, which has also been called the Nonlinear Regression Method, is based on nonlinear regression of equation (2). A variety of non-linear regression methods can be used and produce identical results when the methods converge (Stenstrom *et al.*, 1981) The best estimates of the parameters,  $K_L a$ ,  $C_{\infty}^*$ ,  $C_0$  are selected as the values that minimize the residual sum of squares between equation (3) and the DO-versus-time data. The residual is the difference in concentration between measured DO value at a given time and the DO value predicted by equation (3) at the same time. The non-linear regression technique requires a computer or programmable calculator to estimate the parameters and for this reason was not popular prior to the wide-spread use of personal computers. Equation (2) was more popular because it could be linearized and  $K_L a$  could be estimated by drawing a straight line on graph paper. Equation (2)

can be rearranged when  $t_0 = 0$  as follows:

$$\ln(C_{\infty}^* - C) = \ln(C_{\infty}^* - C_0) - K_L a t \quad (4)$$

The problem is how to estimate  $C_{\infty}^*$ . There were several methods, called *a priori* methods, which used knowledge about the aeration system. For submerged aeration, the hydrostatic pressure of the water column increases the gas pressure inside bubbles, which increases the value of  $C_{\infty}^*$ . Therefore the value of  $C_{\infty}^*$  becomes a function of tank depth and transfer efficiency.

Simplistic models were used for  $C_{\infty}^*$  and the symbol  $C_{st}^*$  will be used to represent the parameter in equation (4) when it is derived from an *a priori* model, which includes surface saturation, mid-depth saturation, bottom saturation, and mid-depth corrected saturation.

The surface saturation model is appropriate for surface aerators and assumes that all the gas transfer takes place at the surface. Hence the value of  $C_{st}^*$  is equal to the handbook value of DO saturation, or  $C_s$ . This assumption is generally true for surface aerators, although surface aerators, especially at high power per unit volume ( $> 1$  hp/1000 ft<sup>3</sup>) may entrain bubbles, which flow around the tank and experience hydrostatic pressure, increasing the value of  $C_{st}^*$ .

In submerged aeration, oxygen transfer occurs throughout the tank volume and  $C_{st}^*$  will vary with depth because of progressive decreases in both hydrostatic pressure and oxygen mole fraction as the bubbles move upward. Equation (5) has been used to estimate  $C_{st}^*$  and accounts for the changes in hydrostatic pressure.

$$C_{st}^* = \frac{\int_0^{z_d} hY(P_a + rz)dz}{z_d} \quad (5)$$

where  $z_d$  = aerator submergence depth, assumed to be equal to liquid height above the aerator

$h$  (m)

$P_a$  = atmospheric pressure (atm)

$H$  = Henry's law coefficient

$Y$  = mole fraction of oxygen in gas phase (0.2095)

$r$  = weight density of water

When  $z = \frac{z_d}{2} = \frac{h}{2}$ , the mid-depth model is defined, as follows:

$$C_{st}^* = C_s \left[ \frac{P_0 + CF \left( \frac{h}{2} \right)}{P_0} \right] \quad (6)$$

where  $P_0$  = Atmospheric pressure @the surface (atm or psi)

CF = water weight density and units conversion factor. Equal to 0.09664 when using atm and meters or 0.433 when using when using psi and feet.

Similarly, when  $z = h$ , the Bottom Saturation Model is obtained. This model assumes that the effective oxygen transfer occurs at the tank bottom. Therefore, the effective saturation concentration is calculated as follows:

$$C_{st}^* = C_s \left[ \frac{P_0 + CF(h)}{P_0} \right] \quad (7)$$

Other methods for estimating  $C_{st}^*$  have been used but all in some way use equations such as (6) and (7). An alternative method is to actually measure  $C_{st}^*$ . This was rarely done because of the time penalty associated with waiting so long for a test to complete. Generally it is necessary to conduct a test to  $5/K_LA$  or  $6/K_LA$  units of time to obtain an accurate ( $\pm 1\%$ ) estimate of  $C_{st}^*$ . It was common practice prior to the Standard to conduct a reaeration test long enough to reach only 70 to 90% of  $C_\infty^*$  (Boyle, et al, 1974), which requires only  $1/K_LA$  or  $2/K_LA$  units of time, or roughly 30% of the time for a more accurate test. The burden of measuring  $C_{st}^*$  is especially onerous for replicate testing.

## COMPARISON OF METHODS

This section shows the differences among the various methods and how they impact to overall estimate of transfer efficiency. Two example data sets were selected, one from a surface aeration test and the second from a diffused aeration system operating at very low air flux (air flow per unit area of tank bottom). Three estimates of  $C_{st}^*$  are demonstrated using the log deficit method as well as the ASCE method (marked as best-fit).

Figure 1 shows the reaeration data, plotted to conform to equation (4). The left panel represents the subsurface aeration system and the right panel shows the surface aerator. The curved lines are

indicative of poor fit. For the diffused aeration system on the left panel, both bottom saturation and surface saturation models show curvature beginning at about 80% of saturation. The mid-depth model is close to but not equal to the best fit model. The right panel shows similar curvature but for mid-depth and bottom saturation. The mid-depth model and the best fit provide similar results.

Figure 2 shows the results of these errors on the overall mass transfer rate, called the Standard Oxygen Transfer Rate (SOTR), when specified at standard conditions. The left vertical axis shows the ratio of the transfer rate obtained using the *a priori* models to the best fit. In the case of the subsurface system, a 20% bias of greater transfer (defined as positive) is obtained if a surface saturation model is used, and a 5% negative bias is obtained if the bottom saturation model is used. For the surface aerator (right panel) there is 10 to 12 % negative bias when the mid-depth and bottom saturation models are used. The best fit and most correct *a priori* models (mid depth for subsurface, surface for surface) differ by approximately 2 to 5%. The best fit model selects the correct value of  $C_{\infty}^*$  with based upon the reaeration data alone.

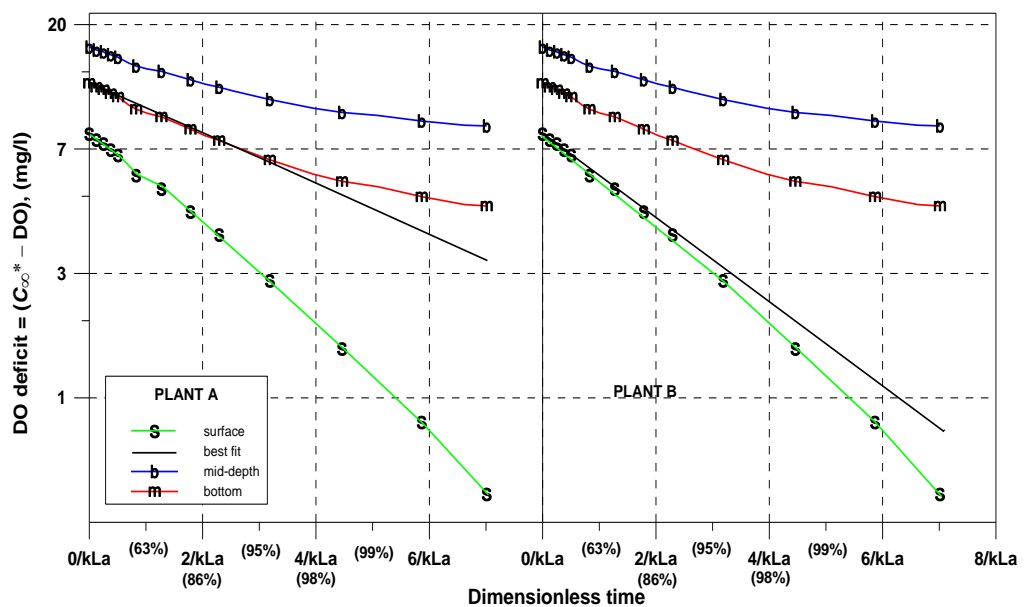


Figure 1. Reaeration Data, Plotted to Conform to the Log Deficit Method of Parameter Estimation

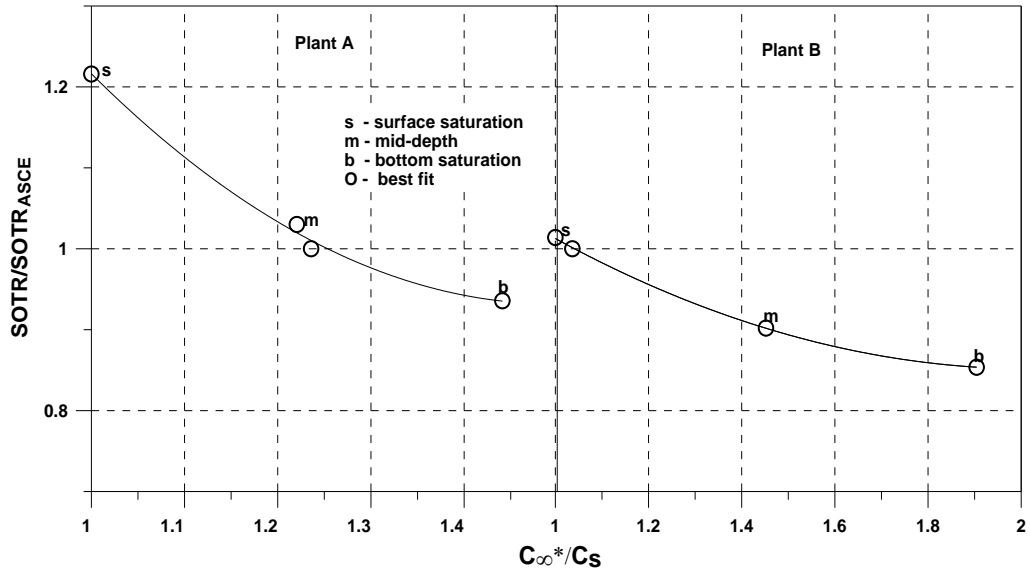


Figure 2. Change in Predicted SOTR as a Function of Equilibrium DO Concentration

The extreme limits of the bias (+22% and -12%) are large by today's methods for specifying aerators. Bids are won and lost by as little as 2% difference in transfer rates. The most troublesome part of the results shown in Figures 1 and 2 is the inability to detect a bias, if the analysis shown in Figure 1 is conducted to only 80%. The curvature of the line is not obvious until the test is conducted to 90% or more of saturation. Therefore it was possible to use the wrong *a priori* model, bias the final results and not know that an error had been made.

To prevent this type of error it is necessary to continue the test until the DO approaches saturation. Unfortunately, this can have an unexpected negative impact on test accuracy and precision. This occurs because of error transformation. When using the log deficit method (equation 4), the residuals are not actual errors in DO concentration, but errors in the log of DO concentration. Taking the logarithm of the error transforms it. Small values of error are made larger while large errors are reduced in size. Therefore, minimizing the log of the residuals does not minimize the difference in the actual residuals. All log deficit methods minimize the log of the error while the ASCE method minimizes the actual error.

A simple example is useful. Suppose the value of  $C_{st}^*$  is 10 mg/L and the error in DO measurement is  $\pm 0.1$  mg/L. At 1.0 mg/L DO concentration, the error in log deficit will be difference between  $\log |10-1.1|$  or  $\log |10-0.9|$  and  $\log |10-1.0|$ , which is  $\pm 0.004$ . At 96% of  $C_{\infty}^*$ , near the end of the test, the error will be the difference in  $\log |10-9.7|$  or  $\log |10-9.5|$  and  $\log |10-9.6|$ , which is 0.09 or -0.12. The relative contribution of the same error in DO measurement is 24 to 31 times greater at the end of the test than at the beginning of the test. The transformed error structure weights measurements at the conclusion of the test more heavily than at the beginning. Also, if the DO measurement error is higher, it may be possible to have undefined error due to a

negative deficit. The error transformation is one possible reason for the former practice of terminating reaeration tests early (Boyle, *et al.*, 1974). The two types of errors, non-uniform residuals and bias due to the incorrect value of  $C_{st}^*$ , require mutually exclusive modifications to the data analysis methodology. The best fit method has neither problem. The error structure is not transformed and it is possible to conduct the test to arbitrarily close to  $C_{\infty}^*$ .

Another difference between methods is the correlation of random error. In fitting equation (3) to experimental data, small, random errors in DO measurement create inversely correlated errors in the parameters estimates for  $K_LA$  and  $C_{\infty}^*$  (an error in DO measurement is compensated by a small increase in the estimate of  $C_{\infty}^*$  and a small decrease in the estimate of  $K_LA$ , *or vice-versa*). When the SOTR is calculated, the estimates of  $K_LA$  and  $C_{\infty}^*$  are multiplied, which partially cancels the net error in SOTR. For this reason, the Standard requires that the estimates of  $K_LA$  and  $C_{\infty}^*$  from each measuring point or probe be multiplied to obtain the SOTR and the SOTR from each measuring point be averaged to obtain the overall SOTR. This improvement due to negative correlation in the errors associated with parameters does not occur in the log deficit procedures.

## **GAS PHASE OXYGEN DEPLETION**

A criticism of the non-steady state reaeration test (regardless of data analysis methods) is the effect of oxygen depletion in the rising bubbles. As the bubbles rise, oxygen is absorbed by the liquid, reducing the oxygen mole fraction in the bubbles. Also, nitrogen and carbon dioxide is stripped from the liquid which further reduces the oxygen partial pressure. The loss of oxygen is greatest in the early part of the reaeration test, where the deficit, and therefore transfer rate, is greatest.

Figure 3 shows this phenomenon for a typical reaeration test. The test was performed according to the ASCE Standard, except that the off-gas from the surface of the tank was collected in a hood and analyzed for oxygen with a Teledyne fuel cell analyzer (Model 320, Teledyne, City of Industry, CA).

The oxygen in the off-gas is depleted in the early part of the test and then returns to 0.2095 mole fraction at the end of the test. The effect of this deficit on parameter estimation and subsequent use of the data for steady-state design calculations was examined by Bailod (1979). He noted that the effect of gas side depletion on parameter estimation was to reduce the estimate of  $K_LA$  and increase the estimate of  $C_{\infty}^*$ . He formulated a conversion equation between “observed”  $K_LA$  and



$C_{\infty}^*$  and “true”  $K_LA$  and  $C_{\infty}^*$  by modeling oxygen transfer in a column, and concluded that the errors in observed  $K_LA$  and  $C_{\infty}^*$  canceled for depths below approximately 30 ft, depending on oxygen transfer rate. In the early discussion of the Standard, it was proposed that the true  $K_LA$  be reported as  $K_LA'$ . In later discussions it was decided not to introduce the concept of true and apparent  $K_LAs$  since the effect was not significant, or even measurable in most cases, for aeration systems used in wastewater treatment.

For this reason, it is not necessary to adjust the value of  $C_{\infty}^*$  for process conditions due to gas phase bubble depletion. In rare cases, such as fermentation systems, or systems using fine pore aeration with pure oxygen, it may be necessary to compensate for gas phase oxygen depletion.

### CONCLUDING REMARKS ON CLEAN WATER TESTING

The ASCE Standard is more than 20 years old and its third revision will soon be published. It has eliminated many of the experimental and data analysis errors previously encountered in clean water testing. The Standard has defined terms to define transfer, such as SOTR (lbO<sub>2</sub>/hr or kg O<sub>2</sub>/hr), Standard Oxygen Transfer Efficiency (SOTE, %), and Standard Aeration Efficiency (SAE, lbO<sub>2</sub>/hp-hr or kg O<sub>2</sub>/kW-hr), and provided conversion methodology for translating these to process conditions. One of its most important contributions is the avoidance of systemic errors by eliminating the need for *a priori* estimates of  $C_{\infty}^*$ . The original objections to the Standard, that it was difficult to understand and that a computer was required, are no longer valid.

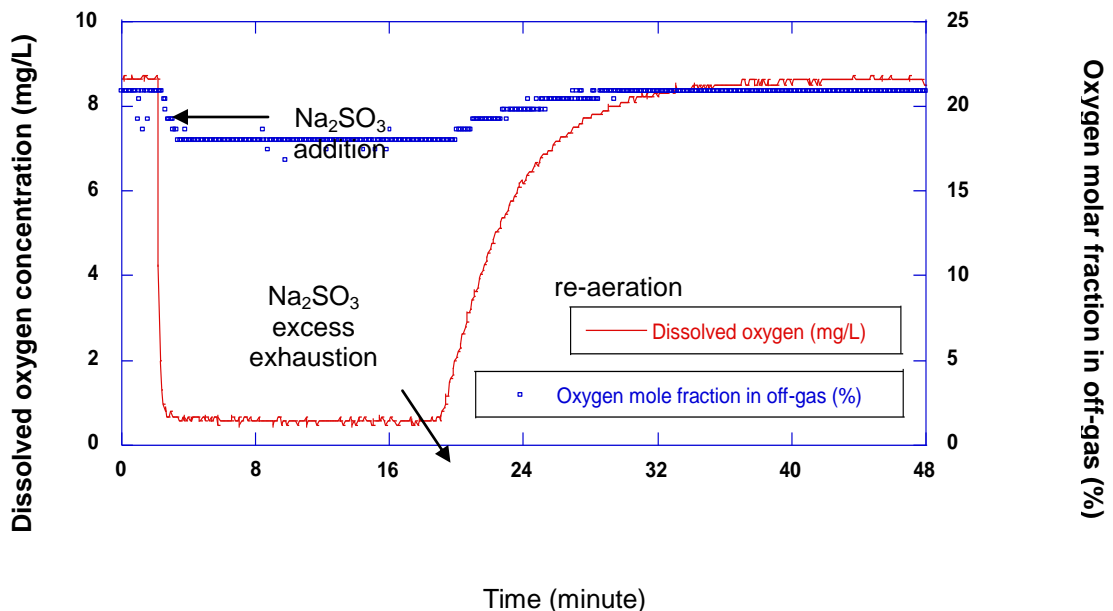


Figure 3. DO Concentration and Oxygen Mole Fraction in the Off-gas During a Clean Water Reaeration Test.

The new release of the Standard contains several important additions, in addition to many small improvements:

1. The Standard now provides specific recommendations for loop reactors (i.e., oxidation ditches) and cites case studies showing how the Standard has been successfully applied to full scale, field clean water tests (Boyle, *et al.* , 1989).
2. The Standard provides a method for estimating oxygen transfer rates for the high purity oxygen activated sludge (HPO-AS) process, using clean water test results in air and the gas phase purities observed or designed for the HPO-AS process.
3. A correction factor to total dissolved solids (TDS) is also recommended. The Standard still requires the TDS of the tap water to be less than 2,000 mg/L, but now provides an empirical correlation to adjust the results to 1,000 mg/L TDS. This is a recommendation in the new Standard, and if supported by a consensus of the users, can become mandatory in the next version of the Standard.
4. The requirement for adding sodium sulfite in dissolved form has been relaxed and can be added as a powder for specific circumstances.
5. A pure oxygen method, which avoids deaeration using nitrogen gas or sodium sulfite is offered as a trial method. The Committee hopes that those using the pure oxygen method can report their results in order to formalize the method for future releases of the Standard.

## **PROCESS WATER TESTING**

The Standards Committee published in-process water testing Standard Guidelines in 1997 (ASCE). These Guidelines codified testing procedures developed or refined by Committee members, manufacturers and consultants, during the proceeding 15 years, which were largely made possible by US EPA and ASCE funding. The Guidelines are currently under review and will undergo improvement to be republished over the next two years.

The Guidelines recommend three types of in-process water testing methods: 1) the non-steady method, using pure oxygen or hydrogen peroxide, for surface or diffused aeration systems; 2) off-gas analysis for diffused aeration systems, and 3) the tracer racer method for both surface and diffused aeration systems. It also describes but does not recommend two other methods, including methods based upon ex-situ oxygen uptake rate measurements and liquid-phase mass balances.

Methods based upon ex-situ oxygen uptake rate measurements, usually called the steady-state method, and using a BOD bottle for uptake measurement, have severe limitations on applicability because of the inability to create conditions in a sample bottle that properly reflect conditions in an aeration basin. The inability to measure an accurate oxygen uptake rate creates artificially low or high oxygen transfer estimates, which have sometimes been explained as biologically enhanced

transfer (Albertson and DiGregorio, 1975). The problems and a history of the errors introduced by ex-situ measurements have been discussed in detail by Mueller and Stensel (1990), who concluded that there was no evidence for biologically enhanced oxygen transfer rates in the activated sludge process. In-situ oxygen uptake measurements, such as those taken by process respirometers, have not been extensively used for in-process testing, and there is little or no long term experience in this use.

The major advance described by the Standard Guidelines is the off-gas analysis method, which was developed by Redmon et al (1983) under US EPA and ASCE sponsorship. The method uses an oxygen gas sensor to measure the oxygen mole fraction in the off-gas. By removing the carbon dioxide and water vapor from the off-gas, and assuming no change in nitrogen fraction, Redmon et al (1983) showed that the OTE could be calculated directly from the mole fraction measurements, and did not rely on volumetric gas flow rate. This technique improved on the methods used previously by a number of investigators, including Sawyer and Nichols (1939), Hover et. al. (1954), Pauling et al (1968), Prit and Callow (1958), Downing (1960), Conway and Kumke (1966) and Leary *et al.* (1968).

#### **OFF-GAS ANALYSIS**

Figure 4 shows a schematic of a set-up to perform off-gas testing. A portable hood is floated on the liquid surface and captures the gas bubbles that reach the surface. The gas flows through an analyzer that measures total gas flow and the oxygen mole fraction of a small slip stream of the gas. Even though the total gas flow is not needed for OTE measurement, it is desirable to measure it, which is usually done by withdrawing a measured flow that precisely balances the pressure under the hood.

The need to measure gas flow rate is to create a flow weighted average transfer efficiency over the entire aeration tank. This is required not only to estimate transfer for tapered aeration systems, but also when there is uneven air flow distribution due to fouled or damaged diffusers.

The hood dimensions are important when performing off-gas analysis in order to sample a representative area of the tank. For fine pore aeration systems, such as discs or domes, the spacing among diffusers may be less than several feet, but for coarse bubble diffusers or tanks that use diffusers to create strong mixing currents (i.e., spiral roll, cross roll), diffusers may be located more than 10 feet apart. Each portion of the tank area must be sampled representative to the entire area, so hood positions must include areas of low air flux (air flow per unit area of tank surface) and high air flux. To reduce the number of separate analysis, a larger hood is used to integrate over high and low flux areas of the tank. Hoods that are 10 feet by 2 feet or 8 feet by 4 feet in dimensions are common. In extreme cases, it is possible to construct a hood to cover an entire tank (Boyle, *et al.*, 1989).

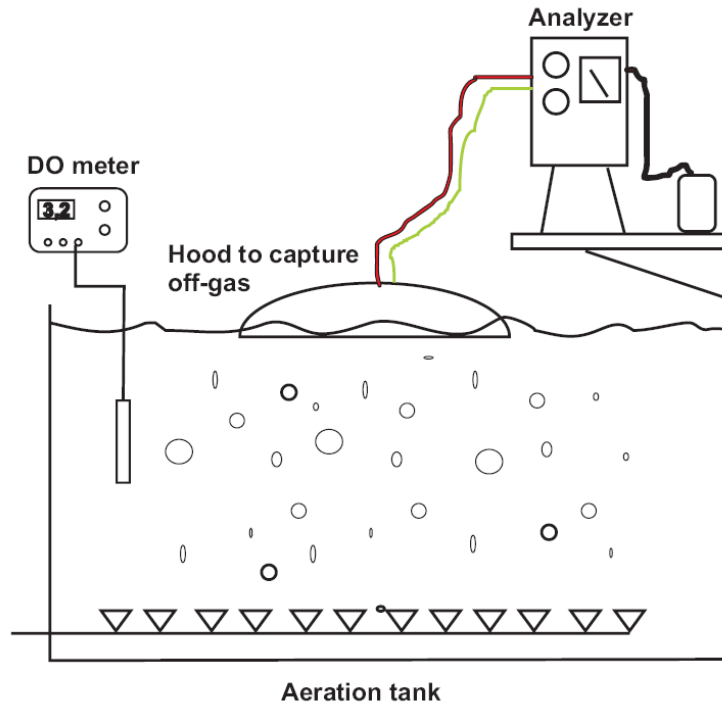


Figure 4. Off-gas test equipment schematic, showing hood, analyzer, DO meter and aeration tank.

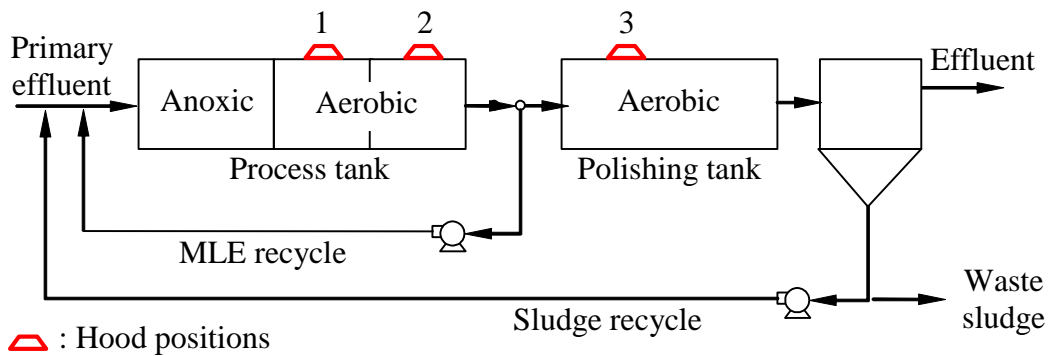


Figure 5. Schematic Diagram of the Nitrifying-Denitrifying Treatment Plant (headworks, primary clarifier, equalization basin and disinfection facilities not shown)

To illustrate the capabilities of off-gas analysis, the results of a 24-hour test are presented, and illustrate the changing in oxygen transfer rates with process loading. Figure 5 is a plant schematic, which is an activated sludge plant that nitrifies and denitrifies using a modified MLE concept. The head works, primary clarifiers and equalization tank are not shown in the figure. Primary effluent flow rate is equalized by diverting excess flow to an off-line storage basin, which is then pumped back into the process during the low flow period. In this way peak loads on the process are reduced.

Figure 6 shows the results of the 24-hour off-gas test along with flow rate and chemical oxygen demand (COD) loading rate. The time scale is noon to noon. The top panel (a) shows the influent flow rate and the influent COD. Note that the maximum flow rate is limited through equalization and that the flow declines to a minimum value at 6 AM morning. The next panel (b) shows the total oxygen demand loading on the plant which was calculated as the product of flow rate and the sum of COD and 4.5 times the ammonia nitrogen concentration. The next panel (c) shows the OTE and air flow rate as determined from off-gas analysis and the air flow rate, also calculated from off-gas analysis. The lower panel (d) shows the oxygen uptake rate, also calculated from off-gas analysis.

The results of this test are useful to designers and clearly show the value of flow equalization. The results are also value for understanding the process dynamics and how the OTE is not a constant value, but changes with plant loading. The  $\alpha$  factor can also be calculated from the data shown in Figure 6, and will be the subject of future work from our laboratory. Design engineers and operators need to plan for a range of transfer efficiencies when designing and operating their treatment plants. It is also interesting to observe the lag between plant loading and oxygen uptake rate, as well as the lag in transfer efficiency and plant loading. The load requires one to two hours to exert its effect on oxygen uptake rate. Also, the low loading period from hours 15 to 21 creates a period of higher oxygen transfer efficiency, which is believed to correspond to reduced surfactant concentrations in the mixed liquor. Trends such as these have been observed by the authors at other treatment plants.

## **CONCLUDING REMARKS**

This paper has described the current state of clean and in-process water oxygen transfer testing. The ASCE Standard, adopted in 1984, eliminated much of the guess work and variability in clean water testing, creating a uniform set of procedures that all manufacturers and consultants can rely upon. The Standard has eliminated several of the key pitfalls of oxygen transfer parameter estimation, including the use of *a priori* methods for selecting the equilibrium oxygen concentration, which can influence overall results by  $\pm 20$  to 25%. The new Standard will contain additional information to assist in the testing of loop (ditch) activated sludge processes, HPO-AS processes and will also have a recommended procedure for eliminating the effects of variable TDS in the test water.

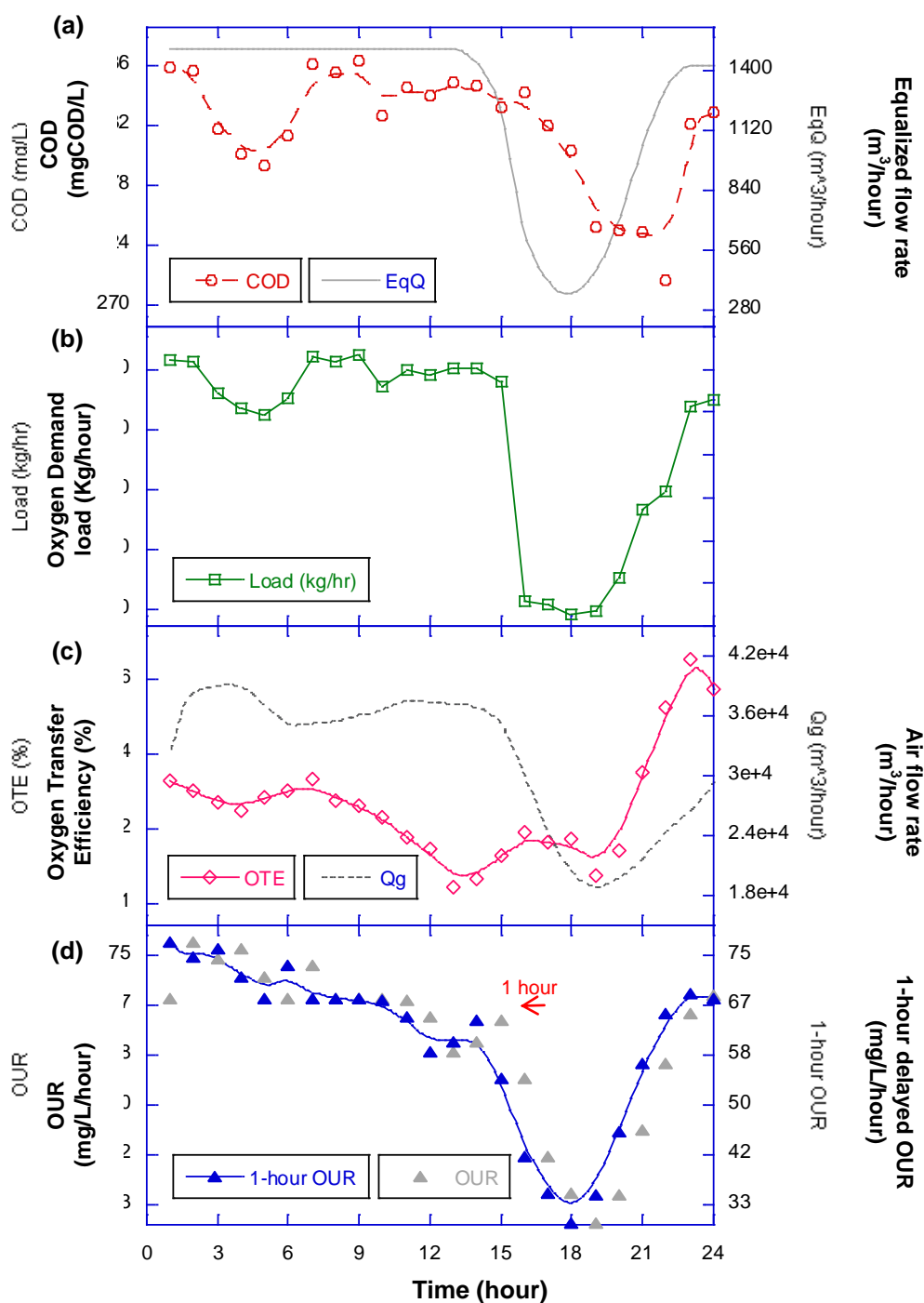


Figure 6. 24-hour off-gas test results: (a) total COD and equalized flow rate of primary effluent; (b) oxygen demand load (COD + 4.5 NH<sub>4</sub>-N); (c) weighted air flow rate from off-gas hood flux and oxygen transfer efficiency; (d) oxygen uptake rate, plotted 1-hour delayed.

The in-process water Standard Guidelines are now nine years old and have had two major impacts on process water testing. The first is encouraging the wide-spread use of off-gas testing for evaluating process performance. Off-gas testing has become the method of choice for diffused

aeration systems. It is shown how it can be used to evaluate oxygen transfer efficiency as a function of process loads as well as show the impacts of flow equalization. Off-gas testing can also be used for pilot plant evaluations or novel processes such as the biological aerated filter (Newman, *et al.* 2005). The second major impact is the reduction in use of the steady-state "BOD" bottle method for estimating transfer rates.

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