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**REAERATION AND AN OXYGEN
TRANSFER MODEL FOR TROPICAL
RESERVOIRS**

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SCHOOL OF CIVIL AND ENVIRONMENTAL
ENGINEERING**

2013

**REAERATION AND AN OXYGEN
TRANSFER MODEL FOR TROPICAL
RESERVOIRS**

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School of Civil and Environmental Engineering

A thesis submitted to the Nanyang Technological
University in fulfillment of the requirement of
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To my parents, my wife,
and my son

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ABSTRACT

Although oxygen transfer has been investigated extensively for several decades, there are however still a number of open questions. Firstly, there is very little information on the effects of temperature on oxygen transfer (reaeration) in water at low turbulence condition. Secondly, how the reaeration rate varies in a water column, especially in a tropical lake or reservoir, is yet to be addressed comprehensively. Finally, there is a knowledge gap in the development of a quantitative model that could describe accurately the rate of mass transfer under various flow conditions, including wind, wave, general surface perturbation, and in quiescent water. As part of the delivery of this study, the author conducted a series of experiments to collect detailed and accurate experimental data which are found to greatly elucidate the reaeration phenomenon.

In this study, the author fabricated a specially designed test-rig system that comprised two main components, namely (1) a jacketed reaeration water column, and (2) an auxiliary oscillating water column, to seek the answers to the questions discussed earlier. Based on the findings of the present experimental study, the author demonstrated clearly that oxygen transfer rate increases with increasing temperature. Also based on the proposed mathematical model, the author deduced that the reaeration rate decreases with water depth as a function of $z^{0.5}$, where z is depth of water below the surface. The author proposed a new characteristic length scale which was known as the diffusive film layer thickness, δ_D . A general quantitative reaeration model, the modified film model, was developed. The model could be used to estimate the mass transfer velocity in various flow conditions. It was also demonstrated that the modified film model could provide good estimates of oxygen transfer rate in the water column under the influence of mechanically generated small amplitude waves. The author went on to demonstrate that the model could be used to unify the results of the present study and those reported in the literature.

Finally, a simplified water quality (DO) model has been developed based on the extended delta method, and incorporated in it a temperature-and-depth dependent

parameter. This model was used to simulate the time series DO profiles at several water depth levels and the vertical distributions of dissolved oxygen at a selected location in Kranji Reservoir, Singapore. The parameters for this model include water temperature, dissolved oxygen concentration, DO saturation, and chlorophyll-a. Based on the quantitative and qualitative criteria of model performance, the proposed model had been shown to simulate DO at different water depths with good accuracy and with the confidence level of better than 95%.

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LIST OF SYMBOLS

A	=	area through which oxygen passes (m^2);
	=	algal concentration (mass/volume);
$A(t)$	=	gas and temperature dependence;
a	=	a constant;
	=	surface divergence (s^{-1});
a_r	=	a constant;
b	=	a constant
	=	the Setschenow salting-out coefficient;
C	=	the bulk concentration of dissolved oxygen at time t (mg/L);
c	=	a constant;
C_o	=	initial concentration (mg/L);
C_s	=	saturation concentration of dissolved oxygen (mg/L);
C_s^z	=	saturation concentration of dissolved oxygen at the depth z (mg/L);
C_z	=	concentration of dissolved oxygen at the depth z (mg/L);
C_w	=	dissolved oxygen at water bulk (mg/L);
C_a	=	oxygen at the air phase (mg/L);
ΔC	=	dissolved concentration difference (mg/L);
D_m	=	molecular diffusivity of dissolved oxygen (cm^2/s);
D	=	dissolved oxygen deficit (mg L^{-1});
D_T	=	the turbulent diffusivity (cm^2/s);
d_o	=	the diameter of the jet (cm);
E	=	activation energy for chemical reaction;
E_T	=	the total diffusivity (cm^2/s);
f	=	the fraction of the day during which the source is active (period of sunlight) (T);
f_c	=	temperature correction factor;
g	=	gravity constant (9.81 m/s^2);

$g(T)$	=	temperature dependent correction coefficient for reaeration rate;
H	=	The wave height (cm);
H_c	=	Henry's constant ($\text{atm m}^3 \text{ mole}^{-1}$);
h	=	the distance from the free surface to the jet centre line (cm);
	=	average water depth (m);
$h(z)$	=	depth dependent correction coefficient for reaeration rate;
I	=	collision factor between molecules;
J	=	the mass flux of dissolved oxygen;
	=	diffusivity coefficient ($\text{gm-cm/s}^2\text{-}^\circ\text{K}$);
K_s	=	the solubility coefficient ($\text{mol L}^{-1} \text{ atm}^{-1}$);
K_T	=	rate of reaction at $T^\circ\text{C}$;
K_L	=	oxygen transfer coefficient (m/s);
k_g	=	gas transfer coefficient in gas phase (m/s);
k_L	=	gas transfer coefficient in liquid phase (m/s);
$K_L/h=K_La=k_2$	=	reaeration coefficient (1/s);
$k(T)$	=	temperature dependent correction coefficient for respiration;
L	=	liquid film thickness (μm);
$l(T)$	=	temperature dependent correction coefficient for photosynthesis;
m	=	the mass of dissolved oxygen;
$m(\text{Chla})$	=	coefficient accounting for the effect of Chlorophyll-a on photosynthesis;
NPP	=	net photosynthesis;
n	=	the Schmidt number dependence;
O_i	=	the measured value of dissolved oxygen (mg/L);
P_{av}	=	the average photosynthesis production rate ($\text{mgL}^{-1}\text{d}^{-1}$);
P_i	=	the simulated value of dissolved oxygen (mg/L);
$P(t)$	=	the daily rate of photosynthetic oxygen production ($\text{mgL}^{-1}\text{d}^{-1}$);
P_g	=	gross photosynthesis;

P_m	=	the maximum oxygen photosynthesis in the stream ($ML^{-3}T^{-1}$);
P_n	=	Net photosynthesis;
p	=	partial pressure (atm);
p_a	=	the partial pressure of gas in the air (atm);
R	=	universal gas constant;
	=	respiration ($mgL^{-1}d^{-1}$);
R_d	=	the dark of the photoautotrophs;
R_l	=	the respiratory losses in the light;
Re	=	the Reynolds number of the reaeration column;
Re_T	=	turbulent Reynolds number;
Re_w	=	the wave Reynolds number;
r	=	surface renewal rate (s^{-1});
S	=	salinity;
$Sc(T)$	=	Schmidt number at $T^{\circ}C$;
$Sc(20)$	=	Schmidt number at $20^{\circ}C$;
T	=	absolute temperature ($^{\circ}K$);
	=	surface renewal time (s);
t	=	time (s or day);
t_s	=	the time expressed as a fraction of the day, at which the source becomes active (T);
u'_L	=	a root-mean-square (RMS) bulk turbulent velocity fluctuation;
V	=	volume of water body (m^3);
	=	the molar volume (V) of O_2 ;
$V_{max}=\pi Hf$	=	the wave maximum velocity at the free surface (m/s);
$x=2.26$	=	the association factor of H_2O ;
z	=	water depth (m);
α	=	a constant;
	=	the dimensionless Ostwald solubility coefficient;
	=	the experimental error (%);

α_1	=	oxygen production per unit of algal mass, mass oxygen/mass algae;
α_2	=	oxygen uptake per unit of algal mass, mass oxygen/mass algae;
β	=	a constant;
δ	=	The Stokes layer thickness
δ_{CBL}	=	concentration boundary layer thickness (μm);
δ_{D}	=	Diffusive film layer thickness (μm);
δ_{e}	=	measured concentration boundary layer thickness (μm);
δ_{SFL}	=	the stagnant film layer thickness (μm);
	=	the characteristic thickness of the viscous sub-layer (μm);
ϵ	=	the rate of energy dissipation by turbulence by unit mass (cm^2/s^3);
μ	=	dynamic viscosity (mPa.s);
	=	specific growth rate of algae (time^{-1});
ν	=	kinetic viscosity of water (cm^2/s);
ν_{20}	=	kinetic viscosity of water (cm^2/s) at 20°C ;
π_1, π_2	=	dimensionless parameters;
θ	=	constant;
ρ	=	water density (kg/m^3);
	=	algal respiration rate (time^{-1});
ρ_{20}	=	water density (kg/m^3) at 20°C ;
σ	=	algal setting rate (time^{-1});
τ	=	the diurnal period (= 1 day);

CHAPTER 1

Introduction

1.1 BACKGROUND

Dissolved oxygen (DO) is one of the most important parameters of water quality. It turns out that DO is the main indicator for a healthy aquatic ecosystem, and it is desirable to maintain DO concentration at an appropriate level to support fish life, protect recreational interests, and ensure desirable aesthetic characteristics of the watercourse. Basically, a water body may be able to tolerate certain increase in biochemical oxygen demand (BOD) without serious consequence on the ecology and aquatic habitat. When it is utilised faster than it is being replenished, the DO concentration in the water body decreases. If DO concentration falls below 5mg/L, it is generally believed that mobile aquatic fauna, i.e. fish, will migrate to areas with higher DO concentration such as when school of fishes move to shallow water and “gulp” for air, while non-mobile species suffer because they are unable to escape from the low-oxygen water. Prolonged very low levels of DO (e.g. <1mg/L) will result in severe stress and occasional death of all organisms requiring a relatively high oxygen concentration to meet their metabolic needs. Furthermore, the absence of DO could result in the growth of microorganisms that produce by-products that cause foul odours in the water and its surroundings. As a matter of fact, a healthy aquatic ecosystem is the principal focus of today’s pollution control activities (Lamb, 1985).

A stream or river, owing to its relatively large velocity, especially a shallow and narrow river, may be considered to be that of a one-dimension flow. Thus, the dissolved oxygen distributions in both the vertical and lateral directions are considered homogeneous. In contrast, a lake or a reservoir displays much more complicated circulation patterns and mixing processes. In large lakes or reservoirs, wind forcing is a key factor in determining a lake circulation and is the major energy source for vertical mixing. For a small (surface area) and deep lakes or reservoirs, wind forcing is usually not significant, usually leading to low flow circulation, and it is generally of not much help in the water quality of the water column. Stratification and quiescent water due to low flow mixing condition are a bane to the water authority, as it generally means that the water quality in the deeper water may be less than ideal. In particular, the concentration of dissolved oxygen there may be low, see Figure 1. 1. However, for a small and shallow tropical reservoir, for example, Kranji reservoir (Singapore), the stratification in terms of dissolved oxygen is less pronounced, see Figure 1. 2. It is noted that the diurnal variation of dissolved oxygen due to photosynthesis and respiration in a river is typically higher than that in a lake as shown in Figure 1. 3 and Figure 1. 4.

Figure 1. 1. Typically simulated and measured DO profiles in Lake Vegoritis in 1993
(Antonopoulos and Gianniou, 2003)

Figure 1. 2. Dissolved oxygen profiles in Kranji reservoir on 7th July 2012 (present study)

Figure 1. 3. Observations of temperature, DO, and DO deficit in Santa Margarita River, Sep 23-25, 1993, at Station 1 (Butcher and Covington, 1995)

Figure 1. 4. Measured DO profiles in Kranji Reservoir (Singapore) at $z=1\text{m}$, July 22-25, 2012 (present study)

The most important mechanism of oxygen transfer in nature is the reaeration process (Herlina, 2005). This reaeration process, which is the focus of this study, is critical to the aquatic habitat as it replenishes dissolved oxygen in polluted water bodies. Thus, understanding and investigating the various factors that may affect the reaeration rate would be fundamental in a reaeration process study.

Reaeration Process

The reaeration rate is dependent on water temperature, transfer characteristics (i.e. degree of turbulence), water depth, oxygen concentration in the atmosphere, pressure, and presence of surfactants. For a turbulent flow, the effects of water depth and air composition are generally not significant and most published papers ignored such effects. Instead most researchers considered only the effects of temperature on the oxygen transfer under various turbulence conditions (Streeter et al., 1936; Downing and Truesdale, 1955; Truesdale and Van Dyke, 1958; Elmore and West, 1961; Metzger, 1968; Bewtra et al., 1970; and Chao et al., 1987). The flow turbulence, leading to turbulence diffusion, has been noted to play an important role in the gas transfer process in addition to molecular diffusion. Several researchers have attempted to study the gas transfer process related to turbulence. The important environmental gases (O_2 , CO_2 , N_2 ...etc) typically have low solubility

and are associated with the boundary layers which are of the order of ten to hundreds of μm “thin” on the liquid side (Herlina, 2005). These liquid boundary layers, in which the molecular diffusion takes place, are found to control the gas transfer process. A number of conceptual models have been developed in an attempt to elucidate the driving force of the process. The simplest model, the two-film theory model, was proposed by Lewis and Whitman (1924). The model assumes that the mass transfer velocity, K_L , was proportional to molecular diffusivity and inversely proportional to the liquid film layer. This model is believed to provide lower value of mass transfer velocity (Herlina and Jirka, 2004, 2008; Woodrow and Duke, 2002;...among others). In contrast, the more elaborate conceptual models, proposed by Higbie (1935) and Danckwerts (1951), show that the transfer velocity is related to the square root of the molecular diffusivity and a surface renewal rate, r , which may be determined experimentally for specific turbulence conditions. Other relevant works include Fortescue & Pearson (1967) and Lamont & Scott (1970) (hydrodynamic models). Beside the conceptual models and hydrodynamic models, various other investigations had focused on relating empirically the mass transfer rate with measured flow condition such as slope of channel, average velocity, etc as given in Churchill (1961), Gulliver & Halverson (1989), and Moog & Jirka (2002). In addition, a number of experimental and numerical works have been conducted. Despite the fact that gas exchange, herein referred to as oxygen transfer, has been extensively investigated to date, there is still a knowledge gap in the development of a general quantitative model that could provide precise predicted values of mass transfer rate in different flow conditions, including low turbulent conditions. Moreover, very little information is known about the effect of temperature on oxygen transfer for low flow turbulence condition. Last but not least, the question of how the reaeration rate varies in a water column and in a lake/reservoir is still open. Detailed and reliable experimental data are much needed to address these open questions. With the improved understanding on oxygen transfer along the water column, it is believed that the knowledge gained would help establish a practical and yet simple water quality (DO) model for the prediction of dissolved oxygen transfer.

1.2 SCOPE AND OBJECTIVES OF STUDY

The turbulence source in the environment may be classified into three main groups: (a) turbulence generated across sheared interface (e.g. wind shear or waves on the ocean or lakes), (b) turbulence generated across an “un-sheared” interface (bottom-shear-induced-turbulence), and (c) buoyant-convection turbulence, i.e. turbulence in lakes/reservoirs owing to surface cooling (Herlina, 2005). Figure 1. 5 illustrates a schematic diagram of the main turbulence sources and their interactions in gas transfer process. This study is focused on the first turbulence source (wind-shear and wave induced turbulence), and especially on the effect of waves on oxygen transfer.

In this study turbulence refers to the effects of water movement and the induced flow fluctuation due to small water surface perturbation.

With the above-mentioned scope and the open questions raised above, the specific goals of this PhD thesis include the followings:

- (1) To further understand the reaeration process at the air-water interfaces;
- (2) To study the effects of temperature on oxygen transfer under low turbulence flow conditions;
- (3) To develop a conceptual model to predict the variation of reaeration rate along the water column;
- (4) To develop a model to account for the effects of surface waves on oxygen transfer using the concept of surface renewal model;
- (5) To establish a universal quantitative model to predict the mass transfer velocity under various flow conditions;
- (6) To develop a simplified water quality (DO) model for tropical lakes/reservoirs.

Figure 1. 5. A schematic Diagram of the dominant turbulence sources in Gas transfer; Type (a) represents the turbulence source investigated in this study

1.3 RESEARCH QUESTIONS

In order to achieve the objectives of this study, the following research questions are pertinent:

- (1) What is the effect of water temperature on oxygen transfer under low turbulence conditions?
- (2) How does the reaeration rate vary in the water column?
- (3) Is the film model valid and universal?
- (4) What are the features that distinguish tropical reservoirs from reservoirs that are not in the tropics?
- (5) Based on the new findings, could a simplified DO model be developed for a tropical lake/reservoir?

1.4 ORGANIZATION OF THE THESIS

This thesis report comprises eight chapters.

Chapter 1 presents current issues associated with dissolved oxygen in water bodies, and the background, scope and objectives, and the research questions of this study.

Chapter 2 contains a review of related works on gas transfer taking place between the atmospheres and underlying water bodies. The basic principles of gas exchange, comprising both chemical and physical parameters are described, followed by detailed review of the effects of physical and chemical factors governing the oxygen transfer across the free surface. Several state-of-the-art models of the gas transport process are then described. A review of bio-chemical processes, including photosynthesis and respiration, is briefly presented. Finally, tropical reservoirs and their characteristics are reviewed.

Chapter 3 describes the experimental setup and measurement equipment of this study. In addition, the field data of Kranji reservoir are presented.

Chapter 4 focuses on the effect of temperature on oxygen transfer.

Chapter 5 demonstrates the investigation of the effect of small surface perturbation or small amplitude waves on reaeration rate.

Chapter 6 illustrates the development of the modified film model.

Chapter 7 shows the establishment of a simplified water quality (DO) model used to predict the dissolved oxygen values of Kranji Reservoir (Singapore).

Finally, **Chapter 8** includes the author's conclusions and recommendations for further study.

CHAPTER 2

Literature Review

2.1 GENERAL INTRODUCTION

Gas transfer across the air-water interfaces is an important research topic in many fields of science and engineering. It is especially important in two engineering applications, and they are (1) environmental engineering (aeration and reaeration processes in lakes and rivers) and (2) chemical engineering (evaporation, mixing and bubbling). A comprehensive understanding of gas exchange process is paramount to many successful applications. This chapter contains a review of related works on gas transfer taking place between the atmospheres and open water bodies. The basic principles of gas exchange, comprising both chemical and physical parameters, are described herein, followed by detailed review of the effects of physical and chemical factors governing oxygen transfer across the free surface. Several state-of-the-art models of the gas transport process are then described. A review of biological processes, including photosynthesis and respiration, is briefly presented. Finally, a review of tropical reservoirs and their characteristics is

described. Figure 2. 1 shows a schematic of the main components of gas exchange at the air-water interfaces.

Based on the number of publications in the scientific and engineering communities, gas exchange at the air-water interface has been a subject of extensive research. However, there are still knowledge gaps, for example those with respect to the development and application of water quality model (DO model) in a tropical lake and reservoir. The author would like to seek answers to the followings:

- (1) What is the effect of water temperature on oxygen transfer?
- (2) How is the dissolved oxygen exchanged at the air-water interfaces and then transferred into deeper water?
- (3) What is the influence of surface perturbation and flow turbulence on oxygen transfer?
- (4) How does the reaeration coefficient vary with water depth?
- (5) What are the emerging issues and challenges in modeling oxygen transfer?

2.2 FUNDAMENTAL CONCEPTS OF GAS EXCHANGE

Gas exchange at the gas-liquid interface can be influenced by many parameters, including chemical, physical, and biological factors. While biological processes (photosynthesis and respiration, for example) may be viewed as a sink and source process in oxygen transfer, the influence of chemical and physical parameters on mass transfer of gases, oxygen in particular, from the atmosphere into the water column holds the interest here and deserves more physically based treatment beyond sink and source.

In general, the concentration gradient across the air-water interface serves as a driving force for gas transfer from the atmosphere into the water column. The concentration gradient, dC/dz , can be described as a function of temperature, salinity (and other chemical properties such as pH), and pressure variations at different altitudes (APHA, 1992). There are also other physical factors including the turbulence and molecular diffusion processes in the liquid medium. The latter refers to the diffusion of gas at the molecular level. The molecular diffusion takes place within a thin layer near to the gas/liquid interface. This thin layer is generally referred to as the stagnant film layer (Lewis and Whitman, 1924) or concentration boundary layer (Herlina and Jirka, 2004, 2008; Woodrow and Duke, 2002; and Gualtieri and Mihailović, 2008). Below this layer, i.e. in the water column, turbulent diffusion dominates. For slightly soluble gases, such as O_2 and CO_2 , the transfer rate is greatly governed by the diffusivity on the liquid side while that on the air side, though with much larger diffusivity, is immaterial when it comes to diffusion across the air-liquid interface.

The flux of oxygen from the atmosphere into water can be described by the Fick's law which states that mass flux of oxygen is proportional to dissolved oxygen concentration gradient in water. The constant of proportionality is known as the diffusion coefficient of oxygen. The transfer is positive from higher to lower dissolved oxygen concentration, i.e.

$$J = \frac{dm}{A dt} = -D_m \left(\frac{dC}{dz} \right) \quad (2.1)$$

where J and m are the mass flux and mass of dissolved oxygen, respectively; t is time; C is bulk concentration of dissolved oxygen at time t ; D_m is molecular diffusion coefficient of dissolved oxygen; A is area through which oxygen passes; and z is the distance in the direction normal to the surface and is positive downwards. Using the two-film theory (Lewis and Whitman, 1924), the concentration gradient across the thickness of the stagnant film layer, δ_{SFL} , can be expressed as Eq. (2.2), i.e.

$$\frac{dC}{dz} \approx -\frac{(C_s - C)}{\delta_{SFL}} \quad (2.2)$$

Substituting Eq. (2.2) into Eq. (2.1), the mass flux of oxygen may be expressed as follows:

$$J = K_L(C_s - C) = K_L \Delta C \quad (2.3)$$

where K_L is oxygen transfer coefficient; C_s is saturation concentration of dissolved oxygen; ΔC is concentration difference.

One may now explore the details of the physical and chemical properties of gas exchange as described in Eq. (2.3).

2.3 PHYSICAL CHARACTERISTICS OF GAS TRANSFER

Gas exchange taking place at the air-water interface is dependent on the molecular and turbulent diffusions. The later is governed by the scale and rapidity of turbulent motions, while the former depends on molecular characteristics and occurs in the thin film layer at the air-water interface.

Basically, kinetic energy induced by wind shear, water wave, and buoyancy flux is transferred into the water column, and is dissipated as turbulence cascades from

larger to smaller turbulent eddies. These eddies lead to mixing within the water body, and are the driver of mass diffusion throughout the water column. The turbulent eddies and mixing motions are eventually attenuated due to viscous forces. At the neighbourhood of the air-water surface turbulent diffusivity is damped and molecular diffusion dominates (Donelan and Wanninkhof, 2002; Bade, 2009). Away from the thin layer of water near the interface, turbulent mixing dominates. This is the basis for the development of the concept of the two-film theory. Detailed description of the model can be found in section 2.4.1. Across the air-water interface, the gas-exchange rate is governed by the lower diffusion rate of the gas or liquid medium of the interface. In this case, the liquid diffusion rate governs the exchange rate across the interface.

An important physical parameter, the Schmidt number (Sc), not only represents the ratio between momentum diffusion and mass diffusion, but also describes the dependence of the film thickness on the kinematic viscosity of water and molecular diffusivity of dissolved oxygen in the water. The Schmidt number is defined as follows:

$$Sc = \frac{\nu}{D_m} \quad (2.4)$$

where ν is the kinematic viscosity of water (cm^2/s); D_m is the molecular diffusivity of dissolved oxygen (cm^2/s). A comprehensive understanding of the effects of temperature and Schmidt number on gas transfer is presented in Chapter 4.

2.4 AIR-WATER GAS TRANSPORT MODELS

Most of the gas-transfer models may be categorised as conceptual, eddy diffusivity, or hydrodynamics models (Brumley and Jirka, 1988). Modeling gas exchange at the air-water interface is of significant importance to environmental engineers and researchers. It is more so now than before because of the perceived climate change of a global scale. The new challenge is that the models developed need to properly describe the relevant phenomenon and to produce reliable quantitative description that is physically meaningful.

2.4.1 Conceptual reaeration models

Conceptual reaeration models may be described as simplified solutions of the one-dimensional (vertical) governing transport equation with no explicit advective component, and may be presented in various forms according to the different initial conditions and boundary conditions (Brumley and Jirka, 1988). Typically, these conceptual models can be included within the class of either film models or surface renewal models.

Film Model. Lewis and Whitman (1924) proposed a simplified concentration profile in a two-phase system by assuming two still surface films, one on the liquid side and the other on the gas side. Each of the surface films has a corresponding gas transfer coefficient, namely k_L and k_g for the liquid and gas phase, respectively. The overall transfer velocity K_L is related to the individual gas transfer coefficients, as in the following resistance-in-series model

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_c k_g} \quad (2.5)$$

where H_c is Henry's constant ($\text{atm m}^3 \text{mole}^{-1}$).

Assuming linear concentration distribution across the liquid film then

$$K_L = \frac{D_m}{\delta_{SFL}} \quad (2.6)$$

where D is the molecular diffusivity and δ_{SFL} is the liquid film thickness. Despite its simplicity merit, the film model is in question whether it may provide good estimate of mass transfer velocity. A number of researchers (Herlina & Jirka, 2004, 2008; and Woodrow and Duke, 2001, 2002) have shown that the film model may underestimate the actual value of mass transfer coefficient. In contrast, Janzen et al. (2010) have recently shown that both the film model and the surface divergence model not only show their good correlation, but also predict well the mass transfer velocity for all of the reported range of Reynolds number.

Penetration Model. Higbie (1935) developed a “penetration model” using the concept of surface renewal effect. His idea was that fresh packages of liquid in the bulk region would be lifted up to the air-water interface where the gas transfer takes place for a certain renewal time (T) as a result of the turbulent motion of the fluid. Thus, the following relationship can be obtained

$$K_L \approx \sqrt{\frac{D_m}{\pi T}} \quad (2.7)$$

Surface Renewal Model. Danckwerts (1951) adopted Higbie’s idea, but modified the constant renewal time (T) to follow an exponential probability distribution of surface renewal rate r ; that is

$$K_L \approx \sqrt{D_m r} \quad (2.8)$$

and $1/r$ may be considered as the mean time between surface renewal events. The surface renewal model is adopted in this study and will be elaborated in detail later.

Film-renewal Model. Combining the film model and surface renewal model, O’Connor and Dobbins (1956) proposed that the interfacial liquid film retains its existence in the statistical sense only and the liquid content of the film is continuously replaced by the liquid from the bulk region. The film-renewal model was proposed as follows:

$$K_L \approx \sqrt{D_m r} \coth \left[\frac{\delta}{\sqrt{D_m/r}} \right] \quad (2.9)$$

Eq. (2.9) becomes Eq. (2.6) for small r and Eq. (2.8) for large r .

Random eddy Model. Harriott (1962) proposed the random eddy model. He suggested that turbulent eddies reaching the water surface could also enhance gas transfer even though the eddies might not have reached the interface. These eddies have a random lifetime and will arrive within a random distance from the interface.

From this distance up to the interface, the transport may be riding on the mechanism of molecular diffusion. In addition, Harriott (1962) assumed that the random lifetime and random distance could be replaced by an independent gamma distribution. The author proposed and derived the following relationship (Eq. (2.10)), where the symbols have the same meaning as before.

$$K_L \approx \frac{\sqrt{D_m r}}{1 + \delta/\sqrt{D_m/r}} \quad (2.10)$$

Surface divergence Model. Brumley and Jirka (1988) proposed a surface divergence model. The authors used the divergence of the tangential velocity in the surface, i.e. surface divergence, to interpret the gas transfer mechanism directly below the air-water interface. They suggested that within a sub-layer in the vicinity of the interface, the mechanism of gas transfer is fully attributable to molecular diffusion. Fluctuations of the surface divergence induce the transport of dissolved gas from this layer across the irrotational Kolmogorov sublayer to the depth where ordinary rotational mixing takes over. Hunt and Graham (1978)'s irrotational source layer theory was used to estimate the Lagrangian time spectrum of the surface divergence in the model developed by Brumley and Jirka (1988) who show that the lower frequency eddies contribute more to the interfacial gas transfer than the higher frequency eddies.

Summary of Conceptual Models

Most of the conceptual models described, except for the film model, have shown that oxygen transfer coefficient, K_L , is dependent on the square root of the molecular diffusivity. In addition, the hydrodynamic parameters influencing the gas transfer process are lumped or embedded in the r or γ term which must be determined experimentally for specific turbulence conditions.

2.4.2 Hydrodynamic models

Hydrodynamic models have been developed based on solutions to the convective-diffusive equation for idealized flow motions, i.e. single scale flow patterns. The

most commonly used flow type may be the steady cylindrical roll cell (Brumley and Jirka, 1988). The following includes several hydrodynamics models. The review is not exhaustive and only selected representative works are presented.

Large Eddy Model. Assuming that the relatively large scale eddies dominate the gas transfer process, Fortescue and Pearson (1967) proposed the “large eddy model”, in which r associated with Eq. (2.8) was defined as u'_L/L . These writers solved the advective-diffusive equation of a roll cell numerically, and suggested the following relationship

$$K_L = a \sqrt{\frac{D_m u'_L}{L}} \quad (2.11)$$

where u'_L is a root-mean-square (RMS) bulk turbulent velocity fluctuation; L is the turbulent integral length scale; and “ a ” is a constant that has a value of 1.46.

Small Eddy Model. Lamont and Scott (1970) considered the small scale eddies as the dominant mechanism controlling the gas transport, defined the r term estimated by $(\epsilon/\nu)^{1/2}$, and proposed the small eddy model as follows

$$K_L = b \sqrt{D_m} \left(\frac{\epsilon}{\nu} \right)^{\frac{1}{4}} \quad (2.12)$$

with ϵ is the rate of energy dissipation by turbulence by unit mass (cm^2/s^3); ν is kinematic viscosity (cm^2/s); b has a value of 0.4. Eq. (2.12) is of the same form as that proposed by Banerjee et al. (1968) and Kitaigorodskii (1984).

Two-Regime Model. Theofanus et al. (1976) proposed a two-regime model based on the fact that both laboratory and field measurements show good correlation with either large eddy or small eddy models. In their model, the large eddy model was related to low turbulent Reynolds numbers Re_T , while the small eddy model was

relevant at high value of Re_T . Using the data of the open-channel flow reported by Brown (1970), Theofanus et al. (1976) suggested the followings:

$$K_L = 0.73u'Sc^{-0.5}Re_T^{-0.5} \text{ for } Re_T < 500 \quad (2.13)$$

$$K_L = 0.25u'Sc^{-0.5}Re_T^{-0.25} \text{ for } Re_T > 500 \quad (2.14)$$

There is another group of hydrodynamic models which has been developed based on the idea of stagnation flow. In contrast to the roll cell models where the surface divergence changes sinusoidally across the surface, the surface divergence associated with stagnation flow is uniform and represents the strength of the flow. Chan and Scriven (1970) solved the convective diffusion equation based on the assumption of a steady stagnation flow and found the instantaneous transfer coefficient to be

$$K_L = \sqrt{\frac{2}{\pi}} \frac{(D_m a)^{1/2}}{\sqrt{1 - e^{-2at}}} \quad (2.15)$$

where “a” is surface divergence and t is exposure time. These authors, however, did not explain how the renewal rate and surface divergence are related to each other.

Using the same approach of stagnation flow but ignoring the time-dependent term, Csanady (1990) found that $K_L = \sqrt{2/\pi}(D_m a)^{1/2}$. This finding is similar to Chan and Scriven (1970)'s result for $(at) \gg 1$. By adopting selected aspects of Chan and Scriven's approach, Brumley and Jirka (1988) proposed a model based on surface divergence fluctuations. A number of other researchers (McCready et al., 1986; Back and McCready, 1988; and Gulliver and Tamburrino, 1995) had also investigated the role of surface divergence fluctuations or the surface divergence spectra.

2.4.3 Eddy diffusivity models

Different from the hydrodynamic models where only a single turbulence scale is treated as the driver of gas transfer process, eddy diffusivity models are true multi-scale models (Brumley and Jirka, 1988). The eddy diffusivity models include the assumption that the predominant turbulence/eddy scale varies within the water column and the total diffusivity E_T is the sum of the molecular diffusivity D_m and the turbulent diffusivity D_t as shown in Eq. (2.16)

$$E_T = D_m + D_t \quad (2.16)$$

Here D_t changes with water depth and follows a power function such as $D_t = \alpha z^n$, where α is a constant and the “n” exponent should be ≥ 2 . Integrating $1/E_t$ from zero to infinite depth, the following relation can be obtained as follow

$$K_L = \left(\frac{n}{\pi}\right) \sin\left(\frac{\pi}{n}\right) \alpha^{\frac{1}{n}} D^{\left(1-\frac{1}{n}\right)} \quad (2.17)$$

It is noted from Son & Hanratty (1967) that for $n=2$ and $n=\infty$ Eq. (2.17) reverts to those of the renewal model ($n=2$) and the film model ($n=\infty$), respectively.

2.5 PHYSICO-CHEMISTRY of GAS EXCHANGE

The flux of gas transferred from the atmosphere into a water body is governed by the physical forcing and the chemical potential gradient of the gas. This gradient is influenced by several factors, including composition of water, the reactivity (ability of a gas to react with other chemicals and solvent) of the gas in question, and the physical characteristics of the gas such as its solubility and diffusion coefficient D (Liss and Merlivat, 1986).

The chemical potential gradient across the air-water interfaces can be described in a number of ways and involves different expressions of solubility. Typically the potential differential can be expressed as follow and in terms of concentration difference

$$\Delta C = (C_w - \alpha C_a) = (C_w - C_s) \quad (2.18)$$

where α is the dimensionless Ostwald solubility coefficient and is defined as the volume of gas at a given temperature and pressure that is dissolved in a unit volume of solvent, and subscripts, “w” and “a”, stand for water and air, respectively. C_s is the equilibrium oxygen concentration given by the Henry’s law. The concentration difference/deficit can also be described as

$$\Delta C = (C_w - K_s p_a) \quad (2.19)$$

where K_s is the solubility coefficient ($\text{mol l}^{-1} \text{ atm}^{-1}$); p_a is the partial pressure of gas in the air (atm). Finally, the difference may be also measured in terms of partial pressure of the gas in air and liquid phases, i.e. $\Delta C = (p_w - p_a)$.

2.5.1 Solubility of Gases

In general, the solubility of most gases is inversely proportional to temperature, typically of the order of 2, and decreases approximately $2\% ^\circ\text{C}^{-1}$ for a slightly soluble gas (for example CO_2 and O_2) (Wilhelm et al., 1977). Henry’s law has been used to quantify the solubility of gases in a solvent, i.e. the solubility of a gas in a solvent is directly proportional to the partial pressure of that gas above the solvent. This law states that for a two-phase system at thermodynamic equilibrium the saturated concentration, C_s , of gas in the liquid phase is proportional to the partial pressure p of the gas in the gas phase

$$p = H_c C_s \quad (2.20)$$

with p is partial pressure (atm); C_s (mole m^{-3}); and H_c denotes Henry’s constant ($\text{atm m}^3 \text{ mole}^{-1}$) which is affected by temperature and the concentration of other solutes in the system (Chapra, 1997; and Smith and Harvey, 2007).

Salinity and pressure at different altitudes also influence the solubility of gases. The solubility of gas in seawater is about 20% less than that in fresh water. The salinity dependence can be described as the Setschenow salting-out coefficient, b :

$$b = \exp(-A(t)S) \quad (2.21)$$

where $A(t)$ is gas and temperature dependence; and S is salinity (Donelan and Wanninkhof, 2002).

2.5.2 Diffusion Coefficient

Molecular diffusion of gases across the air-water interface is one of the driving forces of gas exchange. The diffusion coefficient is gas specific and is dependent on temperature. Over the typical range of temperatures of surface fresh water bodies, the diffusion coefficients increase by a factor of three with temperature. Whilst with salt water the diffusion coefficients are about 5% lower than that in fresh water (Donelan and Wanninkhof, 2002). The molecular diffusion, D_m , can be calculated from the Stokes-Einstein equation with the coefficients of 2.26 (Reid et al., 1977; and Cussler, 1997) and $25.6 \text{ cm}^2/\text{mol}$ for the association factor of H_2O and molar volume of O_2 (Wilke and Chang, 1955), respectively.

For gas transfer investigation, the effect of diffusion is often expressed in terms of the Schmidt number (Sc) (Coantic, 1986; and Calmet and Magnaudet, 1998). Combining Eq. (2.6) and Eq. (2.4), it is possible to see how gas transfer velocity, K_L , can be correlated to Schmidt number, Sc , and how gas transfer coefficients for two different gases may be converted from one gas to another as follows

$$\frac{\delta_{SFL}}{v} = \frac{1}{Sc_1 K_{L1}} = \frac{1}{Sc_2 K_{L2}} \quad (2.22)$$

Typically

$$\frac{K_{L1}}{K_{L2}} = \left(\frac{Sc_1}{Sc_2} \right)^{-n} \quad (2.23)$$

Thus, exchange coefficients may be normalized to a $Sc=600$ for the Schmidt number of CO_2 at $20^\circ C$ in fresh water or to a $Sc=660$ for Schmidt number of CO_2 at $20^\circ C$ in seawater. The gas exchange coefficient of a specific gas x , K_x , at a Schmidt number of 600 (K_{600}) is

$$K_{600} = K_x \left(\frac{600}{Sc_x} \right)^{-n} \quad (2.24)$$

where n is the Schmidt number dependence that is $2/3$ for smooth surfaces and $1/2$ for rough surfaces.

2.6 OTHER FACTORS

2.6.1 Surfactants

Surfactant may influence the gas fluxes at the air-water interface in a number of ways. It may reduce turbulence and diffusion at the water surface, thus reducing the rate of gas transfer (Schmidt and Schneider, 2011). A number of laboratory works using artificial surface films were carried out, i.e. Barger and Garrett (1974), Gaines (1966), and Hühnerfuss and Garrett (1981), who reported on the influence of surfactants on gas exchange. However, it is not easy to adapt the findings obtained experimentally from these investigations to characterize the gas transfer rate in the field, such as that of wave field in lake or the ocean. It is noted that natural water may contain both soluble and insoluble surfactants and may also include proteins, carbohydrates, polysaccharides, hydrocarbons, and humic-type substances (Garrett, 1967; Passow et al., 1994; Van Vleet and Williams, 1983; and Williams et al., 1986) and only minor amounts of lipids (Hunter and Liss, 1977).

The effects of surfactants on gas exchange at air-water interfaces may be grouped into two major categories, namely direct surface effects that occur when insoluble surfactants form closely packed monomolecular barriers on that surfaces that impede molecular diffusion across the interface, and those arising from changes in the hydrodynamic characteristics of water motion at the interface and within the boundary layer below the surface (Davies, 1972; and Liss, 1983). Monomolecular

barriers pose little resistance to gas exchange and thus probably play a minor role in impeding gas exchange in the open ocean (Garrett, 1972; and Liss, 1983). The hydrodynamic effects induced by insoluble surfactants generally produce damping effects on both the gravity and capillary waves (Garrett, 1967; Broecker et al., 1978; and Lucassen, 1982).

Laboratory and field studies have shown that significant suppression of both waves and gas exchange occurred over a wide range of wind speeds when oleyl alcohol (a liquid condensed-type, insoluble surfactant) was spread on the water surface at saturated surface pressures (Broecker et al., 1978; and Brockmann et al., 1982). As the surface pressure of most natural surface films is usually much lower than the pressures generated by the oleyl alcohol (Barger et al., 1974), it may not be possible to extrapolate these latter results to assess the role of capillary wave suppression on the reduction of gas exchange in the marine environment.

There is another explanation for the hydrodynamic effect which, to date, has received little attention among the researchers. Davies (1966), and Metzger and Dobbins (1967) suggested that surfactants dampen eddies impacting on the surface from below by reducing the surface tension, thereby creating a tangential stress opposite to the force of the eddy of clean water approaching the surface in the plane of the air-liquid interface. In effect, the thickness of the viscous sublayer is increased, the rate of surface renewal is reduced, and gas exchange is retarded. The dependence of the surface tension on surfactant concentration for soluble and insoluble surfactants can be estimated experimentally using a setup such as a Langmuir trough (Davies and Rideal, 1963). When it is present at the air-water interface, a surface-active film tends to lower the surface free energy, thus reducing the surface tension (McKenna, 2000). At high surfactant concentration, an additional barrier has to be taken into consideration since gas has to transfer through the air boundary layer, surfactant, and then water boundary layer. Thus, the solubility of the gas in the surfactant layer might affect the transfer rate. Frew (1997) reported that the presence of organic films may damp surface waves and decrease the near-surface turbulence. The effect of surfactants is most pronounced at low wind speeds, since at high wind speeds the wave motions will distribute the

surfactants throughout the water column, and thus reduce their impact on gas exchange (Garrett, 1967; Jarvis et al., 1967; Barger et al., 1974; Broecker et al., 1978; Lazarev and Pokazevev, 1986; and Goldman et al., 1988).

2.6.2 Meteorological Conditions

Despite the fact that the atmosphere pressure, rainfall, and humidity factors may have little effect on gas exchange, the thermal conditions in a lake/reservoir is the principle meteorological factor on gas exchange. The thermal conditions at the air-water interface may affect gas transfer in a number of ways. Heat can be lost from the surface of the water through various mechanisms, including evaporation, sensible heat loss, and long wave radiation (Bade, 2009). The surface layer becomes cooler due to heat loss; and thus convection in the water column takes place as a result of buoyant forces of the upward moving warmer and less dense water below the surface. Thermal convection and penetration of the convective flow into deeper water is another driver of turbulence in the water column, which may explain why gas exchange in lakes may remain relatively high even at low wind speeds (Soloviev and Schlüssel, 1994; Sander et al., 2000; and Jonas et al., 2003). Another consequence of heat loss from the surface is the existence of a cool skin at the top layer of the water column. This layer may be of the order of 1mm in thickness (Wu, 1975, 1984, 1985; and Mcleish and Putland, 1975). It is this cool skin, in turn, that may alter the solubility of gas in the boundary layer and causes a different concentration gradient than would be estimated from a measurement some distance below (Lee, 2002; and Schladow et al., 2002).

2.6.3 Gas Bubbles

Studies on the contribution of bubbles on gas exchange across the air-water interface may be found in Eckenfelder Jr (1959), Kanwisher (1963), Hosoi and Murakami (1968), Kerman (1980), Merlivat and Memery (1983), Keeling (1993), Moutzouris and Daniil (1994), Chang and Liu (1999), and Bortkovskii (2002). The formation of bubbles caused by breaking wave may result in significant enhancement of gas transfer. It has been shown that at wind speed larger than 10

m/s the gas transfer by bubbles, created by breaking waves, become a primary driver; while the gas concentration differential becomes smaller when the wind is strong (Memery and Merlivat, 1985; Thorpe, 1982; Woolf and Thorpe, 1991; Oost et al., 1995; and Leifer et al., 1995).

It has been shown that a positive relationship exists between the gas transfer coefficient and the fractional area of the bubble plumes induced by white-capping waves (Monahan and Spillane, 1984; and Monahan and Torgersen, 1990). The most pronounced impact of bubbles is increased surface area for gas exchange to take place. Tschiersch & Jähne (1980) reported a surface increase of less than 20% even at very high wind speeds. Another important factor is the change in internal pressure of a bubble as it rises through the water column. This increased pressure would determine the concentration gradient at the surface.

Bubble plume studies have also been investigated for their potential in improving water quality in lakes/reservoirs. Because of possible eutrophication and seasonal stratification of lakes/reservoirs, the lake bottom layers may be severely depleted of oxygen, from a biologically desirable level of 5 mg/l to less than 1 mg/l. Therefore artificial oxygen enrichment with air or oxygen plumes may be used to recover the productivity of lakes and reduce the toxicity of lake water (McIssac et al., 1981), as well as accelerating bio-degradation of toxic organic compounds (Murphy, 1990). The bubble plumes may be derived from point sources or line sources (Tsang, 1990). There have been three major theoretical works on gas bubble plumes.

Kobus (1968) proposed the first theoretical model for bubble plumes. The bubbles are assumed to expand isothermally while rising. No gas is absorbed by the ambient water. A constant terminal rising velocity is assumed for the gas bubbles and the source effect on the gas bubble is negligible. Moreover, the plume itself is assumed to expand linearly from its source. In addition, both velocity distribution and density deficit profile are assumed to be Gaussian. Based on the above-mentioned assumptions and applying the Bousinesq approximation, the author then established a set of differential equations, and its solution was used to describe the characteristics of the plume.

A second model, slightly different from Kobus' model, was developed by Ditmars and Cederwall (1974). In this model, the gas bubbles are assumed to reach a constant terminal slip velocity, the velocity relative to the water in the plume which itself is also rising. Kobus' assumption of linear assumption was dropped in Ditmars and Cederwall's model. The expansion of the plume is the result of the natural process of entrainment of the ambient fluid at the perimeter of the plume. They established a set of governing equations which can only be solved numerically.

A third model was developed by Milgram (1983). The Bousinesq approximation is dropped in this model. A set of differential equations were established by studying the plume from a Lagrangian frame of reference. The equations established can only be solved numerically.

2.7 GAS TRANSFER INVESTIGATION

Characterization of the influence of turbulence on gas exchange across the air-water interface has been difficult as the phenomenon is dependent on relative phase velocities, roughness of free surfaces, frictional and adhesive forces, surface tensions, and other parameters (Weber and DiGiano, 1996). Moreover, complex and anisotropic effects of the free surface on turbulence may pose further challenges to the modeling effort (Moog and Jirka, 1999).

According to Gualtieri and Mihailović (2008), the turbulence sources in the environment may be classified into three main groups: (a) turbulence generated across an "un-sheared" interface, (b) combined wind-stream turbulence, and (c) turbulence generated across sheared interface. In addition to the above-mentioned three main turbulent sources, the writer also includes (d) buoyant convective turbulence, especially for lakes/reservoirs. The first case, an "un-sheared" interface is associated with open channel flow where the effects of wind-induced turbulence or wave-induced turbulence on reaeration coefficient are considered negligible compared to the bottom-shear-induced turbulence. The latter is the predominant driving force of gas exchange a surface water flow. Recently, it has been shown that

wind shear poses significant effects on gas transfer rate in natural stream. As a result, the effects of air flow (wind) and water flow need to be considered for a reaeration process. In a lake, however, the primary driving forces of the gas transfer from the atmosphere into a water column is wind stress. This wind stress acts on the water surface, leading to the formation of a shear interface, and increases the rate of gas exchange.

In the following sections, all four turbulent sources are discussed.

2.7.1 Buoyant-convective-induced turbulence

Penetrative convection may be the most important source of vertical mixing in a lake with low wind speeds (as discussed in Section 2.6.2). Convective instability has been studied in the laboratory, see Deadorff et al. (1969) and Kastaros et al. (1977), and in lakes as reported by Imberger (1985), Sander et al. (2000), and Jonas et al. (2003). However, none of those researchers focused on gas transfer. Soloviev and Schlüssel (1994) developed a gas transfer model and considered the effect of convection over a wide range of wind speeds. However, their model was based on oceanic condition in which they assumed surface shear effect in calm atmosphere. It is only until recently that Lee (2002) and Schladow et al. (2002) investigated the phenomenon of gas exchange under convective instability. With the aid of LIF technique, Lee (2002) and Schladow et al. (2002) investigated oxygen transfer across the air-water interface in a water tank and were able to observe the reaeration process, including situation where water with low oxygen concentration interacted with air, and the air and oxygen was transferred from the air by diffusion. Eugster et al. (2003) carried out CO₂ gas flux measurements in lakes under convection using the eddy-covariance method. Their results demonstrated the importance of convective mixing to the process of gas transfer across the air-water interface.

2.7.2 Bottom-shear-induced turbulence

For low wind speed over streams, the predominant driving force of gas exchange in the water column is bottom-shear-induced turbulence. A number of reported works

have attempted to relate the transfer coefficient K_L with stream parameters, such as the mean velocity, bed slope, and average water depth. The relationship may be either empirical, see for example Churchill (1961), Thackston and Krenkel (1969), and Gulliver and Halverson (1989), or semi-empirical with one or two empirically fitted coefficients. Of the semi-empirical equations based on the rate of energy dissipation, there are those reported by Krenkel and Orlob (1963), Tsivoglou and Wallace (1972), and Parkhurst and Pomeroy (1972).

Other semi-empirical equations based on surface renewal model could be found in Gulliver and Halverson (1989), Moog et al. (1999), Moog and Jirka (1999), and Tamburrino and Gulliver (2002).

Brumley and Jirka (1987) conducted detailed measurements of surface hydrodynamics related to gas transfer under the effect of bottom-shear-induced turbulence using a grid-stirred tank. Other investigations on this topic can be found in Jirka and Ho (1990), Chu and Jirka (1992), Chu (1993), McKenna and McGillis (2002), Atmane and George (2002), Tsumori and Sugihara (2006), Xu, et al (2006), and Herlina and Jirka (2004, 2008).

2.7.3 Combined wind-shear and bottom-shear-induced turbulence

Recently, there is increasing awareness that wind shear may pose significant effects on gas transfer rate in natural streams including estuaries. The effects of air flow (wind) and water flow need to be considered in the re-aeration process, see for example Eloubaidy (1969), Eloubaidy and Plate (1972), Mattingly (1977), Plate and Friedrich (1984), Jirka and Brutsaert (1984), Jirka and Chu (1993), Nakayama (2000), Chu and Jirka (2003), and Duan et al. (2009).

Plate and Friedrich (1984) studied the reaeration process of an open channel flow and considered three scenarios, including bottom-generated turbulence, surface-generated turbulence, and the combination of bottom and surface-generated turbulence. These authors proposed a relationship of K_L as a function of the root-mean-square value of the horizontal component of the velocity near the surface σ_u .

Good correlation was reported, but relatively large discrepancies were observed for the three scenarios. Plate and Friedrich suggested using a dissipation velocity u_ϵ to correlate σ_u with mean flow parameters so as to unify the results obtained for different scenarios. Combining with the data of Mattingly (1977), Plate and Friedrich (1984) found a consistent relationship between K_L and u_ϵ for the two distinctly bottom-shear dominated and wind-shear dominated Scenarios.

Jirka and Brutsaert (1984) formulated a criterion to determine whether bottom-shear or wind-shear is the predominant factor for the reaeration process in combined wind/stream driven flows. However, their work only reported limited field measurements that make it not possible to conduct full validation of the proposed criterion. Chu and Jirka (2003) proposed an empirical relationship of wind and stream induced re-aeration by adding the two sources together.

Duan et al. (2009) developed a model based on the two-film theory and the surface renewal theory. Their model correlated the gas transfer rate with the dynamic fluid parameters, i.e. wind speed, stream velocity, kinematic viscosity, and skin-friction coefficient. The writers' results showed good agreement with previous data and they concluded that the model is able to estimate the gas-liquid transfer coefficient in the wind-stream-flow-driven systems.

2.7.4 Wind-shear-induced turbulence

In a lake/reservoir, the primary driving force of gas exchange is wind stress. This wind stress acts on the water surface, leading to the formation of a shear interface, and enhances the rate of gas exchange. A number of researchers investigated the correlation between K_L and surface friction velocity u^* , but their results suggested a lot of discrepancy, see Liss and Slater (1974), Broecker and Peng (1982), Jähne et al. (1979), Jähne et al. (1987), Merlivat and Memery (1983), and Jähne and Haussecker (1998). Comprehensive measurements in the vicinity of the air-water interface under wind-shear-induced turbulence could be found in Wolff et al. (1990), Wolff and Hanratty (1994), Duke and Hanratty (1995), Banner and Peirson (1995), Münsterer et al. (1995), Münsterer (1996), Peirson (1997), Münsterer and

Jähne (1998), and Woodrow and Duke (2001). The actual gas transfer mechanism is elusive. Woodrow and Duke (2002) provided a detailed measurement of the local variation of K_L along the air-water interface using LIF technique. They found detached layers with high oxygen concentration under waves. In addition, the authors also reported that K_L values were much more variable under waves than that for flat water surface.

O'Connor (1983), Kerman (1984), Kitaigorodskii (1984), and Cohen (1983) developed their theoretical models based on rigid wall analogy of the turbulent boundary layer with certain modifications for a free surface. The characteristics of these models were based on the assumption of a smooth surface at low wind speeds and a rough surface at high wind speeds. However, determination of the transition region between low and high wind speeds is still uncertain. There were also reported field measurements of natural streams and the effect of wind-shear on gas transfer, as can be found in Jirka and Brutsaert (1984), Frexes et al. (1984), and Yotsukura et al. (1984).

2.7.5 Effect of mechanically generated waves on Oxygen Transfer

Non-breaking wave-induced turbulence, which is the focus of this study, may be viewed as one that is generated across a sheared interface. Downing and Truesdale (1955) conducted experiments on the influence of mechanically generated waves on oxygen transfer. The wave frequency of 0.6Hz-1.25Hz and various wave heights ranging from 2.8cm to 10.8cm were used in the experiments. These writers reported that increasing either the height or frequency of progressive waves in water caused an approximately linear increase in the rate of oxygen transfer. Daniil and Gulliver (1991) studied the influence of both breaking wave and non-breaking wave on gas transfer across the air-water interface. They proposed a number of expressions that could be used in the surface renewal model and found that the model fitted the experimental data well. The gas-transfer coefficient was shown to be proportional to the maximum vertical wave velocity, πHf , at the water surface, leading to the expression for oxygen transfer coefficient which was the product of wave height

and wave frequency. Further, these authors stated that when breaking waves or bubbles were present, the gas transfer rate increased significantly.

2.8 ARTIFICIAL RE-OXYGENATION

The methods for introducing oxygen into river or lake water column are not discussed in the previous sections, because they are not natural but artificial re-oxygenation processes. These methods are frequently used in practice and are important in maintaining desirable dissolved oxygen concentration in watercourses (Lamb, 1985).

There are several methods to perform artificial re-oxygenation of streams. These methods are presented and described briefly.

Mechanical aeration. There are many studies on the feasibility of using various types of aeration devices to add oxygen directly to streams when needed, but they are seldom used in practice (Hogan et al., 1970; and Lin, 1977).

Turbine venting. In certain hydroelectric power installations oxygenation of water passing through turbines has been accomplished by allowing air to enter at low-pressure points in the system (Raney and Arnold, 1973; Raney, 1977; Bohac, 1989; March and Waldrop, 1990; and Brookshier et al., 1999).

Re-aeration on spillways. Sometimes spillways with roughened surfaces have been constructed to enhance the reaeration of water passing over them (Thomas et al., 1978; Rindels, 1990; and Kells and Smith, 1991).

Addition of oxygen. Occasionally, intermittent addition of oxygen on an as-needed basis could be economical and viable for maintaining the desired DO concentration in some streams (Lamb, 1985).

Addition of hydrogen peroxide. This chemical decomposes to produce DO and is another method for adding oxygen to a stream, especially when needed intermittently (Lamb, 1985).

For lakes or reservoirs, there are certain commonly used methods of artificial aeration including the followings.

2.8.1 Destratification-artificial circulation-aeration

Stratification in a water body is typically not desirable and the condition may be destroyed and water column circulation restored artificially. In shallower, smaller lakes, this restoration may be accomplished by injection of compressed air from a diffuser to the water at the lake bottom. When aeration is the main goal, this simple bubble plume diffuser has been found to be the simplest, most efficient arrangement. The method has been found effective, even for a deep lake (McGinnis et al., 1998). In large, deeper water bodies, the stream of bubbles may be directed by a broad tube of 2-3 meters in diameter to create in-lake circulation (Jørgensen et al., 2005).

2.8.2 Hypolimnetic aeration

This process brings water from the bottom to the surface to be oxygenated and then returned to the bottom without mixing the bottom water with the surface water. There are aerators which can oxygenate the hypolimnion without breaking down the thermocline (Little, 1995; McGinnis and Little, 1999; McGinnis et al., 1998). Burris and Little (1998) used a mathematical model and showed that it was possible to double the oxygen transfer to water in hypolimnetic aerators if the initial bubble diameter were reduced from the more standard 5 mm to just 2.5 mm. The hypolimnetic aeration system has the advantages that the high concentration of elements in the hypolimnion are not transferred to the epilimnion, and do not enhance algae growth (Jørgensen et al., 2005). However, the two main challenges associated with hypolimnetic aeration are evaluating the oxygen consumption of the water body and quantifying the oxygen input capacity of the aeration system (Ashley, 1983 1985; Ashley et al., 1987, 1990).

2.8.3 Hypolimnetic oxygenation

Pure oxygen generated at the lakeshore has been used to increase the oxygen concentrations at the lake bottom without extensive mixing (Gemza, 1997). Oxygen is injected into the water, and with the movement of water created with a propeller, water is circulated from the hypolimnion. The number of reported applications using this method is low (Jørgensen et al., 2005).

2.8.4 Metalimnetic aeration

Metalimnetic aeration oxygenates the water in the metalimnion without destroying either the hypolimnion or the epilimnion (Stefan et al., 1987). The objective is to produce an oxygenated refuge in the metalimnion for *Daphnia* which are members of the Cladocera family and are one of the several small aquatic crustaceans commonly called water fleas because of their saltatory swimming style. A fully submerged bag-type device has been used.

2.8.5 Layer aeration

Kortmann et al. (1982, 1988) and Kortmann (1994) used detailed knowledge of stratification and heat conditions in lakes and reservoirs to achieve redistribution of available heat and oxygen in a stratified lake or reservoir. By using certain specific devices, separate and distinct layers of a lake or reservoir are created and aerated, resulting in the formation of several thermocline-type barriers to vertical diffusion. As a result, the volume and extent of the hypolimnion are reduced. The advantages of this method include creation of the desirable physical and chemical conditions as well as an oxygen supply in the water column through manipulation of the thermal structure. Because it is possible to act selectively, the negative side effects of mixing which often accompany destratification are avoided.

2.8.6 Jets

There are in practice, a number of engineering solutions that have been used to achieve mixing and enhancement of aeration to increase the DO through air

bubbling or mechanical mixer. These methods are energy intensive and in most cases, the effectiveness in terms of mixing and aeration is very much localized. On the other hand, there are natural processes that generate slow but large scale circulation such as that of density current (penetrative convection) due to spatial temperature difference, wind setup or wind stress on the water surface. However, in the case with water body of small surface area, such temperature differential may not exist. The wind-fetch length may be too short to generate effective wind set-up and return flow across the water body.

A potentially plausible approach is to introduce internal flow with low flow speed which could initiate and induce large circulations through the water body. Such a flow could be induced by jet flow, with several jets introduced at strategic levels and locations within the water body. Introduction of jet flow need not be energy intensive as a small potential head difference could generate the desired flow. A jet flow could be generated through a conduit, and driven by small water level difference of the order of centimeters. The jet-flow has the advantage over other forms of flow in that the induced vorticity would cascade through the water body, leading to general circulation within the water body and perturbation of the water surface. It is this water surface perturbation that would enhance reaeration rate at the air-water interface, and the DO-enriched water would be carried throughout the water body through the cascade of vorticity.

Michele and Michele (2002) studied free jet as a driver to improve lake water quality. They found that oxygen-rich water from the surface may be transported down into the hypolimnion using free jet and thus water column would be destratified. Moreover, a free jet entrains oxygen rich and warm epilimnic water on its way down to the deeper water. This water will finally be transferred to the metalimnion. The density differences will make this water travel longer distances. It has been noted that the energy input may be relatively low and would probably not overturn the lake system. A jet started the operation in early spring may produce the most significant effect since the first spring destratification would be destroyed and its development would be delayed to the later part of the year. "...The installation and operation costs are very low, so this technology can be applied for coastal

basins, large and smaller lakes and even fish farming ponds. The oxygen efficiency may be more than an order of magnitude higher compared to other technologies....” (Michele and Michele, 2002)

Nguyen and Tan (2011) studied the effects of Reynolds number and air-water interface on surface jets induced reaeration using PIV measurement. Nine experiments were carried out for different jet normalized depths ($h/d_o=0.55-1.94$) with Reynolds numbers ranging from 1,500 to 6,000. Here h is the distance from the free surface to the jet centre line, d_o is the diameter of the jet. These authors concluded that the air-water interface and Reynolds number have significant effect on the surface jet diffusion characteristics. For submerged surface jets ($h/d_o \leq 0.55$), higher Reynolds numbers result in apparent deeper influence of the jets. The close proximity of air-water interface appears to improve the enhancement of reaeration. For deeper surface jet ($h/d_o \geq 1.11$), the effect of Reynolds number is not pronounced. They also proposed two length scales, d_m and x_m , to characterize the vertical diffusion of the jets. It is shown that for high Reynolds numbers ($Re \geq 3,000$) all the core jet profiles are collapsed into one curve. Moreover, clearly defined relationship was established for different cases studied.

2.9 BIOLOGICAL PROCESSES - PHOTOSYNTHESIS AND RESPIRATION IN THE AQUATIC ENVIRONMENT

The photosynthesis and respiration of the plants (phytoplankton and attached algae) can be important sources and sinks of dissolved oxygen in natural watercourses. Many models have been developed to describe these processes directly in terms of algal growth and respiration. For instance, net algal growth is simulated with the QUAL-II model (Roesner et al., 1981) using the following equation

$$\frac{\partial A}{\partial t} = (\mu - \sigma - \rho)A \quad (2.25)$$

in which A = algal concentration, mass/volume
 μ = specific growth rate of algae, time^{-1}
 ρ = algal respiration rate, time^{-1}

σ = algal settling rate, time⁻¹

The net algal oxygen production minus consumption is simulated by QUAL-II as

$$\frac{\partial C}{\partial t} = (\alpha_1 \mu - \alpha_2 \rho)A \quad (2.26)$$

where C = dissolved oxygen concentration, mass/volume

α_1 = oxygen production per unit of algal mass, mass oxygen/mass algae

α_2 = oxygen uptake per unit of algal mass, mass oxygen/mass algae

The stoichiometric coefficients α_1 and α_2 relate algal growth and death to oxygen production and consumption (see table 3-29 and 3-30 Bowie et al. (1985)).

Phytoplankton and the attached algae are generally modeled as a biomass pool using the same mass balance approach used for nutrients and other constituents. The simpler models lump all algae into a single group, while more complex models distinguish between functional groups such as green algae, diatoms, and blue-green algae. Single-group models are commonly used in rivers, while multi-group models are more common in lakes where long-term simulations of the seasonal succession of different types of phytoplankton are important.

Algal dynamics depends on growth, respiration, excretion, settling, non-predatory mortality, and predation. Although some of these processes can be measured in the field or laboratory, most of the coefficients defining the process rates are usually determined using model calibration. This is necessary since the rates will vary with environmental conditions such as temperature, light, nutrient concentrations, and predator densities as well as with the species composition of the algae, all of which change continually with time. Most processes in algal models are assumed to be temperature dependent.

2.9.1 Light Intensity

Photosynthetic O_2 production and CO_2 consumption take place as the light intensity is gradually increased from zero during the day. At very low light intensities, the photosynthesis and respiration processes show up as a diminution in the rate of O_2 consumption rather than a net liberation of O_2 , i.e. there is significant gross photosynthesis but no net production. The light compensation point is that irradiance¹ at which net gas exchange is zero because gross photosynthesis and respiration are in balance as shown in Figure 2. 2, see the intersection between the graph and the dotted line. This compensation irradiance is not fixed but varies primarily with respiration rate and to a lesser extent the initial slope of the P (photosynthesis rate) versus E (irradiance) curve in Figure 2. 2 (Geider & Osborne, 1992). Beyond this point, liberation exceeds consumption and a net photosynthesis is achieved. With further increase in irradiance, photosynthetic rate, P, begins to decrease again; a phenomenon referred to as photoinhibition. Figure 2. 2 shows an idealized curve of specific photosynthesis rate (P) as a function of irradiance (E) illustrating the maximum photosynthetic rate, P_m , and the irradiance at the onset of light saturation, I_k . α is the initial slope.

Figure 2. 2. Variation of photosynthesis (represented by the generation of O_2) with respect to irradiance, E, according to (Geider & Osborne, 1992)

¹ The radiant flux incident on an infinitesimal element of a surface, containing the point under consideration, divided by the area of that element. It has the units $W \text{ (quanta } s^{-1}) \text{ m}^{-2}$.

2.9.2 Circulation and Depth

The depth through which circulation can occur is limited either by the depth of the bottom or (throughout the year in tropical oceans) by the presence of shallow thermocline. Thus, aquatic photosynthesis takes place best in shallow waters or in waters in which circulation is confined to a shallow layer by thermal stratification. The higher productivity of shallow water also applies to benthic flora. Any surface within the euphotic zone of a water body is usually found to support a productive plant community. This applies not only to the more obvious macrophyte communities such as kelp forests but also to seemingly bare sand and mud surfaces which usually harbour a dense microflora amongst the grains. Further references may be found in Devlin and Barker (1971), Falkowski and Raven (1997), and Kirk (1983).

2.9.3 Temperature

In considering the effects of temperature on aquatic photosynthesis, it is necessary to distinguish between the effects immediately following a change in temperature and the effects obtained if the plants are allowed to adjust to the new temperature for one to several days. A plot of photosynthesis vs. temperature usually gives the type of response curve (Figure 2. 3), although in nature it may not be symmetrical (El-Sharkawy and Hesketh, 1964).

Figure 2. 3. A photosynthesis response curve of the minimum-optimum-maximum type showing the three cardinal points (Devlin & Barker, 1971)

If photosynthesis as a function of irradiance is measured at a series of temperatures (not exceeding the optimum), then it is observed that the maximum photosynthetic rate at light saturation increases with temperature, this is as shown in the P versus E curve (Figure 2. 4; Kirk, 1983).

Figure 2. 4. Photosynthesis rate as a function of irradiance at different temperatures (Kirk 1983)

It is generally found for shallow, productive coastal waters and for inland waters, that both the in situ photosynthetic capacity (the maximum specific photosynthetic rate per unit phytoplankton or macrophyte) and the integral (areal) rate of photosynthesis are positively correlated with the prevailing temperature (Kirk 1983). This is notwithstanding the apparent lack of systematic effect of temperature

on photosynthesis in the oceans. In the case of the whole aquatic ecosystem undergoing slow seasonal temperature changes, there is time both for physiological adaptation by any given species and for changes in dominant species present. Hence, the relation between primary production and temperature could not be so simple at the ecosystem level.

In the marine diatom, *Skeletonema costatum* (after Steeman Nielsen & Jørgensen, 1968; and Steeman Nielsen, 1975), the cells are grown under irradiance of 75×10^{18} quanta $\text{m}^{-2}\text{s}^{-1}$, and exposed to the experimental temperature for 30 minutes before measurements are carried out. In the multicellular red alga *Gigartina stellata* (plotted from data of Mathieson & Burns (1971)), plants are collected from the lower littoral zone of the coast of New Hampshire, USA. The original irradiance values (in foot-candles) have been converted to quantum units.

Kirk (1983) summarized that any optically deep water body at a temperature below the photosynthetic optimum, photosynthesis per unit volume is likely to be limited by light in the lower part of the euphotic zone, by temperature in the upper part of the euphotic zone and by CO_2 everywhere. In water bodies so shallow that adequate light penetrates to the bottom, temperature (apart from CO_2) can become the dominant factor controlling photosynthesis in the whole system.

2.9.4 Temporal Variation in Photosynthesis

Considering diurnal variation, there is no photosynthesis at night. Photosynthesis begins at dawn and ends at dusk. The total photosynthesis of the whole water column roughly follows the approximately sinusoidal variation of solar irradiance during the day (Harris, 1980; Jones and Ilmavirta, 1978; and Talling, 1971). In tropical oceanic waters where there is no seasonal variation in the hydrologic regime, there is usually no pronounced variation in phytoplankton biomass and photosynthesis production. In regions where there is seasonal upwelling of nutrients, there is an accompanying massive increase in phytoplankton and photosynthesis production. Alternating dry and rainy season affects seasonal variation in temperature, insolation and water level, with associated changes in areal photosynthesis.

2.9.5 Estimating Photosynthesis in Aquatic Ecosystems

From the literature, the major problem in determining the compensation depth is the accurate measurement of phytoplankton respiration. Traditionally, respiration has been assumed to be 10% of the maximum rate, and independent of irradiance (Ryther, 1954). Respiratory losses in photosynthetic organism, R_p , can be defined as the rate of electron flow from organic carbon to O_2 with the concomitant production of CO_2 (Falkowski & Raven, 1997). Net photosynthesis, P_n , is the difference between gross photosynthesis, P_g , in the absence of any respiratory losses and the respiratory losses in the light, R_l ,

$$P_n = P_g - R_l \quad (2.27)$$

The three terms are all rates and time dependent as shown in Figure 2. 5 below.

Figure 2. 5. A schematic diagram showing the differences between gross photosynthesis (P_g), net photosynthesis (P_n) and net primary productivity (NPP) over the period of day (Falkowski & Raven, 1997)

At night (indicated by the dark bar in Figure 2. 5) respiration of the photoautotrophs (R_d) leads to a net consumption of O_2 . During the day, P_n , masks respiration. The sum of dark respiratory losses of the photoautotrophs with net photosynthesis is net primary production. NPP is the difference of net photosynthesis and respiration in the dark of the photoautotrophs, R_d ,

$$\text{NPP} = P_n - R_d \quad (2.28)$$

Net photosynthesis, as defined by Eq. (2.28), is the net organic carbon production in the light. Net primary production can (and usually does) include a dark period with an associated respiratory loss of carbon.

2.9.6 Engineering Interpretation

O'Connor and Di Toro (1970) adjusted the temporal form of the photosynthetic oxygen source in streams by a half cycle sine wave. The daily rate of photosynthetic oxygen production P ,

$$P(t) = P_m \sin\left(\frac{\pi(t - t_s)}{f}\right) \text{ when } t_s \leq t \leq t_s + f \quad (2.29)$$

$$P(t) = 0 \text{ when } t_s + f \leq t \leq t_s + 1 \quad (2.30)$$

where P_m is the maximum oxygen photosynthesis in the stream ($\text{ML}^{-3}\text{T}^{-1}$)

t_s is the time expressed as a fraction of the day, at which the source becomes active (T)

f is the fraction of the day during which the source is active (period of sunlight) (T)

In another development, like reaeration, respiration and saturation concentrations of DO, the production equation is also temperature dependent. For streams where temperature variability is small, the delta method of Chapra and DiToro (1991) is useful for scoping DO reaction rate parameters. This method enables a simple graphic fit to reaeration, production and respiration rates and is thus widely used for preliminary interpretation of diel DO studies. However, Butcher and Covington (1995) reported that the use of such methods could yield unrealistic parameter estimates for shallow streams, with a significant range of diel water temperatures. Following assumptions of Chapra and DiToro (1991) at constant temperature, Butcher and Covington (1995) implemented an approximate correction to the

variable temperature. Under variable temperature, the production equations can be represented in van Hoff Arrhenius form,

$$P(t) = P_m \sin\left(\frac{\pi(t - t_s)}{f}\right) i(T) \text{ when } t_s \leq t \leq t_s + f \quad (2.31)$$

where T is the environmental temperature ($^{\circ}\text{C}$), and $i(T)=1.066^{T-20}$

2.10 REVIEW OF TROPICAL RESERVOIRS AND THEIR CHARACTERISTICS

Tropical lakes or reservoirs have received less attention and investigated compared to lakes or reservoirs in the temperate zones (Boon, 1996; Lewis, 2000; MacIntyre et al., 2002; Gal et al., 2003; Romero et al., 2004; Robson and Hamilton, 2004; Bruce et al., 2006, among others). The characteristics of tropical lakes may differ from lakes in other climatic regions in several ways, such as the climate, mixing dynamics and phytoplankton growth (Lewis, 1987; Lewis, 2000; Talling, 2001; MacIntyre and Melack, 2009; Xing et al., 2012). Typically, the physical and biological processes in tropical lakes are driven by higher and longer period of solar radiation, higher primary production with warmer water and lower DO in the water (Lewis, 1987; Gunkel and Casallas, 2002). The seasonal variations of the climate are not as significant as those in the temperate lakes (Mackinnon and Herbert, 1996; Gunkel and Casallas, 2002) and the solar radiation input as well as water temperature do not vary significantly throughout the year in the tropics.

Despite of their unique features and significantly different environment, tropical lakes have seen very limited research performed on them (Talling and Lemoalle, 1998) and even less for shallow tropical lakes (Xing et al., 2012). The following contains discussion on the characteristic features of tropical reservoirs or lakes, including water and heat budgets, thermal stratification, mixing dynamics, and water quality related issues.

2.10.1. Water and Heat budgets

Water budget

The establishment of water budget is useful to describe the hydrological characteristics of lakes or reservoirs (Assouline, 1993). Earlier studies of water budgets in tropical lakes or reservoirs have indicated that for different lakes in the tropical region, the dominant components in the water balance equation may differ (Talling and Lemoalle, 1998). The water budgets of tropical lakes or reservoirs can be characterised by the following:

- Atmospheric parameters (precipitation and evaporation):

Precipitation: i.e., Lake Victoria in East Africa where direct rainfall over the lake is the largest and most variable term (Talling and Lemoalle, 1998; Yin and Nicholson, 1998).

Evaporation: i.e., in closed lakes without surface water outlets such as Lake Naivasha in the East African Rift system where the evaporation accounts for 82 % of the total output in the water budget (Ayenew and Becht, 2008).

- River/tributary inflows: e.g., Lake Abiyata in the Ziway-Shala basin of Ethiopia where the discharge from two rivers draining into the lake is about twice in volume of the direct rainfall over the lake (Legesse et al., 2002; Legesse et al., 2004).
- Groundwater inflow: e.g., Lake Shala in the Ziway-Shala basin of Ethiopia and Lake Magadi in southern Kenya where the groundwater accounts for near half of the total water inflow (Ayenew and Becht, 2008).

Xing *et al.* (2012) established a water budget of the tropical shallow Kranji Reservoir during the year of 2007 using data of water level, reservoir gate operation records, inflow in the main channel as measured using the acoustic Doppler current profilers (ADCP) and inflow predicted using a catchment rainfall/runoff model. It was concluded that the water budget of Kranji Reservoir was dominated by the discharge and catchment inflow, which were very sensitive to the variations in

precipitation. Outflows estimated by using the two approaches for the inflows compared well between them and with the outflow measured at the Kranji Gate confirmed the accuracy of the water budget. XP-SWMM was demonstrated to be useful in predicting water budgets in shallow reservoirs with flow driven by rainfall.

Heat Budget

The study of heat budget is fundamental to establish the thermal balance in the system as it provides direct information on the surface heating and cooling, advective heat transferred by inflows and outflows, and the change of lake heat content. These parameters are essential drivers for the vertical and horizontal thermal stratification and mixing in the lake or reservoir (Lewis, 1983b; Talling and Lemoalle, 1998). In addition, it may aid in studying the variability in the thermal structure and mixing dynamics in a lake or reservoir in both shorter and longer timescales (Xing, 2010).

The interest of the earlier studies on lake heat budgets had focussed on the surface heat fluxes. One-dimensional vertical heat flux models had been applied to various lakes to describe the overall heat balance (e.g., Eggers and Tetzlaff, 1978; Spence et al., 2003; Binyamin et al., 2006; Momii and Ito, 2008). The advective heat associated with inflows and outflows was often considered as a minor source of heat or not measured due to difficulties encountered in assessing this term, and they were thus neglected in the heat budget calculations (e.g., Keijman, 1974; Colomer et al., 1996; Rouse et al., 2003; Binyamin et al., 2006; Momii and Ito, 2008). The findings of many published works on lake heat budgets showed that the input and output of heat energy were dominated by surface heat fluxes including radiation fluxes, latent heat flux and sensible heat flux (e.g., Myrup et al., 1979; Lewis, 1983b; Livingstone and Imboden, 1989; Colomer et al., 1996; Oswald and Rouse, 2004). However, this might not be so for lakes where the water budget was dominated by inflows and outflows (Xing et al., 2012). In such lakes, the advective heat might not be neglected as it was an important component in the heat budget. Xing et al. (2012) concluded that the heat budget of Kranji Reservoir was

dominated by the surface heat flux, while the advective heat flux was also important.

2.10.2. Thermal Stratification and Mixing Dynamics

The thermal stratification and mixing dynamics in tropical lakes or reservoirs are generally affected by external forces such as surface heat fluxes, surface wind field, inflows/outflows, and lake properties, see Han et al. (2000) and Talling and Lemoalle (1998).

Thermal stratification is usually described as an upper warmer layer, called the epilimnion overlying a lower colder layer in the lake, called the hypolimnion. Between the two layers is a region of strong temperature gradient, called the metalimnion (Imberger and Patterson, 1990). The epilimnion is normally considered to be well mixed, responding to mixing induced from the surface wind stress and convective cooling, while the water column is much more stable in the hypolimnion with less mixing and thus limited exchange of heat and dissolved oxygen between the epilimnion and the hypolimnion. However, as Imberger (1985) pointed out, temperature and turbulence intensity are not constant in the surface mixed layer (i.e., the epilimnion), especially when strong surface heating occurs or when the surface layer retreats with reducing wind stress (Imberger and Patterson 1990). The surface layer further responds to diurnal changes in surface fluxes (Imberger, 1985; Imberger and Patterson, 1990). Imberger and Hamblin (1982) proposed the Wedderburn number (W) which indicates the overall dynamics of this layer and accounts for horizontal advection of momentum and mass. In the case where $W \gg 1$, the processes can be deemed as one-dimensional with little tilting of the isotherms and negligible horizontal variations. For $W \ll 1$, the mixed layer tilts in the direction of the wind, causing upwelling at the upwind end of the lake (Monismith, 1986) and corresponding horizontal density gradients will be formed in the surface mixed layer.

Usually, the inflow temperature is lower than surface temperature of reservoir water. When the cold and heavier inflow water enters the lake/reservoir, it plunges and intrudes into the lake/reservoir water below surface (Fischer et al., 1979; Hebbert et al., 1979). The inflow entrains lake water when it flows downstream and causes thermocline erosion (Fischer et al., 1979; Imberger and Patterson, 1990; Han et al., 2000). Wind stress is another essential external force which affects thermal stratification. Surface wind stress introduces momentum and turbulence to the surface mixed layer, and thus mixes the water column (Fischer et al., 1979; Imberger and Parker, 1985; Imberger, 1985). With an increased surface wind stress, the isopycnals, surfaces of constant density in water, rise at the upwind end. This phenomenon indicates that the surface wind stress is balanced by the horizontal pressure gradients created by the tilting isopycnals (Monismith, 1986; Schladow et al., 2004).

Talling and Lemoalle (1998) reviewed mixing dynamics and water temperature cycles in tropical lakes, focusing on deeper tropical lakes and annual cycles of water temperature. Due to the higher radiative heating and lower stability, the thickness of the diurnal mixed layer in tropical lakes is more variable than that of temperate lakes (Lewis, 1987). As a result, convective motions of water between the side arms and the main body of the lake, led by the daytime heating and nighttime cooling, may also contribute to a large degree to the thermal structure and diurnal stratification/destratification cycles (Monismith et al., 1990). In the same fashion, there might be differences in convective processes in tropical lakes (Lewis, 1987).

The thermal structure and mixing dynamics of shallow tropical reservoirs were investigated by Xing (2010) using data collected in the Kranji Reservoir in Singapore. It was shown that temperature stratification of 0.5 to 3.5 degrees was formed during the daylight hours and reduced nightly when cooling occurred. Substantial horizontal redistribution of heat was also observed between the side arms and the main body of the reservoir. The measurements obtained suggested that the phenomenon of stratification in Kranji reservoir was three-dimensional with temperature variations in the vertical, along, and cross-reservoir directions. Vertically, the stratification in the water column depended on the solar radiation,

wind mixing, the penetration of cold inflows and convective cooling. Horizontally, the temperature structure was affected by convective exchanges between shallow arms and main channel, flows towards dam, wind field and reservoir morphometry. The dynamical balance of the system was delicate, with the time scale of changes as short as a day or less. Strong stratification was formed if sufficient net solar radiation was available and reduced almost every day in the reservoir by nighttime cooling. Unlike deeper tropical lakes, where diurnal stratification was often superimposed upon seasonal stratification (Lewis 1973; Talling and Lemoalle, 1998), in shallower lakes like Kranji Reservoir, the whole water column mixes on daily basis for most part of the year. In addition, for shallow lakes like Kranji, notable horizontal variations in thermal structure due to differential heating and spatial differences in the depth of wind mixing are also common (MacIntyre and Melack, 1995; MacIntyre et al., 2002).

The diurnal cycle of stratification observed represents the combined effects of surface heating, wind mixing and inflows/outflows. The data from the field deployment period in 2007 suggested three dynamical regimes: *a solar radiation dominated regime, a windy regime and a cold inflow regime*. These three physical forcing regimes are delineated by two dimensionless numbers, IIW and IWB, with IWB being similar to the Monin-Obukhov length (Imberger, 1985). The solar radiation dominated regime dominates most of the measurement record (86% of the days). Compared to other lakes in the tropical and temperate zones, the tributary inflows and dam outflows in Kranji Reservoir follow a daily time scale and also contribute to the diurnal stratification cycles. Mixing by the wind in Kranji Reservoir can be important at times, but is generally weaker than heating by the incident solar radiation.

2.10.3. The Effect of Shallow Depth

The water depths of tropical lakes also contribute to the differences in stratification cycle and mixing dynamics (Talling, 2001). Most deeper lakes with an average depth exceeding 10 meters in tropical regions only mix once in the “winter” and

stay stratified for the rest of year, i.e., they are warm monomictic lakes. The thermal structure and annual mixing patterns of the warm monomictic tropical lakes have been described in studies of Lake Lanao (Lewis, 1973) and Lake Valencia (Lewis, 1983b), as well as those of Lake Tinaroo (Mackinnon and Herbert, 1996) and Lago San Pablo (Gunkel and Casallas, 2002). In contrast, shallow tropical lakes tend to be polymictic, i.e., mix frequently due to wind mixing and convective cooling at night (MacIntyre and Melack, 2009). The whole water column of shallow tropical lakes may achieve complete mixing on a daily timescale (Lewis, 2000; Talling, 2001). The disparate mixing regimes found in deep and shallow tropical lakes can find their counterparts in the temperate lakes. Deep temperate lakes tend to be dimictic and only achieve complete mixing in spring and fall (Hutchinson and Löffler, 1956; Lewis, 1983a). In contrast shallower temperate lakes, e.g. Clear Lake in California, achieve complete mixing multiple times a year and even partially mix at an almost daily scale (Rueda and Schladow, 2003; Rueda et al., 2003). The mixing dynamics in the shallow polymictic lakes both in tropical and temperate regions are not well studied or understood (Lewis, 1987; Rueda et al., 2003). Furthermore the traditional conceptual model of deep temperate and subtropical lakes in which they have a background stratification that evolves seasonally and is perturbed by distant forcing events (see e.g. Imberger, 1985; Han et al., 2000) may not be adequate to describe the thermal structure and mixing dynamics in shallow tropical lakes well.

2.10.4. Water Quality

The main issues associated with tropical reservoirs are algae bloom, phytoplankton growth, high biological indicators (*E. coli* and *Enterococcus*), and odour (low DO) as a result of excess nutrient (N, P) originated from the reservoir catchment. The overgrowth of toxic producing algae, such as cyanobacteria, has been the main problem in lakes or reservoir world-wide (Leboulanger et al., 2002; Vieira et al., 2005). Published studies have shown that the phytoplankton growth in a lake or reservoir may be affected by a number of factors, such as light climate (Bleiker and Schanz, 1997); meteorological forcing such as radiation fluxes and wind events

(Lewis et al., 1984; Yin et al., 2004); water movement (Byun et al., 2005; Schallenberg and Burns, 1997); nutrients (Pöder et al., 2003; Hunt and Matveev, 2005); and zooplankton and fish (Bouvy et al., 2006).

Significant seasonal variability also exists in the phytoplankton dynamics in tropical lakes (Melack 1979). The seasonal variations of algae concentration and its vertical distribution have been found to be strongly related to seasonal variations of light availability, meteorological forcing and thermal structure in tropical lakes (Talling 1966; Lewis 1978; Melack 1979; Lewis 1986; Gibbs and Vant 1997).

2.11 SUMMARY AND DISCUSSION

Gas exchange at the air-water interfaces has been a subject of extensive research in the literature. Of the conceptual models, the surface renewal model and surface divergence model are believed to be able to describe and model the gas exchange phenomenon well, while it is controversial whether the two-film theory may provide good estimate of the gas transfer coefficient. As one of the aims of this study, the author will then review the original purpose of the two-film model development and attempt to elucidate the validity of this model as presented in Chapter 6.

Basically, to develop a good DO model which is applicable for a watercourse, the model has to take into account all factors (sources and sinks affecting DO budget), especially the important processes such as reaeration, photosynthesis, respiration, BOD, and SOD. In the published studies, it is typically assumed that the water temperature has negligible effect on factors affecting DO budget (O'Connor and Di Toro, 1970) for a river/stream. Following the work reported by O'Connor and Di Toro (1970), Butcher and Covington (1995) implemented an approximate correction to the temperature dependence variable. However, the effects of both water temperature and water depth on the major parameters (i.e. reaeration, photosynthesis, and respiration) that may affect DO budget have not been extensively considered in the modelling of oxygen transfer in a tropical lake/reservoir. This issue is discussed in Chapter 7.

CHAPTER 3

Methodology

3.1 OVERVIEW

To address the research questions, it is the aim of this to seek deeper understanding of the reaeration process at the air-water interface, as well as how dissolved oxygen is transferred into lower layers of a water column. Firstly, the effects of both temperature and turbulence (induced by surface perturbation such as waves) on reaeration process were investigated extensively using a specially designed test-rig. Such phenomenon for quiescent water and low turbulence flow conditions has not been studied extensively and there is very little information available in the literature (see Chapter 2). Therefore, this study would add to the knowledge in the reaeration phenomenon. Secondly, along with the findings obtained, the author attempted to develop a simplified DO model that would be applicable to simulate the vertical distribution of dissolved oxygen in a tropical reservoir in Singapore. To achieve these objectives, the author had designed and fabricated a new experimental system including two main parts, namely (i) a jacketed reaeration water column, and (ii) an auxiliary oscillating water column. In addition, the field data of Kranji reservoir (Singapore) provided by Public Utilities Board (PUB) are fundamental in developing the DO model.

All of the experiments were conducted in the specially designed test-rig located at Maritime Research Centre, Nanyang Technological University. The following sections detail the experiment setup, measurement technique, experimental

conditions of the laboratory experiments, and the description and raw field data of Kranji Reservoir.

3.2 EXPERIMENTAL SETUP AND MEASUREMENT TECHNIQUE

3.2.1 Experimental Components

The reaeration study system comprised a concentric double-cylinder (jacketed water column) and an auxiliary oscillating column (wave maker). A schematic drawing and photograph of the test-rig is shown in Figure 3. 1 and Figure 3. 2, respectively.

Figure 3. 1. A diagrammatic sketch of the DO experiment water column (not to scale); arrows in the jacket indicate direction of circulation of constant temperature water through the system

Figure 3. 2. Photograph of the Test-Rig

3.2.1.1 Jacketed reaeration column and water circulation system

The jacketed water column was made up of 2 concentric cylinders. These cylinders were made of acrylic tubes 2 m in length, making an outer water jacket and an inner test/reaeration column with the diameters of 30 cm and 20 cm, respectively (see

Figure 3. 3). The water jacket was used to maintain the water temperature of the inner water/reaeration column at a desired temperature, and it was also connected to the water circulation system to maintain its water temperature.

The water circulation system consists of a water container (0.1m^3) and a water pump (PEDROLLO; $Q=5\text{-}40\text{l/min}$; $H=5\text{-}38\text{m}$) which was used to pump and circulate the water in the water container and in the water jacket. A heating device was located inside the water container to change its temperature controlled by a thermostat (see Figure 3. 5). The thermostat was used to control the heating device to maintain the water temperature of the water container at pre-set value.

Figure 3. 3. Photographs of Reaeration Column and Auxiliary Column

It is noted that the water container is connected to the water jacket through a water pump and two opposite steel flexible tubes ($d=20\text{mm}$) located at the base of the jacketed water column, see Figure 3. 1. The water flows upwards and then is circulated to the water container by the two flexible heat resistant tubes ($d=25\text{mm}$) connected to the top of the jacketed water column (see Figure 3. 3).

Figure 3. 4. Water Circulation System

Figure 3. 5. Air compressor and Thermostat

3.2.1.2 Auxiliary Oscillating Water Column and Nitrogen Container

The water level oscillation system mainly consisted of an air compressor (Figure 3. 5) and a parallel auxiliary oscillating water column (Figure 3. 3) which was connected to the main/reaeration water column through a 30-cm-tube at the base. The CE air compressor has the characteristics of $Q=35-40$ l/min with the maximum pressure up to 6 Bars, and air tank volume of 3.5 l. In this study, the pressure was operated below 2 Bars, creating a wave height up to 1.5cm. The parallel auxiliary water column has internal diameter of 0.2 m, and 0.6 m long.

Figure 3. 6. The relate used to adjust the frequency of solenoid valve and water wave

Generally, the air pressure above the water level of the side water column was regulated to produce pressure pulses on the water column, and hence generated periodic water level in the side and main water column. The cyclic movement of the water surface simulated vertical harmonic motion at the pre-selected frequency. The frequency and pressure could be adjusted to create mechanical excitation/water level fluctuation of different frequency and height. The driving component of this system was the solenoid valve, 2 Port Sol Valve FKM 230V (VXD2262A-10F-JDOR1), which functioned to create pressure pulses. A relate (Figure 3. 6) was connected to the solenoid valve to adjust its frequency (up to 10 Hz). For example, when the relate is off, the solenoid valve is close and the output pressure of the air compressor and the solenoid valve's pressure increase until the relate is on after a certain period (Δt). As a result, a pressure pulse is created and presses the whole side water column downwards for a specific time (Δt), while the main water column

is moving upwards. After that, the relate is off again, the water level returns to its original location. This process keeps going on, generating the cyclic movement of the water level. It is noted that a controlling valve is used (in addition to the solenoid valve) to balance the pressure above the water level of the auxiliary oscillating water column and the atmosphere pressure when the solenoid valve is close.

In addition, a nitrogen gas container (Figure 3. 7) was connected to the bottom of the reaeration column through a 20-cm-tube to deplete oxygen content inside the reaeration column. The pressure inside the nitrogen gas container may be up to 50 bars, but it was regulated to 2 bars using a pressure regulator. It normally takes about 5-15 minutes to deplete the oxygen concentration inside the reaeration column to the desired initial concentration.

Figure 3. 7. Nitrogen Gas Container

3.2.2 Measurement Equipment – Dissolved Oxygen Meter

Two optical dissolved oxygen (ODO) probes (YSI made; model: ProODO, see Figure 3. 8) were placed close to the free surface ($z=0.065\text{m}$) to measure instantaneous dissolved oxygen concentration in the water column. These two ODO probes were calibrated prior to each and every experiment. The calibration process was followed by YSI ProODO user manual. In this study, 1-point calibration was chosen. Following this calibration process, one needs to moisten the sponge provided in the storage sleeve with a small amount of clean water. It is noted that the sponge should be clean as bacterial growth may consume oxygen and interfere with the calibration. In addition, one must make sure that there are no water droplets on the sensor cap and temperature sensor, and then installs the storage sleeve over the probe. Importantly, the storage sleeve needs to vent to the atmosphere. Then, one may need to wait about 5-10 minutes for the storage container to become completely saturated and to allow the temperature and dissolved oxygen sensors to stabilize.

The specifications of ODO probes are shown in Table 3. 1.

Table 3. 1. ProODO System Specifications (Instrument with Cable & Probe)

	Sensor Type	Range	Accuracy	Resolution
Dissolved Oxygen (%)	Optical (dynamic luminescence quenching lifetime detection)	0 to 500% air saturation	0 to 200% air saturation, $\pm 1\%$ of the reading or $\pm 1\%$ air saturation, whichever is greater; 200 to 500% air saturation, $\pm 10\%$ of the reading	0.1% air saturation
Dissolved Oxygen (mg/L)	Optical (dynamic luminescence quenching lifetime detection)	0 to 50 mg/L	0 to 20 mg/L, ± 0.1 mg/L or $\pm 1\%$ of reading, whichever is greater; 20 to 50 mg/L, $\pm 10\%$ of the reading	0.01 or 0.1 mg/L (auto-scaling)
Temperature		-5 to 70°C	$\pm 0.2^\circ\text{C}$	0.1°C
Barometer		375 to 825 mmHg	± 1.5 mmHg from 0 to 50°C	0.1 mmHg

Source: <http://www.ysi.com/productsdetail.php?ProODO-19>

Figure 3. 8. ODO Meter and ODO Probes

3.3 EFFECT OF TEMPERATURE ON OXYGEN TRANSFER FOR QUIESCENT WATER

3.3.1 Experimental Conditions

In order to study the impact of temperature on oxygen transfer, a number of experiments were conducted using a jacketed water column with a concentric outer and inner cylinder, see Table 4. 2 . A schematic drawing of the experimental setup is shown in Figure 3. 9. A range of water temperature was selected and the temperature ranged from 22°C to 40°C. Two optical dissolved oxygen (ODO) probes (YSI ProODO) were located close to free surface ($z=0.065\text{m}$) to instantaneously measure dissolved oxygen concentration. These two ODO probes were calibrated several times prior to and during each and every experiment run.

Figure 3. 9. A diagrammatic sketch of DO experiment water column

3.3.2 De-oxygenation of Water

Prior to the experiments, nitrogen gas was bubbled through the water column for 15 minutes to purge the dissolved oxygen from the water body to an initial DO concentration of less than 1.5 mg/L. It was noted that the initial dissolved oxygen concentration might not be the same for all the experiments.

3.3.3 Duration of experiments and Measurement Interval

For reaeration studies, the dissolved oxygen is considered to reach its saturation value when the reaeration time reaches a period of $6/K_L a$ (ASCE/EWRI 2-06, 2006) based on the fact that it would typically take at least 22 days for the dissolved oxygen in the water column to reach the saturation level at $T=39.6^\circ\text{C}$. These saturated time values would presumably be longer for lower temperature cases. In this study, the time interval of DO measurement was set at 5 minutes. The

experiment was conducted in accordance to the procedure as stipulated in ASCE/EWRI 2-06.

The results and discussion on this issue are presented in Chapter 4.

3.4 EFFECT OF SURFACE PERTURBATION ON REAERATION

3.4.1 Experiment Setup

14 experiments were performed using a test-rig which comprised a jacketed water column with a concentric double cylinder and a “wave maker”. A schematic drawing of the test-rig is shown in Figure 3. 1. In this study, the wave frequency ranges from 0.125Hz to 0.425Hz and wave height varies from 0.15cm to 1.5cm

The water temperature was set in the range of 30°C to 40°C. Two optical dissolved oxygen (ODO) probes (YSI made; model: ProODO) were placed close to the free surface ($z=0.065\text{m}$) to measure instantaneous dissolved oxygen concentration in the water column. Also, these two ODO probes were calibrated prior to each and every experiment.

It is worth noting the pressure above the reaeration column was atmospheric since it was open to the atmosphere. The oxygen concentration in the air was that of the atmosphere and was treated as constant. There was no circumstance of sub-vacuum being formed and the need for refilling with oxygen. The pressure in the parallel auxiliary column might be positive (above atmospheric) when the solenoid valve was open, and at atmosphere pressure when the solenoid valve was closed. The air pressure in the auxiliary column did not influence the DO concentration in the reaeration column.

3.4.2 Experimental Procedure

The reaeration column was first filled with fresh water to the desired water depth (ranging from 1.6m to 1.7m from base), see Figure 3. 1; valves A, B, and C were all

closed. Then nitrogen gas was bubbled through the column from the bottom for 5 to 10 minutes to purge dissolved oxygen from the water column to the required initial DO concentration (valve B was closed, and valves A and C were opened). Finally, valve C was closed, and valves A and B were opened so that the water levels between the reaeration column and wave maker column were balanced. At the dynamic equilibrium state, the water depth in re-aeration column ranged between 1.1 to 1.2m. It was noted that the initial dissolved oxygen concentration might not had been exactly the same for all the experiments. The duration of the experiment was 24 hours each, except for experiments 3, 4, and 5 which respectively lasted 9, 8, and 7 days so as to estimate the saturated values of DO. The saturation concentration value associated with different run, but the same temperature, is assumed to be the same. The results and discussion of this topic are presented in Chapter 5.

3.5 FIELD MESUREMENTS

Based on the new findings, the author attempted to develop a simplified DO model which is applicable to a tropical reservoir. In this study, Kranji Reservoir was chosen as a case study and its description is illustrated in section 7.3. The studied period was from 22 July 2012 to 25 September 2012. The field data was provided by Water Quality Management and Modelling Division (WQMM), Public Utilities Board (PUB), and included water temperature, dissolved oxygen concentration, DO saturation, chlorophyll-a, and other meteorological parameters such as wind speed, air temperature, rain/shine, etc. These data were used to compare with the simulated results. The DO model was calibrated with the DO data from 22 July 2012 to 19 August 2012. The DO data from 02 September 2012 to 25 September 2012 were used for the validation of the DO model. Generally, the water quality in terms of dissolved oxygen during this studied period is relatively good ($DO > 5\text{mg/L}$). The water temperature varies from 29°C to 31.5°C . The main raw data (DO, temperature, and chlorophyll-a) of Kranji Reservoir are shown in Figure 3. 10 to Figure 3. 21.

Chapter 7 shows the development of the simplified DO model, as well as its application in Kranji Reservoir.

3.5.1 Measured Data Used for the DO Model Calibration

3.5.1.1 Measured Dissolved Oxygen Profiles

Figure 3. 10. Measured DO profiles at different depths of Kranji Reservoir, from Jul 22, 2012 to Aug 05, 2012

Figure 3. 11. Measured DO profiles at different depths of Kranji Reservoir, from Aug 05, 2012 to Aug 19, 2012

3.5.1.2 Measured Water Temperature Profiles

Figure 3. 12. Measured temperature profiles at different depths of Kranji Reservoir, from Jul 22, 2012 to Aug 05, 2012

Figure 3. 13. Measured temperature profiles at different depths of Kranji Reservoir, from Aug 05, 2012 to Aug 19, 2012

3.5.1.3 Measured Chlorophyll-a Profiles

Figure 3. 14. Measured chlorophyll-a profiles at different depths of Kranji Reservoir, from Jul 22, 2012 to Aug 05, 2012

Figure 3. 15. Measured chlorophyll-a profiles at different depths of Kranji Reservoir, from Aug 05, 2012 to Aug 19, 2012

3.5.2 Measured Data Used for the DO Model Validation

3.5.2.1 Measured Dissolved Oxygen Profiles

Figure 3. 16. Measured DO profiles at different depths of Kranji Reservoir, Sep 02-14, 2012

Figure 3. 17. Measured DO profiles at different depths of Kranji Reservoir, Sep 14-25, 2012

3.5.2.2 Measured Temperature Profiles

Figure 3. 18. Measured temperature profiles at different depths of Kranji Reservoir, Sep 02-14, 2012

Figure 3. 19. Measured temperature profiles at different depths of Kranji Reservoir, Sep 14-25, 2012

3.5.2.3 Measured Chlorophyll-a Profiles

Figure 3. 20. Measured chlorophyll-a profiles at different depths of Kranji Reservoir, Sep 02-14, 2012

Figure 3. 21. Measured chlorophyll-a profiles at different depths of Kranji Reservoir, Sep 14-25, 2012

CHAPTER 4

Effects of Temperature on Oxygen Transfer

4.1 INTRODUCTION

The state of the art on the effects of temperature on oxygen transfers is a combination of the surface renewal theory and the two-film theory. Combining Eq. (2.1) with the two-film theory (Lewis and Whitman, 1924), Eq. (2.2), the transfer rate of oxygen in the water body may be expressed as follows:

$$\frac{dC}{dt} = \left(\frac{K_L}{h} \right) (C_s - C) = K_L a (C_s - C) \quad (4.1)$$

where K_L = oxygen transfer coefficient, C_s = saturation concentration of dissolved oxygen, h = average water depth; $a = A/V$; A =area through which oxygen passes;

and V = volume of water body. The term $a=1/h$ and either form is used depending on the application.

The terms (K_L/h) and K_La in Eq. (4.1) can be replaced by k_a and k_2 respectively and are known as the “reaeration coefficient” for the reaeration process in a natural stream/lake. Thus, Eq. (4.1) can also be expressed in the following form:

$$\frac{dC}{dt} = k_2(C_s - C) \quad (4.2)$$

The value of (K_La) or k_2 is dependent on temperature, transfer characteristics (i.e. degree of turbulence), and other factors such as water depth, oxygen concentration in the atmosphere (altitude, for example), pressure, and the present of surfactants. For a turbulent flow, the effects of water depth and surfactants are generally not significant and most researchers ignored such effects; instead they considered only the effects of temperature on the oxygen transfer under various specific turbulence conditions (i.e. Streeter et al., 1936; Downing and Truesdale, 1955; Truesdale and Van Dyke, 1958; Elmore and West, 1961; Metzger, 1968; Bewtra et al., 1970; and Chao et al., 1987). The author is not aware of any published information on the influence of temperature on oxygen transfer rate, as well the variation of reaeration coefficient with depth in a quiescent water column.

To date, it remains open to debate whether oxygen transfer rate increases or decreases with increasing temperature, and under what conditions can the specific temperature correction factor, f_c , be applied. In practice one always corrects for the oxygen transfer rate by making reference to the corresponding value at 20°C, and hence the temperature correction factor, f_c , is simply defined as an exponential (Arrhenius-type) function ($f_c = \theta^{T-20}$). However, it may not provide the physical insight into the nature of water properties; and more important is that the values of θ are locally specified, which could not be scaled up to other physical models or in reality. It is therefore the objective of this chapter to

- (1) present a state-of-the-art review of the effects of temperature on oxygen transfer rate, K_{La} , for turbulent flow conditions;
- (2) propose a reaeration coefficient equation for quiescent and low turbulent conditions;
- (3) verify and demonstrate the validity of the temperature correction factor.

4.2 PREVIOUS CONSIDERATIONS

4.2.1 Effects of Temperature on Oxygen Transfer rate under Turbulence Flow conditions

The question to address is whether the oxygen transfer/reaeration rate increases with temperature. In fact, this proposition appears to be supported by evidence presented by a number of studies. A comprehensive review on this topic could be found in Chao et al. (1987). Generally, the theoretical basis for an increase of oxygen transfer rate with increasing temperature is based on Arrhenius equation that is used to treat the transfer of oxygen between the gas and liquid phases in a similar way to that of a chemical reaction. Absorption of gas molecular into a liquid is considered as a kinetic rate process, and thus the reaeration coefficient following the Arrhenius equation is expressed as follow:

$$K_T = Ie^{-\left(\frac{E}{RT}\right)} \quad (4.3)$$

where K_T = rate of reaction, I = collision factor between molecules, R = universal gas constant, T = absolute temperature, and E = activation energy. One can easily express Eq. (4.3) in the form of $K_T = ae^{bT}$, in which a and b = constants. The parameter K_T is corrected for temperature by making reference to its value at 20°C in the form $K_T/K_{20} = (e^b)^{T-20}$. When (e^b) is replaced by θ , and the equation takes the following form

$$K_T = K_{20}(\theta)^{T-20} \quad (4.4)$$

The validity of Eq. (4.4) appears to be supported by the results of a number of researchers, including Streeter et al. (1936), Downing and Truesdale (1955), Truesdale and Van Dyke (1958), Elmore and West (1961), Metzger (1968), and Bewtra, et al. (1970).

Chao et al. (1987) studied the effects of temperature on oxygen transfer in a constant temperature room where several ambient temperatures (within the range 7°C to 30°C) were selected. The main oxygenation chute was made of a plexi-glass pipe 2.67 m in length and 20.3 cm in diameter. Water flows through the chute at constant flow speed ranging from 0.8 cm/s to 2.8 cm/s. Chao et al (1987) reported that both the measured and the predicted k_2 values increased with temperature when the flow velocity was maintained at 2.8 cm/s. When the flow speed was 1.3 cm/s, the k_2 -temperature curve showed an initial increase followed by decrease. When the velocity was reduced to 0.8 cm/s, the k_2 -temperature relationship depicted a decreasing tendency with temperature. Meeks et al. (1980) and Chao and Galarraga (1981) also reported these behaviors. However, the findings on the k_2 -temperature relationship are not conclusive.

4.2.2 Temperature Correction Factor Models

In practice one always corrects for the oxygen transfer rate by making reference to the corresponding value at 20°C, and hence the temperature correction factor, f_c , is defined as

$$f_c = \frac{K_L(T)}{K_L(20)} \quad (4.5)$$

where $K_L(T)$ and $K_L(20)$ = the value of K_L at $T^\circ\text{C}$ and 20°C , respectively

The conventional approach (Elmore and West, 1961; Bewtra 1970) considered f_c as an exponential (Arrhenius-type) function:

$$f_c = \theta^{T-20} \quad (4.6)$$

where θ was considered as a constant. It is noted that oxygen transfer is a diffusion process and is also influenced by the flow characteristics close to the air-water interface. The parameter K_L (or k_2) is not a “true” reaction rate coefficient, but an equivalent coefficient. Thus, Eq. (4.6) is purely empirical, and θ has been estimated based on oxygen transfer data.

Metzger (1968) reported a θ value ranging from 1.008 to 1.047, and concluded that the temperature correction coefficient is not a constant, but is a function of temperature, and turbulence level among other influences.

Bewtra (1970) studied the effects of temperature on oxygen transfer through diffusion for temperature in the range of 10-30°C and reported a θ value of 1.0192. Elmore and West (1961) carried out a series of carefully controlled experiments in a stirred and well-mixed reactor and determined that $\theta = 1.0241$. This θ -value has been widely used to account for the effects of temperature, see for example Isaac & Gaudy (1968). The same θ -value has been recommended by ASCE (1984, 2006). While the empirical relationships are practical and useful, there is a need to account for the effect of temperature in a comprehensive model. As a departure from the Arrhenius-type temperature correction factor, Metzger and Dobbins (1967) and Metzger (1968) used the film penetration model for K_L as follow:

$$K_L = (Dr)^{\frac{1}{2}} \coth \left(\frac{rL^2}{D_m} \right)^{\frac{1}{2}} \quad (4.7)$$

in which r = surface renewal rate of the liquid; L = liquid film thickness; and D_m = molecular diffusivity of the gas in the liquid film. When the surface film is neglected, i.e. there is no renewal of the film and $r = 0$, the value of $K_L = D_m/L$ (the film model). When r is large, the K_L value approaches $(D_m r)^{1/2}$ (the renewal model). Daniil and Gulliver (1988) used Metzger’s and Dobbin’s assumptions, a Stokes-type relation, $D_m \nu \rho / (T+273) = \text{constant}$, and ρ_{20}, ν_{20} = the values of ρ and ν at 20°C, respectively, and derived the following expressions:

for the renewal model:

$$f_c = \left(\frac{T + 273}{293} \right)^{0.5} \left(\frac{v_{20}}{v_T} \right)^{0.125} \quad (4.8)$$

and for the film model:

$$f_c = \left(\frac{T + 273}{293} \right) \left(\frac{v_{20}}{v_T} \right)^{1.75} \frac{\rho_{20}}{\rho_T} \quad (4.9)$$

Coantic (1986) proposed a model for gas transfer across the air-water interface and reported that K_L is a function of the Schmidt number, $Sc = \nu/D_m$, in which $K_L \propto Sc^n$, where n varies between $-2/3$ and $-1/2$ depending on the agitation level. Later Daniil and Gulliver (1988) suggested adopting Coantic's equation associated with $Sc^{-1/2}$ for the conversion factor from one temperature to another and for all gas under turbulent transport conditions as in the following form.

$$f_c = \left[\frac{Sc(20)}{Sc(T)} \right]^{1/2} = \left(\frac{T + 273}{293} \right)^{1/2} \left(\frac{v_{20}}{v_T} \right) \left(\frac{\rho_{20}}{\rho_T} \right)^{1/2} \quad (4.10)$$

4.3 THEORETICAL CONSIDERATIONS

4.3.1 Absorption of oxygen into quiescent water

A mathematical model has been developed for a completely stagnant situation, where the hydrodynamic effects are negligible (Socolofsky and Jirka, 2002). It is assumed that the initial oxygen concentration along a water depth is C_o , which is less than the saturated value of oxygen C_s . The air-water interface is then instantaneously exposed to the air (oxygen source). Owing to the concentration deficit ($C_s - C_o$) between the two phases, oxygen has the tendency to diffuse and dissolve into the water until the water column reaches a uniform concentration of

C_s . It is noted that the surface layer reaches saturation earlier, and the rate is lower with depth as the diffusion process in water is a much slower process away from the surface.

A one-dimensional governing transport equation for quiescent water may be described as below:

$$\frac{\partial C}{\partial t} = D_m \frac{\partial^2 C}{\partial z^2} \quad (4.11)$$

The boundary and initial conditions are:

$$C = C_s, z=0, t>0$$

$$C = C_o, z>0, t=0$$

$$C = C_o, z=\infty, t>0$$

The solution of Eq. (4.11) for diffusion into a “semi-infinite” liquid associated with above conditions is

$$C(z, t) = C_o - (C_s - C_o) \operatorname{erfc} \left[\frac{z}{\sqrt{2\delta}} \right] \quad (4.12)$$

where $\delta = \sqrt{2D_m t}$ is the characteristic thickness of the viscous sub-layer or the concentration boundary layer; z is water depth (positive downwards). It is plausible that this viscous sub-layer is thicker for quiescent water.

Based on Eq. (4.12), one can derive an expression for boundary flux at the air-water interface ($z=0$) using Fick's law. Writing the flux law for the stagnant case in 1D, one may obtain

$$J_z = uC - D_m \left. \frac{\partial C}{\partial z} \right|_{z=0} = -D_m \left. \frac{\partial C}{\partial z} \right|_{z=0} \quad (4.12a)$$

Since $u=0$ (stagnant water), substituting Eq. (4.12) to Eq. (4.12a), one can compute J_z as follows

$$J_z(t) = -(C_s - C_0) \sqrt{\frac{D_m}{\pi t}} \quad (4.12b)$$

In addition, the boundary flux can be written as

$$J_z(t) = -K_L(C_s - C_0) \quad (4.12c)$$

As a result, the gas transfer coefficient can be defined as

$$K_L = \sqrt{D_m/(\pi t)} \quad (4.13)$$

Eq. (4.13) was used to develop the penetration model of Higbie (1935). Danckwerts (1951) modified Higbie's model to allow for a random distribution of surface ages, leading to the relation $K_L \sim (D_m r)^{1/2}$, where r was defined as the rate of surface renewal. It can be seen that K_L becomes very low after a time, unless the surface is renewed by mixing or by convection (Dankwerts, 1951). In fact, the applicable range of Eqs. (4.12) and (4.13) is limited to turbulent flow conditions. Thus developing a new model for quiescent water or low turbulent flow condition is necessary.

4.3.2 Proposed Reaeration Coefficient in a Quiescent Water and Low Turbulence Flow Conditions

In order to define the reaeration coefficient for DO transfer in a quiescent water body, a dimensional analysis of the phenomenon based on a set of relevant variables was performed. The variables are listed in Table 4. 1.

Table 4. 1. Variables for dimensional analysis

Variable	Symbol	Dimensions
Reaeration coefficient	$K_L a$	T^{-1}
Molecular diffusivity of oxygen into water	D_m	$L^2 T^{-1}$
Water density	ρ	ML^{-3}
Dynamic Viscosity	μ	$ML^{-1} T^{-1}$
Kinematic Viscosity	ν	$L^2 T^{-1}$
Water depth	z	L
Gravity constant	g	LT^{-2}

Considering the variables involved in oxygen transfer process as given in Table 4. 1, there must exist a functional relationship of the following

$$f(K_L, a, z, g, \mu, \rho, D_m) = 0 \quad (4.14a)$$

By using the approach of dimensional analysis, one obtains the following dimensionless parameters:

$$f(\pi_1, \pi_2) = 0 \quad (4.14b)$$

The dimensionless parameters π_1 and π_2 are

$$\pi_1 = K_L a \frac{z^{1/2}}{g^{1/2}} = \frac{K_L a z}{\sqrt{g z}} \quad (\text{a form of Froude Number})$$

$$\pi_2 = Sc = \frac{\mu}{\rho D_m} = \frac{\nu}{D_m} = \text{Schmidt number}$$

The general equation relating these two dimensionless parameters can be written as

$$\pi_1 = \phi(\pi_2) \quad (4.15)$$

$$\text{Or } K_L a \frac{z^{1/2}}{g^{1/2}} = \phi \left(\frac{v}{D_m} \right) \quad (4.16)$$

By examining the functional relationship of Eq. (4.16), the equation may also be expressed as a power function as shown in Eq. (4.17).

$$K_L a \frac{z^{\frac{1}{2}}}{g^{\frac{1}{2}}} = c \left(\frac{v}{D_m} \right)^{\beta} \quad (4.17)$$

in which c and β are constants. Eq. (4.17) can be further expressed as below

$$K_L a = \frac{cg^{\frac{1}{2}}}{z^{\frac{1}{2}}} \left(\frac{v}{D_m} \right)^{\beta} = \frac{cg^{\frac{1}{2}}}{z^{\frac{1}{2}}} S c^{\beta} \quad (4.18)$$

The author used Eq. (4.18) to perform a correlation analysis of the variable $K_L a$, v , z , g , and D_m . The constants c and β are determined using a least squares curve fitting technique based on the experimental data of $K_L a$ and T (see Table 4. 3).

The author also proposed that the oxygen transfer rate under quiescent water condition may be expressed as Eq. (4.19), where K_L is defined as $K_L a \times z$ from Eq. (4.18).

$$K_L = cg^{1/2} z^{1/2} S c^{\beta} \quad (4.19)$$

As compared to Eq. (4.13), the oxygen transfer coefficient, K_L , is not only a function of molecular diffusion, but also the water depth, z , for quiescent water.

4.3.3 Proposed Temperature Correction Factor

Based on Eq. (4.5) and substitution of Eq. (4.18), the author obtains

$$f_c = \frac{K_L a(T)}{K_L a(20)} = \frac{\left(\frac{cz^{1/2}}{g^{1/2}} \left(\frac{v}{D_m} \right)^\beta \right)_T}{\left(\frac{cz^{1/2}}{g^{1/2}} \left(\frac{v}{D_m} \right)^\beta \right)_{20}} = \left(\frac{v_T}{v_{20}} \right)^\beta \left(\frac{D_{m20}}{D_{mT}} \right)^\beta \quad (4.20)$$

Molecular diffusivity can be calculated using the Stokes-Einstein equation (Wilke, 1949) expressed in the following form:

$$D_{mT} = J \frac{T}{\mu} \quad (4.21)$$

in which J is a constant ($\text{gm-cm/s}^2\text{-}^0\text{K}$) independent of the water temperature; $\mu = \rho v$ is the dynamic viscosity of water (centipoises). Thus, the ratio of molecular diffusivity of Eq. (4.20) can be rewritten as below:

$$\frac{D_{m20}}{D_{mT}} = \left(\frac{J \frac{273 + 20}{\rho_{20} v_{20}}}{J \frac{273 + T}{\rho_T v_T}} \right) = \left(\frac{293}{273 + T} \right) \left(\frac{v_T}{v_{20}} \right) \left(\frac{\rho_T}{\rho_{20}} \right) \quad (4.22)$$

Substituting Eq. (4.22) in Eq. (4.20), one can obtain the temperature correction factor for quiescent water condition as following

$$f_c = \left(\frac{293}{273 + T} \right)^\beta \left(\frac{v_T}{v_{20}} \right)^{2\beta} \left(\frac{\rho_T}{\rho_{20}} \right)^\beta \quad (4.23)$$

It is worth noting that Eq. (4.23) is used as the conversion factor from one temperature to another under quiescent water or low turbulent transport condition.

4.4 RESULTS AND DISCUSSION

The experimental performance is described in section 3.3. It is noted that the temperature was uniform in water column and the overlying air. The experimental conditions are summarized in Table 4. 2. The water temperature at various cases was varied from 21.6°C to 39.6°C. The measured DO concentration were obtained by averaging the two ODO-Probes-value curves at a fixed depth, $z=0.065\text{m}$. The

maximum span of concentration change measured from the two probes was 0.1 mg/L and the standard deviation (SD) was 0.07 for each experiment. Thus, the results in Figure 4. 1 were only presented in average values.

4.4.1 Saturation Dissolved oxygen concentration

The saturation dissolved oxygen concentration for tap water was found to be significantly less than the reported DO saturation values for distilled water (Benson and Krause, 1984) of 8.5% after correction for temperature and barometric pressure. The difference was found to range from 0.46 mg/L to 0.76 mg/L, plausibly due to the characteristic of the tap water in the laboratory.

Table 4. 2. Summary of Experiment Conditions and Results

No.	T (°C)	C _o (mg/L)	C _s (mg/L)	Measured DO concentration	Predicted DO concentration	Truncation of Initial Data (%)
				K _L a ^a (1/day)	K _L a ^b (1/day)	
1	21.6	1.52	8.14	0.152 (0.144÷0.166)	0.154	18.67
2	27.7	1.24	6.96	0.186 (0.177÷0.194)	0.188	17.81
3	29.4	1.25	6.79	0.203 (0.194÷0.210)	0.198	18.41
4	32.2	1.16	6.71	0.222 (0.214÷0.232)	0.215	17.29
5	35.1	1.20	6.38	0.228 (0.222÷0.234)	0.234	18.81
6	39.6	1.10	5.93	0.264 (0.253÷0.274)	0.265	18.55

^aCalculated using Eq. (4.24)

^bCalculated using Eq. (4.25)

4.4.2 Reaeration Coefficient (K_La)

For low turbulent flow condition, it is plausible to assume that the water column may be divided into multiple sub-layers with two ODO probes in each sub-layer. Each sub-layer is considered to be homogeneous and the saturation dissolved oxygen concentration is constant and has its own value in that sub-layer. Then the results obtained for each sub-layer (depth, z) can be analyzed by using a simplified mass transfer model to estimate the reaeration coefficient, K_La, and the steady-state DO saturation concentration, C_s^z. The model of Brow and Bailod (1982) is adopted here, and is given by

$$C_z = C_s^z - (C_s^z - C_o)\exp(-K_L a t) \quad (4.24)$$

where C_z = DO concentration at the depth z ; C_s^z = determination point value of the steady-state DO saturation concentration at the depth z as time approaches infinity; C_o = initial DO concentration; and $K_L a$ = reaeration coefficient at depth z .

Using nonlinear regression analysis of Eq. (4.24), the values of oxygen transfer rate $K_L a$ are calculated and shown in Figure 4. 1 and listed in Table 4. 2 as the measured values. It is noted that the value of $K_L a$ is dependent of how C_s^z is assumed. Eq. (4.24) can be rearranged into the form of $(C_s - C)/(C_s - C_o) = \alpha \exp(-K_L a t)$. Therefore, the best value of $K_L a$ is associated with $\alpha=1$. In order to provide the confidence range of $K_L a$ according to this study α is chosen to vary between 0.95 and 1.05. It is found that the value of $K_L a$ obtained lie within ± 0.01 (day^{-1}) as shown in Figure 4. 2.

Figure 4. 1. Estimation of Reaeration coefficients under various temperatures

Figure 4. 2. Oxygen transfer rate, $K_L a$, and temperature relationship under non-turbulence condition

4.4.3 Determination of $K_L a$ and temperature correction factor

The measured physical parameters (z , g , T , v , and D_m) were analyzed using Eq. (4.17) so as to estimate the values of c and β . These values were in turn substituted in Eq. (4.18) and Eq. (4.23) to determine the values of $K_L a$ and temperature correction factor, f_c . It is noted that the value of J in Eq. (4.21) for quiescent water is $0.714 \times 10^{-7} \text{ gm-cm/s}^2 \cdot ^\circ\text{K}$ (International Critical Tables (1929)).

Based on the results shown in Table 4. 3, the respective values of c and β are estimated as 8.42×10^{-6} and -0.666 ($-2/3$) using linear regression ($R^2 = 0.986$, $P < 0.01$). The value of reaeration coefficient can be estimated by substituting the above-mentioned respective values of c and β into Eq. (4.18), which yields Eq. (4.25):

$$K_L a = \frac{8.42 \times 10^{-6} g^{1/2}}{z^{1/2}} \left(\frac{v}{D_m} \right)^{-2/3} = \frac{8.42 \times 10^{-6} g^{1/2}}{z^{1/2}} (Sc)^{-2/3} \quad (4.25)$$

in which ν is kinematic viscosity (cm^2/s); D_m is water molecular diffusivity (cm^2/s); $g=9.81 \text{ m/s}^2$; $K_L a$ is reaeration coefficient (1/s). The values of $K_L a$ obtained based on Eq. (4.25) is in good agreement with the relationship reported by Coantic (1986) and Jähne et al. (1987) for smooth surface condition based on $Sc^{-2/3}$. Figure 4. 3 shows the comparison between the experimental measured and estimated $K_L a$.

The temperature correction factor equation, Eq. (4.26), can be obtained by substituting the value of $\beta=-2/3$ in Eq. (4.23).

$$f_c = \left(\frac{T + 273}{293} \right)^{2/3} \left(\frac{\nu_{20}}{\nu_T} \right)^{4/3} \left(\frac{\rho_{20}}{\rho_T} \right)^{2/3} \quad (4.26)$$

Table 4. 3. Intermediate results showing calculation of predicted $K_L a$

T	ν (cm^2/s)	D_m (cm^2/s)	g (m/s^2)	ν/D_m	$k_L a z^{1/2}/g^{1/2}$	$\log(\nu/D_m)$	$\log(k_L a z^{1/2}/g^{1/2})$
21.6	0.0097	2.1824×10^{-5}	9.80665	442.58	1.432×10^{-7}	2.6460	-6.8440
27.7	0.0084	2.5624×10^{-5}	9.80665	328.20	1.753×10^{-7}	2.5161	-6.7563
29.4	0.0081	2.6738×10^{-5}	9.80665	303.27	1.913×10^{-7}	2.4818	-6.7183
32.2	0.0077	2.8626×10^{-5}	9.80665	267.28	2.092×10^{-7}	2.4270	-6.6795
35.1	0.0072	3.0650×10^{-5}	9.80665	235.59	2.148×10^{-7}	2.3722	-6.6679
39.6	0.0066	3.3929×10^{-5}	9.80665	195.38	2.488×10^{-7}	2.2909	-6.6042

Figure 4. 3. Comparison between Measured $K_L a$ and Predicted $K_L a$ Values

4.4.4 Determination of reference Reaeration coefficient $K_{La}(20)$

A number of models, corresponding to Eqs. (4.8), (4.9), (4.10) and (4.26), were used to estimate the value of oxygen transfer rate at 20°C, and the values obtained are listed in Table 4. 4. It is clear that the result obtained from the author's proposed model agrees well with the extrapolated value of oxygen transfer rate ($K_{La}(20) = 0.146$) at this reference temperature based on the best-fit curve ($K_{La}=0.0810\text{Exp}(0.0302T)$, see Figure 4. 2). Based on the values of $K_{La}(20)$ obtained from various model, the author deduced that the proposed model is closer to Film model than of the Surface Renewal model.

Table 4. 4. Estimation of K_{La} at 20°C with various models

T°C	Density (ρ) kg/m ³	Kinematic Viscosity (ν) mm ² /s	Proposed Model		Free Surface Model		Renewal Model		Film Model	
			f_c	$K_{La}(20)$	f_c	$K_{La}(20)$	f_c	$K_{La}(20)$	f_c	$K_{La}(20)$
21.6	997.873	0.0097	1.057	0.144	1.042	0.146	1.008	0.151	1.076	0.141
27.7	996.309	0.0084	1.290	0.144	1.210	0.154	1.036	0.180	1.401	0.133
29.4	995.817	0.0081	1.360	0.149	1.259	0.161	1.043	0.195	1.503	0.135
32.2	994.955	0.0077	1.479	0.150	1.341	0.166	1.056	0.210	1.681	0.132
35.1	993.992	0.0072	1.609	0.142	1.429	0.160	1.069	0.213	1.879	0.121
39.6	992.357	0.0066	1.823	0.145	1.569	0.168	1.088	0.243	2.218	0.119
Average				0.146		0.159		0.199		0.130
STD				0.003		0.008		0.031		0.008

4.4.5 Model Comparison

One could find the comparison among various models and experimental data for turbulent flow condition in Danniil and Gulliver (1988). Figure 4. 4 shows a set of data from Elmore and West (1961) that was used to validate Daniniil and Gulliver's proposed equation for turbulence flow condition.

Here the author aims to investigate the reaeration phenomenon in quiescent water or low turbulent condition. The effects of temperature would be more pronounced for low oxygen transfer coefficients, see Metzger and Dobbins (1967) and Danniil and Gulliver (1988)). In Figure 4. 4, the author's proposed model (Eq. (4.26)), the results of Metzger and Dobbins (1967) for low mixing condition and the author's experimental results for non-turbulent condition are presented for ease of

comparison. It is clear that these data fitted well with Eq. (4.26). This finding lends confidence to the use of the author's proposed equation as the choice model for this study.

Figure 4. 4. Comparison of Equations and Experimental Data for Temperature Correction Factor f_c against Temperature

4.5 CONCLUSIONS

Effects of temperature on reaeration rate were investigated based on laboratory experiments. The Schmidt number obtained lies between 195 and 443 and the study is for the condition of low or non-turbulence flow condition. A mathematical model for estimating reaeration coefficients and a temperature correction factor were proposed. The findings of the study include the followings:

1. The experimental results demonstrate clearly that oxygen transfer rate increases with increasing temperature;
2. A mathematical model for oxygen transfer rate prediction at different temperature and water depth for quiescent water and low turbulence flow has

been established (Eq. (4.25)). The simulated results of the proposed model fitted well with the experimental data.

3. Based on the model it can be deduced that reaeration rate decreases with water depth and the magnitude decreases as a function of $z^{0.5}$, where z is depth of water below the surface. This finding forms the basis for the development of the simplified DO model in Chapter 7. In addition, a new relationship is developed for the transformation of the reaeration rate constant for a temperature to another (Eq. (4.26)).

CHAPTER 5

Effect of Small Surface Perturbation or Small Amplitude Waves on Reaeration

5.1 INTRODUCTION

Reaeration is a process by which oxygen in the atmosphere diffuses across the interface between the atmosphere and an open water body such as a river, lake, and ocean. This physical diffusion process, like molecular and turbulent diffusions, ultimately takes place at the molecular diffusion level. For slightly soluble gases, such as O_2 and CO_2 , the transfer rate is greatly governed by the diffusivity on the liquid side while that on the air side, though with much larger diffusivity, is immaterial when it comes to diffusion across the air-liquid interface. The gas transfer across this interface is typically described using the Fick's law which states that the flux of oxygen from the atmosphere into water is proportional to the dissolved oxygen concentration gradient in water. The constant of proportionality is

known as the coefficient of oxygen diffusion. The transfer is positive from higher to lower dissolved oxygen (DO) concentration, i.e.

$$\frac{dm}{A dt} = -D_m \left(\frac{dC}{dz} \right) \quad (5.1)$$

where m = the mass of dissolved oxygen; t = time; C = bulk concentration of dissolved oxygen at time t ; D_m = molecular diffusivity of dissolved oxygen; A = area through which oxygen passes; and z = distance in the direction normal to the surface and is positive downwards. Using the two-film theory (Lewis and Whitman, 1924), the concentration gradient across the stagnant film layer, δ_{SFL} , is defined as in Eq. (5.2). The validity of the two-film theory will be elucidated and presented in chapter 6.

$$\frac{dC}{dz} \approx - \frac{(C_s - C)}{\delta_{SFL}} \quad (5.2)$$

Substituting Eq. (5.2) and $m = CV$ into Eq. (5.1), the transfer rate of oxygen in the water column may be expressed as follows:

$$\frac{dC}{dt} = \frac{D_m}{\delta_{SFL}} \frac{A}{V} (C_s - C) = \frac{K_L}{h} (C_s - C) = k_2 (C_s - C) \quad (5.3)$$

where $K_L = k_2 h = D_m / \delta_{SFL}$ = oxygen transfer coefficient; C_s = saturation concentration of dissolved oxygen; h = average water depth, and $k_2 = K_L / h$ is the reaeration coefficient. Eq. (5.3) has been widely used by a number of researchers to estimate the value of the reaeration coefficient under various scenarios (Herlina and Jirka, 2004, 2008; Downing and Truesdale, 1955; Daniil and Gulliver, 1991). The solution is obtained by integrating Eq. (5.3) with respect to time. Introducing the initial condition $C = C_o$ at time $t=0$ yields

$$\ln(C_s - C_o) - \ln(C_s - C) = k_2 t \quad (5.4)$$

and k_2 may be estimated as the gradient of the linear plot of the left hand side term of Eq. (5.4) as a function of time. In general, the reaeration coefficient, k_2 , may be considered as a lump parameter resulting from the combination of a number of factors, including (i) various types of surface agitation induced by waves or wind, (ii) turbulence level in the water, (iii) temperature of the water, (iv) the presence of soluble and insoluble surface contaminants, and (v) forced or natural convection. Indeed, the reaeration coefficient is not only dependent on the molecular diffusion, but also on the turbulent intensity. According to Gualtieri and Mihailović (2008), there are three categories of turbulence sources: (a) turbulence generated across an “un-sheared” interface, (b) combined wind and stream turbulence, and (c) turbulence generated across sheared interface. Detailed review can be found in section 2.7.

Wave induced turbulence may be viewed as the one that is generated across a sheared interface. Downing and Truesdale (1955) carried out experiments on the influence of mechanically generated waves on oxygen transfer. They reported that increasing either the height or frequency of progressive waves in the water caused an approximately linear increase in the rate of oxygen transfer for high turbulent conditions. Daniil and Gulliver (1991) studied the influence of both breaking wave and non-breaking wave on air-water gas transfer. These authors proposed a number of expressions which constituted the surface renewal model that fit the experimental data well. The gas-transfer coefficient was shown to be proportional to the vertical wave velocity at the water surface, leading to the dependence of oxygen transfer coefficient on the product of wave height and wave frequency. Further, these authors stated that when breaking waves or bubbles were present, the gas transfer velocity increased significantly.

This chapter presents the findings on the effects of mechanically generated waves on oxygen transfer rate under laminar flow environment for which there is little reported information in the literature. A dedicated test rig was designed and fabricated to investigate reaeration process under low turbulence condition as detailed in section 3.4. Eq. (5.5) proposed by Daniil and Gulliver (1991) is adopted to describe the reaeration process, and the diffusive film thickness, δ_D , is proposed

to unify the reaeration process in a still water body with surface perturbation (surface wave, ripples, for example).

5.2 PREVIOUS CONSIDERATION - Surface Renewal Model

The concept of surface-renewal model $K_L \sim (D_m r)^{1/2}$ first proposed by Danckwerts (1951) is considered in this study. Here r is defined as the rate of surface renewal (1/s). Daniil and Gulliver (1991) reported that their proposed surface-renewal model is applicable to describe the gas exchange phenomenon associated with mechanically generated wave. In their study, r was expressed in terms of the wave characteristics and defined as $\frac{a_r^2 V_{\max}}{H} \text{Re}_w$, where the wave height (H) was the characteristic depth and $\text{Re}_w = V_{\max} H / \nu$ was wave Reynolds number. Here $V_{\max}$ was defined as $\pi H f$, a_r was a constant, and f was wave frequency. These authors found that $K_L \text{Sc}^{1/2}$ is proportional to Hf and proposed the following relationship:

$$K_L \text{Sc}^{1/2} = c H f + b \quad (5.5)$$

in which Sc =Schmidt number = ν/D_m ; c and b are constants; $c=0.0159$ and $b=0$ as reported by Daniil and Gulliver (1991). The term $K_L \text{Sc}^{1/2}$ is a parameter that measures the rate of oxygen transfer and Sc accounts for the effects of temperature.

5.3 RESULTS AND DISCUSSION

The experimental results are presented in Table 5. 1 and Table 5. 3. The fluid viscosities, ν and μ , were functions of temperature and determined according to (Kestin, et al. 1978), and D_m was calculated from the Stokes-Einstein equation (see Eq. (5.6))

$$D_m = 7.4 \times 10^{-8} \frac{(xM)^{1/2} T}{\mu V^{0.5}} \quad (5.6)$$

The coefficients were 2.26 (Reid et al., 1977; and Cussler, 1997) and 25.6 cm²/mol for association factor (x) of H₂O and molar volume (V) of O₂ (Wilke and Chang,

1955), respectively. This study does not aim to evaluate the accuracy of this equation and the calculation as the experiments had not been designed for this purpose.

All measured values of DO were based on the average of the two measured DO values measured using the two DO probes at a fixed depth, $z=0.065\text{m}$.

5.3.1 Estimation of Reaeration Coefficient (k_2)

The maximum span of concentration change measured from the two probes was 0.1 mg/L and the standard deviation (SD) was 0.07 for each experiment. Thus, the results in Figure 5. 1 were only presented in average values. Using Eq. (5.4), the experimental results of DO concentration over time after de-oxygenation are plotted and shown in Figure 5. 1. The gradients of the fitted straight lines yield the values of k_2 , which are in turns used to determine K_L , see Table 5. 3.

Table 5. 1. A summary of Experimental Conditions and parameters

No.	C_o (mg/L)	C_s (mg/L)	T ($^{\circ}\text{C}$)	ν (cm^2/s)	D_m (cm^2/s)	$Sc=\nu/D_m$	H (m)	F (Hz)
R1	1.26	6.70	30.0	0.0080	2.563×10^{-05}	312	0.0015	0.275
R2	2.64	6.70	30.0	0.0080	2.563×10^{-05}	312	0.003	0.275
R3	1.35	6.70	30.0	0.0080	2.563×10^{-05}	312	0.004	0.275
R4	1.21	6.26	35.7	0.0071	2.936×10^{-05}	243	0.004	0.275
R5	1.17	5.87	39.4	0.0067	3.192×10^{-05}	208	0.004	0.275
R6	2.99	6.70	30.0	0.0080	2.563×10^{-05}	312	0.002	0.125
R7	1.36	6.70	30.0	0.0080	2.563×10^{-05}	312	0.004	0.125
R8	1.25	6.26	35.7	0.0071	2.936×10^{-05}	243	0.004	0.125
R9	1.21	5.87	39.4	0.0067	3.192×10^{-05}	208	0.004	0.125
R10	2.97	6.70	30.0	0.0080	2.563×10^{-05}	312	0.0065	0.125
R11	4.11	6.70	30.0	0.0080	2.563×10^{-05}	312	0.015	0.125
R12	1.28	6.70	30.0	0.0080	2.563×10^{-05}	312	0.0015	0.425
R13	1.23	6.26	35.7	0.0071	2.936×10^{-05}	243	0.0015	0.425
R14	1.15	5.87	39.4	0.0067	3.192×10^{-05}	208	0.0015	0.425

Figure 5. 1. Distribution of DO concentration with time for various water level perturbations (constant temperature at 30°C)

5.3.2 Discussion on Flow Condition

To evaluate the flow turbulence conditions of these experiments, the Stokes layer thickness (i.e. Hino et al. (1976)) is adopted. Basically, the Stokes layer thickness is defined as follows

$$\delta = (2\nu/\omega)^{1/2} \quad (5.7)$$

with $\omega = 2\pi/T$ (T = period of oscillating motion) and the Reynolds number defined in term of the oscillating mean velocity amplitude U and the Stokes layer thickness is describes as below

$$Re_\delta = \frac{U\delta}{\nu} \quad (5.8)$$

The term Re_δ may also be related to Re_d through $Re_d = 2\lambda Re_\delta$, where Re_d is defined as Ud/ν and the Stokes parameter (λ), the ratio of the radius ($d/2$) and the Stokes

boundary-layer thickness, is defined as $\lambda = \frac{d/2}{\delta} = \frac{d}{2}(\omega/2\nu)^{1/2}$. The main parameters are summarised in the Table 5. 2 below.

Table 5. 2. Estimation of Reynolds numbers

No.	H (m)	f (Hz)	ν (m ² /s)	$\omega=2\pi f$	$U=\pi Hf$ (m/s)	$\delta=(2\nu/\omega)^{1/2}$	$\lambda=d/(2\delta)$	Re_d	$Re_\delta=U\delta/\nu$
R1	0.0015	0.275	8.0071×10^{-07}	1.73	0.00130	0.000963	103.85	324	1.6
R2	0.003	0.275	8.0071×10^{-07}	1.73	0.00259	0.000963	103.85	647	3.1
R3	0.004	0.275	8.0071×10^{-07}	1.73	0.00345	0.000963	103.85	863	4.2
R4	0.004	0.275	7.13541×10^{-07}	1.73	0.00345	0.000909	110.01	968	4.4
R5	0.004	0.275	6.6508×10^{-07}	1.73	0.00345	0.000878	113.94	1039	4.6
R6	0.002	0.125	8.0071×10^{-07}	0.79	0.00079	0.001428	70.01	196	1.4
R7	0.004	0.125	8.0071×10^{-07}	0.79	0.00157	0.001428	70.01	392	2.8
R8	0.004	0.125	7.13541×10^{-07}	0.79	0.00157	0.001348	74.17	440	3.0
R9	0.004	0.125	6.6508×10^{-07}	0.79	0.00157	0.001302	76.82	472	3.1
R10	0.0065	0.125	8.0071×10^{-07}	0.79	0.00255	0.001428	70.01	637	4.6
R11	0.015	0.125	8.0071×10^{-07}	0.79	0.00589	0.001428	70.01	1471	10.5
R12	0.0015	0.425	8.0071×10^{-07}	2.67	0.00200	0.000775	129.10	500	1.9
R13	0.0015	0.425	7.13541×10^{-07}	2.67	0.00200	0.000731	136.76	561	2.1
R14	0.0015	0.425	6.6508×10^{-07}	2.67	0.00200	0.000706	141.65	602	2.1

In this study, U is defined as the maximum velocity and equal to πHf (Daniil and Gulliver, 1991). The experiments were performed for the values of Reynolds number Re_δ ranging from 1.4 to 10.5 (or for the values of Reynolds number Re_d in the range of 196 to 1471) and for the values of the Stokes parameter λ from 70 to 142. Sergeev (1966) reported the critical value of Reynolds number of 500, 550 as suggested by Hino et al. (1976). Based on the classification of the types of oscillatory flow (Hino et al. (1976), the flow condition of this study is laminar flow as its Reynolds number ranges from 1.4 to 10.5.

5.3.3 Diffusive Film Layer Thickness (δ_D)

In addition to adopting the surface renewal model (Eq. (5.5)), the author also draw on the two-film theory. The model has merits in simplicity and being intuitive. In fact, Janzen et al. (2010) has shown that the film model and the surface divergence model estimated well the oxygen transfer coefficients under the range of Reynolds

number reported in the literature. The diffusive film thickness, δ_D instead of δ_{SFL} , may be viewed as a characteristic length scale to describe the reaeration process (see chapter 6). It is shown clearly that the thickness of this layer δ_D decreases with increasing turbulence intensity, see Table 5. 3. Moreover, this proposed thickness may be estimated as the ratio between the molecular diffusivity (D_m) and oxygen transfer coefficient (K_L); that is $\delta_D = D_m/K_L$. Here D_m is the physical fluid property of the diffusivity of the gas in liquid, and K_L is determined experimentally. Note that δ_D is in the order of mm, as shown in Table 5. 3.

Table 5. 3. A summary of the experimental results and parameters

No.	H.f (m/s)	k_2 (1/day)	$K_L = k_2 h^{\#}$ (m/s)	$\delta_D = D_m/K_L$ (m)	$K_L Sc^{1/2}$
R1	4.125×10^{-4}	0.263	1.218×10^{-6}	2.11×10^{-3}	2.152×10^{-5}
R2	8.250×10^{-4}	0.325	1.505×10^{-6}	1.70×10^{-3}	2.659×10^{-5}
R3	1.100×10^{-3}	0.379	1.755×10^{-6}	1.46×10^{-3}	3.101×10^{-5}
R4	1.100×10^{-3}	0.445	2.060×10^{-6}	1.43×10^{-3}	3.212×10^{-5}
R5	1.100×10^{-3}	0.495	2.292×10^{-6}	1.39×10^{-3}	3.308×10^{-5}
R6	2.500×10^{-4}	0.279	1.278×10^{-6}	2.01×10^{-3}	2.258×10^{-5}
R7	5.000×10^{-4}	0.347	1.606×10^{-6}	1.60×10^{-3}	2.839×10^{-5}
R8	5.000×10^{-4}	0.409	1.894×10^{-6}	1.55×10^{-3}	2.952×10^{-5}
R9	5.000×10^{-4}	0.456	2.111×10^{-6}	1.51×10^{-3}	3.047×10^{-5}
R10	8.125×10^{-4}	0.437	2.023×10^{-6}	1.27×10^{-3}	3.576×10^{-5}
R11	1.875×10^{-3}	0.621	2.875×10^{-6}	8.92×10^{-4}	5.081×10^{-5}
R12	6.375×10^{-4}	0.280	1.296×10^{-6}	1.98×10^{-3}	2.291×10^{-5}
R13	6.375×10^{-4}	0.327	1.514×10^{-6}	1.94×10^{-3}	2.360×10^{-5}
R14	6.375×10^{-4}	0.363	1.681×10^{-6}	1.90×10^{-3}	2.426×10^{-5}

[#]Note: h = water depth in the reaeration column (=0.4m) and the bulk DO concentration was considered homogeneous.

The time scale in the abscissa of Figure 5. 1 may be presented in terms of speed, in this case, inverse of speed, i.e. t/δ_D . Figure 5. 2 is Figure 5. 1 re-plotted with the abscissa expressed in t/δ_D . It can be seen from Figure 5. 2 that the data for various wave conditions collapse into a straight line. Indeed, Eq. (5.4) could have been re-written with the right hand side term expressed as $(k_2 \delta_D) \left(\frac{t}{\delta_D} \right)$. Based on Figure 5. 2,

the gradient of the best fitted curve yields the value of $k_2\delta_D=D_m/h=5.58\times10^{-4}$ m/day. It is noted that the product $k_2\delta_D=D_m/h$ contains two parameters, k_2 and δ_D which define the reaeration process. In fact, δ_D may be viewed as a universal length scale that reflects the variation of reaeration with depth under various external forcing. One could visualize that under a certain external influence [forcing] (temperature, wave, wind, ship wake, etc) or a combination of external influences the reaeration process would be reflected in the terms k_2 and δ_D . The interesting and significant point is that the product of these two parameters has been shown to be a constant. Therefore, one needs only to determine either k_2 or δ_D , whichever is more readily available, to establish the other. For instance, if one can measure δ_D directly, then the corresponding reaeration coefficient can be determined readily.

Figure 5. 2. Temporal distribution of DO concentration under various water level perturbations presented with respect to time scaled diffusive film layer thickness (δ_D) (constant temperature at 30°C)

5.3.4 Statistical Analysis and Modified Surface Renewal Model Development

A linear least-squares regression analysis was performed and significance of correlation coefficient was also tested for the data obtained in the present study. The Student's t-tests and statistical significance were performed using commercial software [Origin 8.5 (OriginLab) and Excel 2007 (Microsoft)]. The significance, P-value corresponding to the two-tailed test was estimated to be less than 0.001.

Figure 5. 3 shows the relationship between $K_L Sc^{1/2}$ and H_f based on experiments carried out for the present study. The wave frequency ranges from 0.125Hz to 0.425Hz and wave height varies from 0.15cm to 1.5cm. The results are plotted in Figure 5. 3 where the constant, “c”, is found to be 0.0158 ($K_L Sc^{1/2} = 0.0158 H_f + 1.72 \times 10^{-5}$, $R^2 = 0.74$, $P < 0.001$) and is comparable with the value of 0.0159 reported by Daniil and Gulliver (1991) (wave frequency range of 1.59Hz-2.65Hz and wave height from 0.70cm to 5.35cm). Another reported work in this area, Downing and Truesdale (1955) performed experiments with wave frequency of 0.6Hz-1.25Hz for various wave heights ranging from 2.8cm to 10.8cm. Using their data, the constant, “c”, has been estimated to be 0.0163, which is also comparable with that obtained in this study.

Figure 5. 3. Variation of $K_L Sc^{1/2}$ with H_f ($P < 0.001$)

The author found a way to unify these three sets of data. After evaluating the basis and development of the surface renewal model, and knowing that there is inevitable

large degree of errors in the experimental measurements, the author proposes to include an error factor, α , in the surface renewal model as described herein.

By definition, an experimental/measurement error is the relative deviation from the true value, and may be represented as follow:

$$\text{error} = \frac{\text{True value} - \text{Measured value}}{\text{True value or Measured value}} = \frac{\text{True value}}{\text{Measured value}} - 1 \quad (5.9)$$

The denominator could be the true value or the measured value if the error is small. In this case, the author chooses to use the measured value as the denominator. Then by rewriting Eq. (5.9) one obtains

$$\text{True value} = (1 + \text{error}) \times \text{measured value} \quad (5.10)$$

In our context, the true value is given by the function $(cHf + b)$. The measured value is expressed as $(K_L Sc^{1/2})$. Therefore, Eq. (5.10) may be expressed as

$$(cHf + b) = (1 + \text{error}) \times (K_L Sc^{1/2}) \quad (5.11)$$

With the error represented by α , one can consequently derive Eq. (5.12).

$$K_L Sc^{1/2} = \frac{(cHf + b)}{(1 + \alpha)} \quad (5.12)$$

Eq. (5.12) reverts to Eq. (5.5) when $\alpha=0$. The constant, α , defines the error bound of the experimental data. In this way, Eq. (5.12) not only describes the surface renewal process, but also provides an indication of the error band of the measured data.

Figure 5. 4 shows the comparison of the present results (expressed in terms of $K_L Sc^{1/2}$ as a function of (Hf)). Also included are the data extracted from Daniil and Gulliver (1991) and Downing and Truesdale (1955). The dot lines ($\alpha=\pm 10\%$) and the dash lines ($\alpha=\pm 20\%$) represent the confidence interval of 10% and 20%,

respectively. Figure 5. 4 indicates that most of the data fall within the $\pm 20\%$ band. It may be deduced that the surface renewal model, Eq. (5.12), clearly describes very well the reaeration process for wave frequency between 0.125Hz and 2.65 Hz, and wave height from 0.15 cm to 10.8 cm.

Figure 5. 4. Variation of $K_L Sc^{1/2}$ with Hf for various wave conditions

5.3.5 Effects of Wave Height and Frequency on Oxygen Transfer Coefficient

In order to evaluate the effects of both wave height and wave frequency on oxygen transfer, and for ease of presentation, the author used Eq. (5.12) and set $\alpha=0$, $c=0.0158$, and $b=1.72 \times 10^{-5}$ in the illustration shown in Figure 5. 5. Figure 5. 5 shows clearly that higher wave frequency results in higher values of $K_L Sc^{1/2}$, hence higher oxygen renewal rate, for a constant wave height. For a constant wave frequency, higher wave height results in higher oxygen renewal rate. Figure 5. 5 also reflects very well the (H, f) space occupied by the present study and those by Daniil & Gulliver (1991) and Downing and Truesdale (1955). One may also deduce

intuitively from Figure 5. 5 that for a surface wave of small amplitude, the surface renewal rate is independent of the frequency. In the limit, the value of $K_L Sc^{1/2}$ approaches the value of 1.72×10^{-5} m/s for a still water surface.

Figure 5. 5. Effects of wave height and frequency on Oxygen transfer (K_L)

5.4 CONCLUSIONS

The effects of mechanically generated waves on oxygen transfer were investigated. This study focused on small amplitude wave similar to those produced by ripples. The wave frequency ranged from 0.125Hz to 0.425Hz for different wave heights, H , which ranged from 0.15cm to 1.5cm. A modified surface renewal model was proposed and the model successfully unified the findings of the present study and those reported by Daniil and Gulliver (1991) and Downing and Truesdale (1955). The findings of this chapter include the followings:

1. It was found that the diffusive film layer thickness, δ_D , may be adopted as the characteristic length to describe the reaeration process;
2. For a constant wave height, oxygen renewal rate increases with wave frequency; similarly, oxygen renewal rate increases with wave height for a constant wave frequency.

CHAPTER 6

The Modified Film Model

6.1 INTRODUCTION

In order to predict the rate of mass transfer, a number of gas transfer models have been proposed and they may be classified into three major groups, namely conceptual models (Lewis and Whitman, 1924; Danckwerts, 1951; and Brumley and Jirka, 1988), eddy diffusivity models (i.e. Son and Hanratty, 1967), and hydrodynamics models (Fortescue and Pearson, 1967; Lamont and Scott, 1970; and Brumley and Jirka 1988). Based on the surface renewal model and hydrodynamic models, i.e. Danckwerts (1951) and Brumley and Jirka (1988), it is showed that oxygen transfer velocity, K_L , was dependent on the square root of the molecular diffusivity of dissolved oxygen. However, the hydrodynamic parameters influencing the gas transfer process were still embedded in some lumped rate terms which must be determined experimentally and under specific turbulence conditions. In contrast, the two-film model (Lewis and Whitman, 1924) assumes that the oxygen transfer velocity, K_L , is proportional to the molecular diffusion coefficient of dissolved oxygen.

Despite the fact that various theoretical models and different empirical formulations have been proposed to date, there is still no general consensus on the method to estimate the rate of oxygen transfer. It is therefore the objective of this chapter to develop a general gas transfer model which will be applicable to a surface water body and under a general environmental flow condition and small water surface perturbations.

6.2 BOUNDARY LAYER THICKNESSES AND MODEL DEVELOPMENT

6.2.1 Boundary Layer Thicknesses

In the literature, a number of boundary layer thicknesses have been proposed and used in the development of various reaeration models. These thicknesses include the stagnant film layer thickness (δ_{SFL}), the concentration boundary layer thickness (δ_{CBL}), and the measured concentration boundary layer thickness (δ_e). The meaning of diffusive film layer (δ_D) will be elaborated later. The definitions of these various boundary layer thicknesses, essentially proportional to D/K_L , are illustrated in Figure 6. 1. Typically it is assumed that the oxygen concentration at the surface is at saturation concentration (C_s), and the DO concentration in the bulk of the water column is C_b ($C_b < C_s$). Transition of the concentration takes place through the boundary layer. Lewis and Whitman (1924) assumed that this transition is linear, see the linear transition curve from the air-water surface (C_s) to the bulk (C_b). However, later works by Chu and Jirka (1992) and Herlina and Jirka (2004, 2008) showed that the transition is not linear but may follow the shape of an “exponential” curve as shown in Figure 6. 1.

Figure 6. 1. Definition sketch of various boundary layers used in the study of the reaeration process; those layer values are presented in Table 6. 1; C_s is the saturation DO concentration; C_b is the DO concentration at the bulk of water

Chu and Jirka (1992) proposed a measured concentration boundary layer thickness, δ_e , which was used as a normalizing parameter in their proposed mean

concentration profiles. In their study, the normalized mean concentration profiles was described as an exponential function as follow

$$\frac{C - C_b}{C_s - C_b} = e^{\frac{-z}{\delta_e}} \quad (6.1)$$

where δ_e is referred to as the measured concentration boundary layer thickness and is defined as the depth (z) where the value of the normalized concentration $(C - C_b)/(C_s - C_b) = 1/e = 37\%$.

Jähne and Haußecker (1998) presented yet another boundary layer thickness, the concentration boundary layer (CBL) thickness, δ_{CBL} , which is defined as the intercept of the tangent to the concentration profile at the surface and the bulk water column. Later, Herlina and Jirka (2004, 2008) and Woodrow and Duke (2001, 2002) adopted this boundary layer in their gas exchange studies.

In addition to these above-mentioned boundary layers, other boundary layers have also been reported by Magnaudet and Calmet (2006) and Schulz and Schulz (1991). They are not discussed herein as they are not directly relevant to this study.

Although a number of various boundary layers have been proposed to date in the works related to gas exchange, none of them has been found to characterize the reaeration process satisfactorily. In this study, the author proposes to define a new parameter, diffusive film layer thickness (δ_D) which could be adopted as the characteristic length. The definition and significance of δ_D will be elaborated later.

6.2.2 Development of the Modified Film Model

Lewis and Whitman (1924) proposed a simplified concentration profile in a two-phase system by assuming two still surface films, one on the liquid side and the other on the gas side. Each of the surface films has a corresponding gas transfer coefficient, namely k_L and k_g for the liquid and gas phase, respectively. The overall

transfer velocity K_L is related to the individual gas transfer coefficients, as in the following resistance-in-series model

$$\frac{1}{K_L} = \frac{1}{k_L} + \frac{1}{H_c k_g} \quad (6.2)$$

where H_c is Henry's constant ($\text{atm m}^3 \text{ mole}^{-1}$).

It is noted that Lewis and Whitman (1924)'s purpose of proposing the two-film model was to estimate the relative importance of gas-phase and liquid-phase resistances among various gases with their different solubilities (Herlina 2005). The two film model shows that the gas-side resistance is generally negligible compared to that of the liquid-side for gases of low solubility (e.g. O_2 , CO_2 , and N_2). Therefore, the linear assumption was found to be adequate for that purpose and the following relationship was obtained

$$K_L = \alpha \frac{D_m}{\delta_{\text{SFL}}} \quad \text{or} \quad \delta_{\text{SFL}} = \frac{\alpha D_m}{K_L} \quad (6.3)$$

with δ_{SFL} as the stagnant liquid film layer and $\alpha=1$. Eq. (6.3) is also referred to as the film model in the literature. The validity of $\alpha=1$ is elaborated later.

Despite its merit in simplicity, the film model has been questioned whether it may provide good estimate of the oxygen transfer velocity. Based on the boundary layers, i.e. δ_{CBL} or δ_e , Herlina and Jirka (2004, 2008) and Woodrow and Duke (2001, 2002) showed that the film model predicted lower value of oxygen transfer velocity than expected. Janzen et al. (2010) recently found that the film model and the surface divergence model show good correlation, as well as producing good estimate of the mass transfer velocity for all turbulence flow conditions considered in their study. The present author adopts the approach of Janzen et al. (2010) to develop the modified film model as will be elaborated later.

Table 6. 1. A summary of parameters and coefficients used to develop the modified film model

Author	Flow conditions	K_L (m/s)	D_m/K_L (μm)	δ_{CBL} (μm)	δ_e (μm)	$\delta_{\text{SFL}}^{(2)}$ (μm)
Herlina (2005)	Stirred Grid	4.16×10^{-6}	474	865	697	474
		5.58×10^{-6}	354	618	470	354
		6.82×10^{-6}	289	549	395	289
		7.93×10^{-6}	249	503	387	249
Herlina and Jirka (2004)	Stirred Grid	6.70×10^{-6}	295	$559^{(1)}$	420	295
Woodrow and Duke (2001, 2002)	Waves	8.59×10^{-6}	230	366	$246^{(1)}$	230
		1.04×10^{-5}	190	298	$185^{(1)}$	190
		8.80×10^{-6}	225	336	$219^{(1)}$	225
Chu and Jirka (1992)	Stirred Grid	7.90×10^{-6}	250	$382^{(1)}$	260	250

$D_m(20^\circ\text{C}) = 1.97 \times 10^{-5} (\text{cm}^2/\text{s})$; all parameters and coefficients are normalized at 20°C
⁽¹⁾ $\delta_{\text{CBL}} = 1.11 \delta_e + 93$ based on the data reported by Herlina (2005)
⁽²⁾ δ_{SFL} estimated using Eq. (6.3)

Table 6. 1 shows a summary of parameters and various boundary layer thicknesses used to develop the proposed modified film model. The data used are collected from Chu and Jirka (1992), Herlina and Jirka (2004), Herlina (2005), and Woodrow and Duke (2001, 2002) for various flow conditions and water surface perturbation, including waves and stirred grids. Using the published data presented in Table 6. 1, one may obtain the following correlation equations (Eqs. (6.4) and (6.5)) among different boundary layer thicknesses and D_m/K_L as shown in Figure 6. 2.

$$\delta_e = 1.80 \frac{D_m}{K_L} - 147 \quad (R^2 = 0.93, P < 0.0001) \quad (6.4)$$

$$\delta_{\text{CBL}} = 2.01 \frac{D_m}{K_L} - 73 \quad (R^2 = 0.94, P < 0.0001) \quad (6.5)$$

Figure 6. 2. Correlations among different boundary layer thicknesses (δ_{SFL} , δ_e , and δ_{CBL}) and D_m/K_L ; the data used are reported by Chu and Jirka (1992), Woodrow and Duke (2001, 2002), Herlina and Jirka (2004), and Herlina (2005) as shown in Table 6. 1

6.2.2.1 Diffusive Film Layer Thickness (δ_D)

It is noted that the thicknesses of the various film layers, as computed in Table 6. 1, are $\delta_{CBL} > \delta_e > \delta_{SFL}$. The thickness of δ_{SFL} appears to be inconsistent with its original definition as shown in Table 6. 1. This inconsistency is the result of conceptual definition of the thickness from water surface to the depth which shows bulk DO concentration, while the equation proposed as a function of D_m/K_L with the constant of proportionality taken as unity. In fact this constant coefficient of unity is shown here to be inconsistent with the physical definition. Instead, it is hereby proposed that a new term, diffusive film layer, δ_D be used instead, and

$$\delta_D = \frac{D_m}{K_L} \quad (6.6)$$

Based on the results in Table 6. 1, one may readily establish the relationships between the various measured boundary layer thicknesses and $\delta_D (=D_m/K_L)$ as in Eqs. (6.7) and (6.8). Figure 6. 3 shows the correlation between δ_D and δ_{CBL} under various turbulence flow conditions. A similar figure (not shown in this thesis) may also be obtained for the relationship between δ_D and δ_e .

$$\delta_D = 0.47\delta_{CBL} + 51 \quad (R^2=0.97, P<0.0001) \quad (6.7)$$

$$\delta_D = 0.56\delta_e + 75 \quad (R^2=0.96, P<0.005) \quad (6.8)$$

Figure 6. 3. Correlation between δ_{CBL} and $\delta_D (=D_m/K_L)$ ($R^2=0.97$, $P<0.0001$) under various wave-induced and bottom-shear-induced turbulences.

In this study, the writer proposes two approaches to estimate the diffusive film layer thickness. In the first approach, the diffusive film layer thickness, δ_D , may be defined as the ratio between the molecular diffusivity (D) of dissolved oxygen and the measured oxygen transfer coefficient (K_L), i.e. $\delta_D = D_m/K_L$. It is noted that this approach is used once the mass transfer velocity, K_L , has been determined experimentally.

In the second approach, the diffusive film layer thickness may be estimated using its established function with the concentration boundary layer (δ_{CBL}) or the measured concentration boundary layer (δ_e) as shown in Eqs. (6.7) and (6.8), respectively. The boundary layer thickness, δ_{CBL} or δ_e , is typically measured using the laser-induced fluorescence (LIF) technique (Herlina and Jirka, 2004, 2008). The diffusive film layer is then determined using its relationship with δ_{CBL} or δ_e . Finally, the oxygen transfer velocity is estimated based on the diffusive boundary layer thickness from Eq. (6.6).

The author further proposes that the diffusive film layer thickness may be used as the “z” term in Eq. (6.1) and the new equation is then:

$$(C - C_b)/(C_s - C_b) = \text{Exp}(-\delta_D/\delta_e) = \text{Exp}(-(0.56 + 75/\delta_e)) \quad (6.9)$$

As the value of δ_e ranges from 185 to 697 as shown in Table 6. 1, the normalized concentration at $z=\delta_D$ varies accordingly from 0.38 to 0.51. That the normalized concentration at the diffusive film layer is not constant suggests that it is a function of the degree of flow turbulence or perturbation at the water surface, with the lower value associated with higher degree of perturbation. Based on Figure 6. 2, it is also worth noting that the diffusive film layer thickness (δ_D) approaches δ_e for high turbulence conditions (i.e. $\delta_e < 250\mu\text{m}$), while it is closer to the depth (z) where $C = (C_s + C_b)/2$ for lower turbulence conditions. Based on the data at hand, it appears that δ_D is equal to δ_e when $\delta_e = 170 (\mu\text{m})$.

6.3 WORKING EXAMPLES

The first example uses the present experimental data, Figure 6. 4. It can be seen in Figure 6. 4 that the data for various water surface perturbation (wave conditions) collapse into a straight line. Based on Figure 6. 4, the gradient of the best fitted curve yields the value of $k_2\delta_D = D_m/h = 5.58 \times 10^{-4} \text{ m/day} = 6.46 \times 10^{-7} \text{ cm/s}$ at 30°C . This constant relationship, albeit with different coefficient, also holds for other

temperatures investigated in this study as illustrated in Table 6. 2. Datasets used are cases R1, R13, R14 shown in Table 5. 1 and Table 5. 3.

Figure 6. 4. Temporal distribution of DO concentration under various water level perturbations presented with respect to time scaled film thickness (δ_D) (constant temperature at 30°C)

The second example is based on the various experimental results reported by Chu and Jirka (1992), Herlina and Jirka (2004), Herlina (2005), and Woodrow and Duke (2001, 2002), see Table 6. 2. Figure 6. 5 presents the correlation between $k_2\delta_D$ and D/h for various cases. It is found that the constant of proportionality is taken as unity. As a result, it can be deduced from Figure 6. 5 that the proposed relationships ($k_2\delta_D = D/h$) also hold for those above-mentioned studies.

Table 6. 2. Parameters and coefficients used to validate the modified film model

Author	K_L (cm/s)	h (cm)	$T^\circ\text{C}$	k_2 (1/s)	δ_D (μm)	$k_2\delta_D$ (cm/s)	D_m/h (cm/s)
Herlina (2005)	4.16×10^{-4}	48.6	20	8.55×10^{-6}	458 ⁽¹⁾	3.91×10^{-7}	4.06×10^{-7}
	5.58×10^{-4}	48.5		1.15×10^{-5}	341 ⁽¹⁾	3.95×10^{-7}	4.07×10^{-7}
	6.82×10^{-4}	48.5		1.41×10^{-5}	309 ⁽¹⁾	4.35×10^{-7}	4.07×10^{-7}
	7.93×10^{-4}	49.0		1.62×10^{-5}	287 ⁽¹⁾	4.65×10^{-7}	4.03×10^{-7}
Herlina and Jirka (2004)	6.70×10^{-4}	47.2	20	1.42×10^{-5}	314 ⁽¹⁾	4.46×10^{-7}	4.18×10^{-7}
Woodrow and Duke (2001, 2002)	8.59×10^{-4}	1.1	20	7.81×10^{-4}	223 ⁽¹⁾	1.74×10^{-5}	1.79×10^{-5}
	1.04×10^{-3}	1.1		9.47×10^{-4}	191 ⁽¹⁾	1.81×10^{-5}	1.79×10^{-5}
	8.76×10^{-4}	1.1		7.96×10^{-4}	209 ⁽¹⁾	1.66×10^{-5}	1.79×10^{-5}
Chu and Jirka (1992)	7.90×10^{-4}	40.0	20	1.98×10^{-5}	230 ⁽¹⁾	4.55×10^{-7}	4.93×10^{-7}
Present study	1.22×10^{-4}	40.0	30	$(3.04 \pm 0.116) \times 10^{-6}$	2105 ⁽²⁾	$(6.41 \pm 0.244) \times 10^{-7}$	6.41×10^{-7}
	1.51×10^{-4}	40.0	35.7	$(3.78 \pm 0.116) \times 10^{-6}$	1939 ⁽²⁾	$(7.34 \pm 0.224) \times 10^{-7}$	7.34×10^{-7}
	1.68×10^{-4}	40.0	39.4	$(4.20 \pm 0.116) \times 10^{-6}$	1899 ⁽²⁾	$(7.98 \pm 0.220) \times 10^{-7}$	7.98×10^{-7}

$D_m(20^\circ\text{C}) = 1.97 \times 10^{-5}(\text{cm}^2/\text{s})$; $D_m(35.7^\circ\text{C}) = 2.49 \times 10^{-5}(\text{cm}^2/\text{s})$; $D_m(39.4^\circ\text{C}) = 3.19 \times 10^{-5}(\text{cm}^2/\text{s})$

⁽¹⁾Estimated based on Eq. (6.7)

⁽²⁾Estimated based on Eq. (6.3)

Figure 6. 5. The correlation between $k_2\delta_D$ and D_m/h for various studies

6.4 CONCLUSIONS

This study presents the author's attempt in the development of a universal reaeration model which may be applicable to most environmental flow conditions (including water surface perturbation induced by wind, waves, and water flow). A specially designed test-rig had been fabricated to study the effect of waves on oxygen transfer for low turbulence conditions. The wave frequency range was from 0.125Hz to 0.425Hz for various wave heights, H , which varied from 0.15cm to 1.5cm. A comprehensive review of the application of the film theory reveals that the length scales, i.e. δ_{CBL} and δ_e , had been used for the film theory, but they tend to underestimate the oxygen transfer velocities. The main findings of this chapter include the followings:

1. Based on the data reported in the literature, the author proposes the diffusive film layer thickness (δ_D) which is then adopted as the characteristic length scale for the reaeration process. The diffusive film thickness may be defined as the ratio between the molecular diffusivity (D_m) of the dissolved oxygen and the measured oxygen transfer coefficient (K_L). Alternatively, the diffusive film thickness may be determined from the measured value of δ_{CBL} and δ_e based on Eqs. (6.7) and (6.8), respectively;
2. It is found that the value of normalized concentration at the diffusive film layer thickness is dependent on the degree of water surface perturbation;
3. Based on the author's experiments and published experimental data by others, the author demonstrates that the modified film model is valid for most surface water body subject to small water surface perturbations.

CHAPTER 7

Simplified Dissolved Oxygen (DO) Model in a Tropical Reservoir

7.1 INTRODUCTION

In addition to the previous findings, this chapter describes the development of a proposed water quality (DO) model and its application to a shallow tropical reservoir (Kranji Reservoir) in Singapore.

In general, a comprehensive water quality (DO) model applicable to a watercourse has to include all the factors (sources and sinks) affecting the DO budget in the watercourse. The DO sources normally include dissolved oxygen (DO) associated with the inflows, primary production (photosynthesis), and reaeration; while DO sinks comprise DO associated with the outflows, respiration, biochemical oxygen demand (BOD), and sediment oxygen demand (SOD). In addition, a comprehensive simulation of a dynamic DO model must also include the effects of both temperature and water depth on the sources and sinks.

For streams in which the depth variation of temperature and flow turbulence are small, the delta method of Chapra and Di Toro (1991) can be used to estimate

reaeration, photosynthesis, and respiration rates using relatively simple graphical fits. As it is simple to use, the delta method has been widely used for preliminary evaluation of diurnal DO investigation. Briefly, the delta method was based on the assumptions that the rates of reaeration and respiration and saturation value of DO are constant, while photosynthesis may be described as a simple sinusoidal function during the daylight hours. However, the delta method may produce significant errors in the estimation of the rate parameters when significant diurnal fluctuations in water temperature are observed since the rates of reaction and DO saturation concentration are temperature dependent. By adopting the assumptions of Chapra and DiToro (1991), and introducing an approximate correction to the temperature-dependence variable, Butcher and Covington (1995) showed that their model provided more accurate parameter estimates for streams with significant variability of temperature.

Gelda et al. (1996) attempted to estimate the reaeration coefficient in Onondaga Lake, N.Y., based on the whole-lake approach. They studied the recovery of dissolved oxygen in a medium-sized lake following an annual lakewide depletion event. The reaeration coefficients associated with the post-turnover recovery periods of 2 years were determined based on the assumption that the net sum (S) of all oxygen sources (not including reaeration) and sinks is constant during the recovery periods. This approach is relatively simple and may provide a preliminary estimation of reaeration coefficient. However, the approach might result in misleading estimates of reaeration coefficients when it is applied into a dynamics lake or reservoir.

In a stratified lake, the thermocline prevents oxygen transfer from the epilimnion to the hypolimnion. Therefore, during the stratification period the oxygen sources are confined only to the epilimnion. The oxygen sinks, including respiration of the organisms living in the hypolimnion and the oxidation of large quantities of reduced substances (COD), cause depletion. As a result, the dissolved oxygen profile in the lakes is stratified.

There are two groups of stratification models, namely the mixed type/integral and the eddy diffusion/differential models (Hostetler and Bartlein, 1990). Dissolved oxygen distribution may be described together with the temperature distribution or as a sub-model of an ecological model (Newbold and Liggett, 1974; Martin et al., 1985; Fang and Stefan, 1995; and Antonopoulos and Gianniou, 2002).

In this chapter, a simplified water quality model of DO in a shallow tropical reservoir is developed. The model includes the parameters that account for the effects of both water temperature and water depth on reaeration coefficient, respiration, and primary production. Basically, the model is established based on the extension of the delta method. The model is then solved numerically.

7.2 MODEL DEVELOPMENT

The author attempts to develop a simplified water quality model for a lake or reservoir based on an extended delta method (Chapra and Di Toro, 1991). The delta method was established based on the assumptions that the spatial variability of dissolved oxygen deficit, D , is relatively insignificant compared to temporal variability and that the saturation DO concentration and respiration is constant. The mass balance for D in a stream may be described as

$$\frac{dD}{dt} + k_2 D = R - P(t) \quad (7.1)$$

where D = dissolved oxygen deficit (mg L^{-1}); t = time (d); k_2 = reaeration rate (d^{-1}); R = respiration ($\text{mgL}^{-1}\text{d}^{-1}$); and $P(t)$ = primary production ($\text{mgL}^{-1}\text{d}^{-1}$). In the delta method, $P(t)$ is estimated approximately as a half sine wave during the daylight hours, and set to zero at night:

$$P(t) = P_{av} \frac{\pi\tau}{2f} \sin\left(\frac{\pi(t - t_s)}{f}\right), t_s \leq t \leq t_s + f \quad (7.2a)$$

$$P(t) = 0, t_s + f \leq t \leq t_s + \tau \quad (7.2b)$$

where P_{av} = the average photosynthesis production rate ($\text{mgL}^{-1}\text{d}^{-1}$); t_s = the time expressed as a fraction of the day, at which the source becomes active (T); f = the photoperiod ($=0.535$ days); and τ = the diurnal period ($= 1$ day).

As discussed above, the delta method is relatively simple and is widely used for preliminary evaluation of diurnal DO investigation. However, the model may lead to significant errors when the rates of reaeration, respiration, and photosynthesis are dependent on water temperature (i.e. Butcher and Covington, 1995) and water depth. The aim of the extended model is to establish a DO model which takes into account the effects of both water temperature and depth. The water column is divided into multiple layers so that each layer is considered totally mixed. The proposed model applied at various locations is considered as 1-D. In addition, the reaeration rate, k_2 , and respiration are assumed to vary with water temperature and depth, while photosynthesis can be described as a function of time, temperature, and concentration of chlorophyll-a. With these assumptions, the delta method can be extended and modified with correction coefficients as follow:

$$\frac{dD}{dt} + k_2(20)g(T)h(z_o)D = R(20)k(T) - P(t)l(T)m(\text{Chla}) + \frac{dC_s}{dt} \quad (7.3)$$

where $k_2(20)$ = reaeration coefficient at 20°C (mgL^{-1}); $Sc(T) = \nu/D_m$ = Schmidt number at $T^\circ\text{C}$; $R(20)$ = average respiration rate at 20°C at the water depth z ; z_o is the normalised depth referenced by 1m water column from the water surface.

$$g(T) = [Sc(T)/Sc(20)]^{-1/2} \text{ (Daniil and Gulliver, 1998)} \quad (7.4)$$

$$h(z) = 1/(z_o)^{1/2} \text{ for } z > 1\text{m}; \quad (7.5a)$$

$$= 1 \text{ for } z \leq 1 \text{ (} z \text{ is water depth and positive downwards)} \quad (7.5b)$$

$$k(T) = 1.08^{T-20}; \quad l(T) = 1.066^{T-20} \text{ (Bowie et al., 1985)} \quad (7.6)$$

$$m(\text{Chla}) = [\text{Chla}(t)/\text{Chla}_{av}]^{1/\alpha} \quad (7.7)$$

$g(T)$ described as a function of Schmidt number ($n=-1/2$) is used instead of 1.024^{T-20} (Elmore and West, 1961) as it provides the insight into the nature of water properties; Eq. (7.5 a) is adopted with reference to Eq. (4.25) where the reaeration

rate is present as a function of $z^{1/2}$, while Eq. (7.5 b) shows that the reaeration rate is uniform within the 1m layer below the water surface; $Chla(t)$ is the Chlorophyll-a concentration at water depth z at time t ; $Chla_{av}$ is the average chlorophyll-a concentration in period studied. α is a constant to control the impact of chlorophyll-a on photosynthesis. The term dC_s/dt in Eq. (7.3) represents the change of saturated DO due to temperature.

Eq. (7.3) is an ordinary differential equation with temperature-and-depth-dependent coefficients. This equation may be approximated in finite difference in time between times t and $t + 1$ and D_{t+1} can be obtained as Eq. (7.8) below

$$D_{t+1} = D_t - k_2(20)g(T)h(z)D_t\Delta t + R(20)k(T)\Delta t - P(t)l(T)m(Chla)\Delta t + C_{s,t+1} - C_{s,t-1} \quad (7.8)$$

where Δt = the time increment; It is noted that the differential on D is expressed in forward difference, while that on C_s is expressed as a central difference.

As a result, the DO concentration at time $t+1$ can be estimated as follow:

$$C_{t+1} = C_{s,t+1} - D_{t+1} \quad (7.9)$$

Eq. (7.9) is then used as the basic equation to simulate the following parameters, namely: $k_2(20)$, $R(20)$, P_{av} , and α . The algorithm starts at the third time step after the first two observations as input. Eq. (7.8) is then used to do the time stepping ($\Delta t=25$ mins) and propagate over the complete period to produce a time series C_t which can then be compared with measured values $C_t^{Measured}$. Finally, the relevant coefficients can be determined using optimization technique such as the minimization of the error-squared of the predictions, $\sum_{t=1}^n (C_t - C_t^{measured})^2$.

As in most numerical/finite difference work, stability and convergence are two important issues to consider. The author evaluated the discretised equation terms by terms and found that the equation is robust and there is no ill condition for which instability or blow up of the solution would take place. Various time steps have

been tested right at the beginning of the simulation work. The author found that the solution based on 75 minutes, 50 minutes, and 25 minutes produced essentially the same result in the test solutions. In other words, the solution converges. The author finally settled on 25 minutes as a matter of personal preference and convenient time step to use in the presentation. The findings on the stability and convergence are consistent with the experience of other researchers such as Butcher and Covington (1995) and Gelda et al. (1996).

7.3 KRANJI RESERVOIR DESCRIPTION

Singapore has an equatorial climate with a mean annual rainfall and evaporation of 2,400 mm and 1,674 mm, respectively. The Kranji Reservoir is located in the northwestern part of Singapore, facing the Johor Straits which separates Singapore from West Malaysia (1°25'N, 103°43'E). In the past, Kranji catchment supported mainly vegetable farming, pig farming and prawn farming activities (Appan, 1977). Parts of the catchment have become urbanized and the current land use within the catchment is varied, ranging from forested to high density housing areas. Some vegetable farming, chicken farming, horticulture and aquaculture activities exist today (Chua, 2009).

Kranji Reservoir has a maximum water surface area of 2.8 km² and storage volume of about 9.6×10⁶ m³. The annual inflow to the reservoir is about 45.2×10⁶ m³, which is about 4.7 times the reservoir volume. The length of main channel of Kranji Reservoir is about 4 km with a maximum depth of about 20 m and average depth of about 5 m. It is surrounded by a mixed catchment with a total area of 556 ha, of which about 17.8% of the land area is residential, 5.4% is agricultural, 0.2% is industrial, and 76.6% is undeveloped (Gin, 2010). There are four major tributaries flowing into Kranji Reservoir: Sungei Kangkar, Sungei Tengah, Sungei Peng Siang, and Sungei Pang Sua which has been diverted into Kranji Reservoir since the end of 2005. Kranji Reservoir is almost entirely fed by dry weather flow and storm runoff from the four tributaries and direct precipitation on the reservoir. It is generally mesotrophic with typically average chlorophyll-a concentration of 7 µg/L during the investigated period from Jul 22 to Sep 25, 2012. The reservoir has been used to

supply water for Choa Chu Kang Treatment Works. Maps of Singapore, Kranji Reservoir and its catchment are shown in Figure 7. 1.

Figure 7. 1. (a) A map of Singapore and location of Kranji Reservoir (Xing, 2011) and (b) a map of the Kranji Reservoir and surrounding catchment (Chua, 2009)

7.4 MODEL APPLICATION IN KRANJI RESERVOIR

The proposed DO model was applied here to simulate the distribution of dissolved oxygen in Kranji Reservoir from 22 July 2012 to 25 September 2012. The data during this period was provided by Public Utilities Board (PUB), and included water temperature, dissolved oxygen concentration, DO saturation, chlorophyll-a, and other meteorological parameters such as wind speed, air temperature, rain/shine etc. These data were used to compare with the simulated results. The DO model was calibrated with the DO data from 22 July 2012 to 19 August 2012. The DO data from 02 September 2012 to 25 September 2012 were used for the validation of DO model. It is noted that during the studied period the monthly mean rainfall is relatively small, $\leq 158\text{mm}$, calculated by averaging the monthly total rainfall for each month for the 27 year period (1982-2008) (National Environment Agency, 2009), and thus the effect of rainfall intensity is considered to be less significant compared to these above-mentioned factors. The main raw data (DO, temperature, and chlorophyll-a) of Kranji Reservoir are given in Figure 3. 10 to Figure 3. 21 (Chapter 3).

A quantitative procedure was used to evaluate the proposed model based on the root mean square error ($\text{RMSE} = (\sum_{i=1}^n (P_i - O_i)^2 / n)^{1/2}$), the mean absolute errors ($\text{MAE} = \frac{1}{n} \sum_{i=1}^n (|P_i - O_i| \times 100\% / O_i)$), the maximum absolute errors (MaxAE) difference between the measured (O_i) and simulated (P_i) values of dissolved oxygen, and the Nash-Sutcliffe Efficiency ($\text{NSE} = 1 - [\sum_{i=1}^n (O_i - P_i)^2 / \sum_{i=1}^n (O_i - O^{\text{mean}})^2]$).

All constants and coefficients determined were found to fall within their respective ranges given in the literature (Bowie et al., 1985). In this study, these values were first estimated based on literature value and corrected during the calibration procedure.

7.4.1 DO Model Calibration

In order to estimate the values of parameters and coefficients, the author used the established optimization routine included in a commercial spreadsheet package (Excel 2007) which yielded quick estimation of parameters based on the technique of minimizing the prediction error-squared. The results obtained using both the delta method (DM) and the proposed DO model (PM) are shown in Table 7. 1. It can be seen clearly that the proposed DO model yielded better prediction values at different water depths compared to those predicted using the delta method even though the same optimization routine was used in both models (MaxAE and NSE criteria).

Table 7. 1. Parameter and coefficient values used in the DO model simulation.

z, m	k ₂ (20) (d ⁻¹)		R(20) (mgL ⁻¹ d ⁻¹)		P _{av} (mgL ⁻¹ d ⁻¹)		MaxAE (%)		MAE (%)	NSE		RMSE (mgL ⁻¹)
	DM	PM	DM	PM	DM	PM	DM	PM	PM	DM	PM	PM
1	0.3	0.300	1	0.51	0.8	0.48	17.23	14.77	3.06	0.113	0.41	0.26
2	0.3	0.212	1	0.50	0.8	0.48	19.80	14.76	3.27	-0.360	0.13	0.27
4	0.3	0.150	1	0.47	0.8	0.48	22.33	12.95	3.60	-1.090	0.07	0.29
6	0.3	0.120	1	0.45	0.8	0.48	25.44	15.68	4.36	-1.340	-0.12	0.34
8	0.3	0.106	1	0.44	0.8	0.48	26.24	15.96	5.91	-0.57	-0.32	0.45

Note: DM: the delta method; PM: the proposed model based on extended delta method; MaxAE: the maximum absolute errors; MAE: the mean absolute errors; NSE: the Nash-Sutcliffe Efficiency; RMSE: the root mean square error.

Based on the simulated results of k₂(20) as listed in Table 7. 1, one may deduce that the reaeration rate decreases with water depth and the magnitude decreases with $z^{1/2}$, which is consistent with the finding reported in Chapter 4 of this thesis. The estimated results of k₂(20) are comparable with those (0.22 d⁻¹ in 1989 and 0.13 d⁻¹ in 1990) reported by Gelda et al. (1996). Here, the average photosynthetic production rate, P_{av}, is considered constant throughout the water column. In contrast, the respiration rate decreased with water depth due to the decrease in dissolved oxygen in the lower depth of the water column. Based on the average water depth of 8m, the average area rates of photosynthesis and respiration in Kranji Reservoir are estimated at 3.84 and 3.79 gm⁻²day⁻¹, respectively. Those rates are within the range of 0 to 36 g.m⁻²day⁻¹ as summarized by Bowie et al. (1985).

The maximum absolute errors at various water depths are also included in Table 7. 1. Here, the error is defined as $|P_i - O_i| \times 100\% / O_i$. It can be seen that the maximum absolute error is less than 15% for water depth less than 4m and corresponds to RMSE of less than 0.3 (mg/L), and it is less than 16% for the greater depths with RMSE of less than 0.45 (mg/L). The mean absolute errors (MAE) of the simulated values associated with 1, 2, and 4m are found to be 3.06%, 3.27%, and 3.60%, respectively, and they are 4.36% and 5.91% for 6m and 8m depth, respectively. Therefore it can be concluded that the proposed DO model produces better prediction for those water depths closer to free surface, i.e. for $z \leq 6m$. The same conclusion can be reached based on NSE. For the case of 8m depth, although the measured data fluctuates widely (see Figure 7. 10 and Figure 7. 11), the DO model still provided good estimated values with the confidence interval of 6%. The fluctuations in the measured data may be attributed to benthic chemical and biological activities, BOD and SOD for instance. It is noted that the coefficient, α , is found to provide the best fits when it is set to a value of 2.

Figure 7. 2 to Figure 7. 11 are comparison of the measured and simulated DO in Kranji Reservoir for various water depths. The author found that the confidence interval of 4% is associated with depths less than 4m, while those of 5% and 6% are at depths of 6m and 8m, respectively.

DO vs Time at z=1m

Figure 7. 2. Simulated and measured DO profiles in Kranji Reservoir at z=1m, Jul 22 to Aug 05, 2012

DO vs Time at z=1m

Figure 7. 3. Simulated and measured DO profiles in Kranji Reservoir at z=1m, Aug 05 to Aug 19, 2012

DO vs Time at z=2m

Figure 7. 4. Simulated and measured DO profiles in Kranji Reservoir at z=2m, Jul 22 to Aug 05, 2012

DO vs Time at z=2m

Figure 7. 5. Simulated and measured DO profiles in Kranji Reservoir at z=2m, Aug 05 to Aug 19, 2012

DO vs Time at z=4m

Figure 7. 6. Simulated and measured DO profiles in Kranji Reservoir at z=4m, Jul 22 to Aug 05, 2012

DO vs Time at z=4m

Figure 7. 7. Simulated and measured DO profiles in Kranji Reservoir at z=4m, Aug 05 to Aug 19, 2012

DO vs Time at z=6m

Figure 7. 8. Simulated and measured DO profiles in Kranji Reservoir at z=6m, Jul 22 to Aug 05, 2012

DO vs Time at z=6m

Figure 7. 9. Simulated and measured DO profiles in Kranji Reservoir at z=6m, Aug 05 to Aug 19, 2012

DO vs Time at z=8m

Figure 7. 10. Simulated and measured DO profiles in Kranji Reservoir at z=8m, Jul 22 to Aug 05, 2012

DO vs Time at z=8m **Figure 7. 11.** Simulated and measured DO profiles in Kranji Reservoir at z=8m, Aug 05 to Aug 19, 2012

7.4.2 DO Model Validation

The parameters ($k_2(20)$, $R(20)$, and P_{av}) and coefficient α determined from model calibration are used without change in the validation of the proposed model. The criteria for evaluating the performance of the model are based on RMSE, MaxAE, MAE, and NSE of the DO for different water depths, see Table 7. 2. Generally, the simulated DO values are in good agreement with the measured values. The mean absolute errors (MAE) are less than 4.1% for those at depths less than 4m, and the largest error of 4.46% is associated with 8m depth. In addition, the RMSE values for all depths are less than 0.4 mg/L. The discrepancies between simulated and measured DO are observed at depths deeper than 6m. The maximum errors, approximately 20% ($z > 6$ m), are observed for two days, day-248 and day-249, during which the biological activities produce substantial quantity of dissolved oxygen (super saturation), see Figure 7. 18 and Figure 7. 20.

Table 7. 2. Parameters and coefficients for proposed DO model validation

Z (m)	$k_2(20)$ (d⁻¹)	R(20) (mgL⁻¹d⁻¹)	P_{av} (mgL⁻¹d⁻¹)	MaxAE (%)	MAE (%)	NSE	RMSE (mg/L)
1	0.300	0.51	0.48	16.80	3.15	0.378	0.30
2	0.212	0.5	0.48	14.18	3.41	-0.060	0.29
4	0.150	0.47	0.48	16.10	4.10	-0.450	0.34
6	0.120	0.45	0.48	19.54	4.18	0.010	0.35
8	0.106	0.44	0.48	19.93	4.46	0.030	0.39
The constant $\alpha=2$							

Figure 7. 12 to Figure 7. 21 show the computed and observed values of DO at various depths in Kranji Reservoir. The confidence intervals were found to be 4% for $z \leq 4$ m and 5% for $z \geq 6$ m.

The above good results clearly demonstrate that the proposed model works well for the Kranji Reservoir.

DO vs Time at z=1m

Figure 7. 12. Simulated and measured DO profiles in Kranji Reservoir at z=1m, Sep 02-14, 2012

DO vs Time at z=1m **Figure 7. 13.** Simulated and measured DO profiles in Kranji Reservoir at z=1m, Sep 14-25, 2012

DO vs Time at z=2m **Figure 7. 14.** Simulated and measured DO profiles in Kranji Reservoir at z=2m, Sep 02-14, 2012

DO vs Time at z=2m

Figure 7. 15. Simulated and measured DO profiles in Kranji Reservoir at z=2m, Sep 14-25, 2012

DO vs Time at z=4m **Figure 7. 16.** Simulated and measured DO profiles in Kranji Reservoir at z=4m, Sep 02-14, 2012

DO vs Time at z=4m

Figure 7. 17. Simulated and measured DO profiles in Kranji Reservoir at z=4m, Sep 14-25, 2012

DO vs Time at z=6m

Figure 7. 18. Simulated and measured DO profiles in Kranji Reservoir at z=6m, Sep 02-14, 2012

DO vs Time at z=6m

Figure 7. 19. Simulated and measured DO profiles in Kranji Reservoir at z=6m, Sep 14-25, 2012

DO vs Time at z=8m

Figure 7. 20. Simulated and measured DO profiles in Kranji Reservoir at z=8m, Sep 02-14, 2012

DO vs Time at z=8m

Figure 7. 21. Simulated and measured DO profiles in Kranji Reservoir at z=8m, Sep 14-25, 2012

7.4.3 Sensitivity Analysis

A sensitivity analysis of the model inputs using Eq. (7.8), including reaeration rate ($k_2(20)$), photosynthesis (α and P_{av}), and respiration ($R(20)$), has been performed and the results are shown in Figure 7. 22. In this model, the four above-mentioned input parameters have to be determined based on the best-fit values. The estimated results are reported in Table 7. 2. In order to evaluate the sensitivity of each parameter/constant with respect to the model performance, a deviation of $\pm 20\%$ was introduced for one parameter at a time while holding the other parameters constant. The results are shown in Figure 7. 22. It is noted that the rates of reaeration ($k_2(20)$) and respiration ($R(20)$) also varied with water depth. Therefore, their values at different depths are altered accordingly. Here, $k_2(20, 1m)$ and $R(20, 1m)$ are referred to as the reaeration rate and respiration rate at 1m, respectively.

Based on the findings of the sensitivity analysis (Figure 7. 22), the photosynthesis-related oxygen production and respiration-related oxygen depletion are the most important processes in the DO model since they show the most significant impacts on the DO profiles. The increase in the value of P_{av} (photosynthesis) results in a significant increase in the computed values of DO profiles (Figure 7. 22 (c)), while the opposite trend for $R(20)$ can be seen for respiration, see Figure 7. 22 (d). The results are reasonable and are to be expected as the photosynthesis process enhances DO concentration, leading to increased simulated values of DO; and the opposite is observed for the respiration process. Based on Figure 7. 22 (b), the reaeration process shows less impact on computed DO profiles. A similar behavior of photosynthesis process is observed to reaeration process. These results are logical and intuitive as the reaeration process is normally a slow process of a much longer time scale compared to that of photosynthesis and respiration. The constant, α , is observed to produce less effect on the computed DO distribution as shown in Figure 7. 22 (a). Nevertheless this constant has its role and place in the model.

The author has also evaluated the contributions of photosynthesis and respiration and other physical environmental factors. With reference to the description of the reaeration process (Eq 7.8), one can isolate each factor (reaeration, respiration, and photosynthesis) in the equation and consider their contribution to the concentration of DO. For example, let's consider the variations of different factors at the depth $z = 1m$ for three days as shown in Figure 7. 23 below.

Figure 7. 22. Sensitivity analysis for constants and parameters α , $k_2(20)$, P_{av} , and $R(20)$ and oxygen profiles on Jul 27, 2012.

Figure 7. 23. A comparison of the relative contribution of photosynthesis, respiration, and reaeration on DO concentration at the depth of 1m

It is clear that in region 1 (night time), the model is sensitive to respiration and reaeration. However, the model is sensitive to photosynthesis and respiration in region 2 (day time). It may be deduced from the same figure that averaged over a 24-hour cycle, reaeration contributes to about 15% of the overall DO in a water column. The effect of surface perturbation would not be insignificant.

7.5 CONCLUSIONS

A water quality (DO) model has been developed and used to simulate the DO distributions at various depths for Kranji Reservoir during the period from 22 July 2012 to 25 September 2012. The proposed model was based on the extended delta method, which has incorporated in it a temperature-and-depth dependent factor to the relevant parameters (reaeration, photosynthesis, and respiration) of the Delta method. The model was solved using the finite difference method. The data input parameters for this model include water temperature, dissolved oxygen concentration, DO saturation, and chlorophyll-a, which are readily available.

The proposed model may be considered as a simplified DO model as it has not taken into consideration the effects of other meteorological data such as rainfall, wind speed and

direction, and air temperature, and biochemical and chemical activities (BOD and SOD). Future studies on this issue need to take into account the variability of meteorological conditions at the reservoir

The main findings of this segment of the study may be summarized as below.

1. Based on the quantitative and qualitative criteria of model performance, the proposed model has been shown to simulate DO at different water depths with good accuracy and with the confidence interval of less than 5%. The largest errors (approximately 20%) were observed at 6m and 8m depths;
2. Based on the sensitivity analysis, the two main biological processes, including photosynthesis and respiration, are found to have significant effects on the computed values of DO profiles. The reaeration process is a slow process but operate on a longer time scale. The constant, α , associated with the effect of chlorophyll-a shows less impact on the DO profiles, but it remains a relevant and significant factor in the model.

CHAPTER 8

Conclusions and Recommendations

8.1 CONCLUSIONS

Based on the findings and the knowledge gaps identified in the literature survey, this study aimed to address the following questions about the oxygen transfer:

- (1) What is the effect of water temperature on oxygen transfer under low turbulence conditions?
- (2) How does the reaeration rate change along the water column?
- (3) What is the effect of turbulence, i.e. waves, on oxygen transfer?
- (4) Is the film model valid?
- (5) Based on the new findings, could a simplified DO model be developed for a tropical lake/reservoir?

In order to seek the answers to the above-mentioned questions, the author had designed and fabricated a specially designed test-rig system comprising two main parts, namely a jacketed reaeration water column, and an auxiliary column. All the experiments were performed in this specially designed system. In addition, field data had been used in the study (courtesy Public Utilities Board (PUB), Singapore).

The findings of this study are summarized in the following:

- Based on the laboratory experiments, it can be concluded conclusively that oxygen transfer rate increases with increasing temperature. The proposed mathematical model (Eq. (4.25)) has been found to predict well the oxygen transfer rate for low turbulent condition. In addition, the reaeration coefficient decreases with water depth and the magnitude decreases as a function of $z^{0.5}$. A new relationship has been developed for the conversion of the reaeration rate constant from a temperature to another.
- A modified surface renewal model has been proposed and the model successfully unified those data obtained in this study and reported in the published papers. Interestingly, the proposed surface renewal model shows that for a constant wave height, oxygen renewal rate increases with wave frequency; similarly, oxygen renewal rate increases with wave height for a constant wave frequency.
- Based on the data reported in the literature, the writer proposed the diffusive film thickness, δ_D , to be the characteristic length for describing the reaeration process. The diffusive film thickness may be defined as the ratio between the molecular diffusivity (D_m) of dissolved oxygen and the measured oxygen transfer coefficient (K_L). Alternatively, the diffusive film thickness may be determined based on its established function with δ_{CBL} or δ_e . In addition, based on the author's experiments and published experimental data by others, the author demonstrates that the modified film model is valid for most surface water body subject to small water surface perturbation.
- A water quality (DO) model has been successfully developed and applied to model the DO profiles for Kranji Reservoir. Based on the quantitative and qualitative criteria of model performance, the proposed model has been shown to simulate DO at different water depths with good accuracy and with the confidence interval of better than 95%. In addition, based on the sensitivity analysis, the two main biological processes, i.e. photosynthesis and respiration, are found to have significant effects on the computed values of DO profiles.

8.2 RECOMMENDATIONS

The findings obtained in this study have established the comprehensive understanding of how dissolved oxygen is exchanged at the air-water interfaces and transported into the deeper parts of the water column. However, there are still open questions and relevant issues which have not been addressed in this study. These issues need further investigation and include the followings:

- (1) What are the effects of water characteristics, i.e. water surface tension, surfactants, and domestic, pharmaceutical, and industrial wastewaters, on oxygen transfer coefficient?
- (2) This study has only focused on the turbulence source induced by waves, so could a general quantitative model of prediction of oxygen transfer velocity be developed for the combined turbulence sources of both wind and wave?
- (3) Could the simplified DO model be applied for stratified lakes/reservoirs?
- (4) The proposed model presented in this study may be considered as a simplified DO model as it has not taken into account the effects of other meteorological data such as rainfall, wind speed and direction, and air temperature, and biochemical and chemical activities (BOD and SOD). Therefore, future studies on this issue need to take into account the variability of meteorological conditions at the reservoir.

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