Air–water mass transfer and tracer gases in stormwater systems

H.I. Madsen, J. Vollertsen and T. Hvitved-Jacobsen

Section of Environmental Engineering, Aalborg University, Sohngaardsholmsvej 57, 9000 Aalborg, Denmark
(E-mail: him@bio.aau.dk; jv@bio.aau.dk; thj@bio.aau.dk)

Abstract Reaeration is a central quality parameter for the performance of environmental systems such as ponds receiving urban and road runoff. Tracer gases can be used to measure reaeration rates in these systems. The methods comprise injection of a volatile tracer into an environmental system and subsequently measurement of the emission of the volatile tracer. The physical basis of such methods is the existence of a constant ratio between the air–water mass transfer coefficient for oxygen and the corresponding mass transfer coefficient for the volatile tracer gas. This constant ratio is often not clearly defined in the literature due to difficulties in both experimental procedures and handling of data. In this study such methods are evaluated and an experimental procedure and a corresponding data processing procedure for a general and reliable determination of mass transfer rates are presented. Propane is selected as an example of an appropriate tracer gas and the ratio between the mass transfer coefficients of oxygen and propane is determined.

Keywords Air–water mass transfer; oxygen; propane; reaeration; tracer gas

Introduction
Tracer gases have been widely applied for measurement of reaeration rates in environmental systems, e.g. rivers, lakes and sewers. The methodology comprises injection of a volatile tracer into the environmental system and subsequently measurement of the emission of the volatile tracer. The method is based on the existence of a constant ratio (R) between the mass transfer rate for oxygen (K(O₂)) absorbed by a water volume and the mass transfer rate for a volatile tracer gas (K(tracer)) desorbed from the same water volume, \( R = \frac{K(O_2)}{K(tracer)} \). The ratio (R) is assumed to be constant, and independent of temperature, turbulence and the presence of impurities (Rathbun et al. 1978; Boumansour et al. 1995; Madsen et al. 2006).

A correct determination of the ratio (R) is crucial for the application of a new tracer gas. The ratio can be determined both theoretically and experimentally, however, different methods yield different values, making it problematic to determine a correct value for specific cases. The objective of this study is therefore to develop a general procedure for determination of mass transfer rates for the purpose of determining the ratio between the mass transfer rates of oxygen and a tracer gas. This is done by analyzing, discussing and improving experimental and data handling procedures. Propane is chosen as an example of an appropriate tracer gas, but the procedure is developed for general application.

Background
An often applied concept for understanding the mass transfer at the air–water interface is the two-film theory. This theory is based on molecular diffusion through two stagnant films at the air–water interface: a liquid film and a gas film (Lewis and Whitman 1924). The importance of the two films can be described by the magnitude of Henry’s law constant (Liss and Slater 1974). Oxygen and propane have similar Henry’s law constants and
for both gases the resistance to mass transfer lies mainly in the liquid film. Another well established theory dealing with mass transfer at the air–water interface is the surface-renewal theory (King 1966), which is more appropriate under high turbulence conditions. Both mass transfer theories predict a correlation between the mass transfer coefficients ($K_{La}$) and the coefficients of molecular diffusion ($D$), Eq 1.

$$R = \frac{K_{La}(O_2)}{K_{La}(C_3H_8)} = \left( \frac{D(O_2)}{D(C_3H_8)} \right)^n$$

where $K_L$ is the gas transfer velocity in the liquid (m d$^{-1}$), $a$ is the specific interface area, surface area per unit volume (m$^2$ m$^{-3}$) and $n$ is a constant ($-$). The value of $n$ depends on the level of turbulence, where $n = 1$ for non-turbulent conditions (two-film theory) and $n = 1/2$ for turbulent conditions (surface-renewal theory).

Difficulties appear when determining the ratio from measured or estimated diffusion coefficients. Measured diffusion coefficients are unavailable for many compounds due to time consuming and costly experiments, and conflicting data have been reported for others. Consequently, estimated values are often used, however, the estimation methods are not equally appropriate for all compounds. Diffusion coefficients for oxygen and propane estimated by the method of Othmer and Thakar (1953) results in $R = 1.89$ ($n = 1$) or $R = 1.38$ ($n = 1/2$). The ratio ($R$) between the mass transfer coefficients of oxygen and propane has previously been measured by several authors, cf. Table 1.

The different authors referred to in Table 1 state the ratio as either a mean value of measured $K_{La}$(oxygen)/$K_{La}$(propane) ratios or as the slope of a best-fit line in a plot of $K_{La}$(propane) versus $K_{La}$(oxygen). However, applied on the same dataset, the two methods can result in different values, cf. Rathbun et al. (1978), Table 1.

One widely discussed problem in the determination of oxygen transfer rates concerns the calculation of the oxygen transfer coefficient. Different methods have been proposed by e.g. Brown and Baillod (1982), Boyle et al. (1974), and Rathbun et al. (1978). Using different methods can lead to significant differences in the value of $R$. The different methods are discussed later in this paper.

Prior to measuring the oxygen transfer rate, deoxygenation or supersaturation of the water is required. The use of sodium sulfite and cobalt chloride for deoxygenation can cause problems with the simultaneous use of Winkler determinations (Naimie and Nelson 1978). Furthermore, experiments performed with Winkler determinations and varying pH showed significant variations for both deoxygenation by sodium sulfite and deoxygenation by nitrogen gas (Naimie and Nelson 1978). In order to solve this problem, Naimie and Nelson (1978) suggest the use of a phosphate buffered system maintained at pH 6.9 or less if Winkler determinations are used. There was no effect of pH on the measured oxygen mass transfer rates in experiments where the oxygen concentration was measured.

<table>
<thead>
<tr>
<th>Author</th>
<th>No. of tests</th>
<th>$R$ Mean value</th>
<th>Std dev. Mean value</th>
<th>$R$ Slope</th>
<th>Std dev. Slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rathbun et al. (1978)</td>
<td>34</td>
<td>1.43</td>
<td>0.11</td>
<td>1.39</td>
<td>0.0291</td>
</tr>
<tr>
<td>Rainwater and Holley (1984)</td>
<td>27</td>
<td>1.36</td>
<td>0.09</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Bales and Holley (1986)</td>
<td>45</td>
<td>1.468</td>
<td>0.241</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Boumansour et al. (1995)</td>
<td>~45</td>
<td>1.389</td>
<td>0.025</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hebrard et al. (2000)</td>
<td>~20</td>
<td>–</td>
<td>–</td>
<td>1.396</td>
<td>0.091</td>
</tr>
<tr>
<td>Bicudo and James (1989)</td>
<td>24</td>
<td>–</td>
<td>–</td>
<td>1.365</td>
<td>0.030</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td><strong>268</strong></td>
<td><strong>1.41</strong></td>
<td><strong>0.54</strong></td>
<td><strong>1.38</strong></td>
<td><strong>0.51</strong></td>
</tr>
</tbody>
</table>
with a probe (Naimie and Nelson 1978). None of the authors referred to in Table 1 specify at which pH the experiments were performed.

**Methods**

**Experimental procedure**

The ratio between the air–water mass transfer coefficients of oxygen and propane was determined in batch reactors 90 times, 45 initial test experiments and 45 main experiments (cf. Table 2). The experiments were performed in a 3 L Erlenmeyer flask, cf. Figure 1. In order to avoid contamination by microorganisms, glass equipment and oxygen probes were flushed with boiling water and 70% ethanol, respectively. A flow of water saturated air through the headspace of the Erlenmeyer flask removed desorbed propane gas continuously and maintained a constant oxygen concentration in the gas phase. The water phase was mixed using a magnetic stirrer (120 rpm). Constant temperatures (20°C) in the water and air phases were achieved by placing the flask in a water bath. The water saturated air was prepared by bubbling air through a flask filled with water and placed in the water bath.

Oxygen in the water phase was initially stripped with nitrogen to a level below 0.1 mg L$^{-1}$ and propane saturated water was added. The DO concentration was measured using an oxygen sensor with 12 mm Teflon membrane (Mettler Toledo, Switzerland) and logged with a computer every minute until saturation occurred. The accuracy of the oxygen sensor is ±30 ppb. The oxygen sensor was calibrated with a two-point calibration, zeroing gel (Mettler Toledo, Switzerland) and air saturated water. Prior to the experiments the DO probes were checked for linearity against Winkler determinations (APHA et al., 1998) according to ASCE Standard (1984). At each calibration, Winkler determination was done as a reference.

The method applied for measurement of the propane concentration is the headspace technique described by e.g. Bales and Holley (1986) and Thene and Gulliver (1990). The concentration in the original water sample is determined from the headspace in an infusion bottle by a mass balance and equilibrium partitioning based on the ideal gas law and Henry’s law. A Chrompack CP900 gas chromatograph with a flame ionization detector (FID) was used for the analysis of propane.

In this study 2 mL samples for propane analysis were drawn through a stainless steel tube with a syringe and passed to a closed 38 mL infusion bottle. A minimum of 10

**Table 2** Summary of the parameters varied in the procedure for measurement of the mass transfer rates. A * indicates the procedure that was used in the main experiments (45 experiments)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Variation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane gas type</td>
<td>*F-gas containing min. 95% propane from BP Gas</td>
</tr>
<tr>
<td></td>
<td>Test gas containing 1.1% propane in air from Duotec A/S</td>
</tr>
<tr>
<td>Start propane concentration</td>
<td>High concentration (~100 mg L$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td>*Mean concentration (1–10 mg L$^{-1}$)</td>
</tr>
<tr>
<td></td>
<td>Low concentration (20–50 µg L$^{-1}$)</td>
</tr>
<tr>
<td>Oxygen measurement</td>
<td>*Ingold/Mettler Toledo probe</td>
</tr>
<tr>
<td></td>
<td>Fiber optic oxygen microsensor</td>
</tr>
<tr>
<td></td>
<td>Winkler titration</td>
</tr>
<tr>
<td>Water type</td>
<td>Distilled water</td>
</tr>
<tr>
<td></td>
<td>MilliQ water</td>
</tr>
<tr>
<td></td>
<td>*Glass distilled water</td>
</tr>
<tr>
<td>Water volume</td>
<td>1.5 L water</td>
</tr>
<tr>
<td></td>
<td>*2.4 L water</td>
</tr>
<tr>
<td>Propane sample volume</td>
<td>*2 mL</td>
</tr>
<tr>
<td></td>
<td>10 mL</td>
</tr>
</tbody>
</table>
samples for propane analysis were drawn at each experiment with time intervals of 1–3 hours. No preservation was done, as propane is rather stable in clean water, and the samples were analyzed within a few days. A minimum of 3 samples were analyzed from each headspace, ensuing a standard deviation of 2–3%.

The influence of a number of experimental conditions was tested in order to optimize the procedure for measurement of the mass transfer rates, cf. Table 3. A few experiments (2–10) were done with each setting after which the optimal setting was chosen. Finally, 45 experiments were done without further adjustments.

**Procedures for estimation of the oxygen mass transfer coefficient**

As previously mentioned, a number of graphical and numerical methods have been used to estimate the oxygen mass transfer coefficient. They are all based on the same model, Eq. 2, derived from Fick’s first law of diffusion.

\[
\frac{dC}{dt} = K_{La} \cdot (C_S - C)
\]

where \( C \) is the concentration of oxygen/propane (mg L\(^{-1}\)), \( C_S \) is the concentration of oxygen in equilibrium with the atmosphere (mg L\(^{-1}\)) and \( t \) is the time (s, h, d).

**Table 3** Methods for estimation of the oxygen mass transfer coefficient

<table>
<thead>
<tr>
<th>Method</th>
<th>Equation</th>
<th>( C_S )</th>
<th>Brief explanation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 Standard value saturation</td>
<td>3</td>
<td>Standard value</td>
<td>Linear least square analysis. ( C_S ) is a standard value obtained from literature and corrected for temperature and pressure</td>
</tr>
<tr>
<td>2 Measured saturation</td>
<td>3</td>
<td>Measured</td>
<td>Linear least square analysis. ( C_S ) is determined from the experiment as time goes to ( \infty ) (( C_{\infty} ))</td>
</tr>
<tr>
<td>3 Direct</td>
<td>2</td>
<td>Not necessary</td>
<td>Linear least square analysis. ( \Delta C/\Delta t = (C_{i+1} - C_i)/(t_{i+1} - t_i) ) are plotted against the mean value ( (C_i + C_{i+1})/2 ) and the slope of the line is ( K_{La} )</td>
</tr>
<tr>
<td>4 Exponential 3-parameter</td>
<td>4</td>
<td>Estimated</td>
<td>Nonlinear least square analysis with the variables ( K_{La}, C_S ) and ( C_0 )</td>
</tr>
<tr>
<td>5 Exponential 2-parameter</td>
<td>4</td>
<td>Measured</td>
<td>Nonlinear least square analysis with the variables ( K_{La} ) and ( C_0, C_S ) is determined from the experiment as time goes to ( \infty ) (( C_{\infty} ))</td>
</tr>
</tbody>
</table>
After integration of Eq. 2, an equation expressed on logarithmic form (Eq. 3) or exponential form (Eq. 4) is found.

\[
\ln\left(\frac{C_S}{C}\right) = -K_{La}t + \ln\left(\frac{C_S}{C_0}\right) \tag{3}
\]

where \( C_S \) is the concentration of oxygen/propane at saturation (mg L\(^{-1}\)) and \( C_0 \) is the concentration of oxygen/propane at time 0 (mg L\(^{-1}\)).

\[
C = C_S - (C_S - C_0) \exp(-K_{La}t) \tag{4}
\]

Several authors have reviewed the advantages and disadvantages of methods for estimation of the oxygen mass transfer coefficient (Table 3): Boyle et al. (1974), Brown and Baillod (1982), ASCE Standard (1984) and Rathbun et al. (1978). Most of these researchers conclude that the three-parameter nonlinear least square analysis (method 4) is the most appropriate, but none of the authors listed in Table 1 uses this method.

Rathbun et al. (1978) compared a linear least square method (methods 1 and 2), a two- and a three-parameter nonlinear least square method (methods 5 and 4, respectively). They found that the two-parameter nonlinear least square method was best due to unreasonable values for the saturation concentration of oxygen resulting from the three-parameter nonlinear least square method. The linear least square method was rejected, because it weights the observed concentrations as though the experimental error was a constant percentage of the concentration making the experimental error dependent on the concentration, which is not always the case (Rathbun et al. 1978).

The five different estimation methods for calculation of the oxygen mass transfer coefficient (cf. Table 3) are compared and discussed in this study. The RMSE (root mean square error) value is used for evaluation of the performance of the model. The estimated \( C_S \) and \( C_0 \) values from method 2 were used to calculate the RMSE in method 4.

Procedure for estimation of the propane mass transfer coefficient

Calculation of the mass transfer coefficient of propane is more simple as \( C_S = 0 \), whereby integration of Eq. 2 results in Eq. 5, which can be solved by a linear least square analysis.

\[
\ln(C) = -K_{La}t + \ln(C_0) \tag{5}
\]

Results and discussion

The water used in the main experiments was glass distilled water (pH = 7), because it was found in the initial test experiments that demineralized water was not sufficiently clean to obtain reaeration rates without interference from an oxygen demand of microorganisms.

A traditional oxygen probe (Clark sensor) consumes oxygen, which may result in an error in the measurement of oxygen mass transfer rates. Measurements with the Clark sensor were therefore checked against measurements with a fiber optic oxygen microsensor, having no oxygen consumption. Figure 2 shows that there was no significant difference between the measurements obtained by the two probes.

The method for determination of propane mass transfer rates was tested for a possible influence of the sample volume on the propane mass transfer rate. Figure 3 indicates that there was no such influence. Furthermore, the initial propane concentration and the water volume had no influence on the measurement result (results not shown). The propane mass transfer rates were also measured with two different types of propane gases (cf. Table 2) in order to examine a possible impact of the gas type. For the gases tested, no differences between the mass transfer rates were found (results not shown).
Figure 4 shows the mean ratios between the oxygen mass transfer coefficients estimated by the five methods listed in Table 3 and the propane mass transfer coefficients estimated by Eq. 5, calculated from the 45 main experiments. Applying the Student t-test, the $R$ values are tested to be equal at the 95% level of confidence. The RMSE value calculated between the measured and the modeled oxygen concentration shows that method 4 simulates the data best (cf. Figure 4). One disadvantage of method 4, claimed by Rathbun et al. (1978), is unreasonable values for $C_S$. $C_S$ was found to 8.98 mg L$^{-1}$ with a standard deviation of 0.13 mg L$^{-1}$ and compared with the standard value of 9.09 mg L$^{-1}$ at 20°C and 1 atm (APHA et al., 1998), the values obtained for $C_S$ are reasonable. An advantage of method 4 is that the experiment does not have to be continued until saturation occurs. The preferred method is therefore method 4.

The value of $R$ can either be calculated as a mean value, Figure 4, or from the slope of a best-fit line in a plot of $K_{La}(propane)$ versus $K_{La}(oxygen)$, Figure 5. Using estimation method 4, the mean value is calculated to 1.56 with a standard deviation of 0.12, and the slope to 1.56 ($R^2 = 0.91$), i.e. the two approaches give identical results. Based on statistical analysis of the variability, a recommended number of repetitions of the ratio $R$ determination are 7–10 (Walpole et al., 1998).

The calculated mean value of $R$ using method 1 is smaller ($R = 1.45$) than the values of $R$ calculated using the remaining methods and in addition, method 1 fits the data rather poorly compared to method 4 (cf. Figure 4). Method 1 is the most frequently used method.

---

**Figure 2** Testing of the experimental procedure. Dissolved oxygen measurement with two different oxygen probes (Clark sensor and fiber optic microsensor)

**Figure 3** Testing of the experimental procedure. Propane measurements with 2 and 10 mL propane samples, respectively
estimation method by the authors listed in Table 1, and the result of method 1 in this study is also closer to their mean value.

The experimental procedure used in this study yields no interference with pH, as the oxygen concentration was measured with a probe. Furthermore, the air temperature was controlled and kept at the same temperature as the water. This was not done by any of the authors listed in Table 1. The magnitude of this error source is, however, not known. Propane gas is heavier than air and might under quiescent conditions accumulate near the water surface, resulting in errors in the measurements of the propane mass transfer rates. However, in the present experimental setup, a constant flow through the gas phase resulted in a completely mixed gas phase without propane gas.

Bales and Holley (1986) measured the ratio between the air–water mass transfer coefficients of oxygen and propane by 45 experiments distributed on three test series resulting in a mean value of 1.47 (cf. Table 1). In the first test series (26 experiments), they obtained a mean value of 1.56, while in the two following test series (9 experiments each), the mean value obtained was 1.35 and 1.37. They could not find any explanation for the high mean value in the first test series. However, the mean value measured in the first test series fits well with the mean value obtained in this study.

In this study, the measured mean ratio between the mass transfer coefficients of oxygen and propane is within the range of the $R$ values calculated from the estimated diffusion coefficients by the method of Othmer and Thakar (1953). The value of $n$ in this

![Figure 4](https://iwaponline.com/wst/article-pdf/56/1/267/437258/267.pdf)

Figure 4 $R$ and RMSE values from the 45 main experiments

![Figure 5](https://iwaponline.com/wst/article-pdf/56/1/267/437258/267.pdf)

Figure 5 The ratio between the air–water mass transfer coefficients of oxygen and propane, respectively
study is calculated to 0.73 (Eq. 2), whereas most other authors have typically found the value of $n$ to be around 0.5, cf. Table 1. The value of $n$ found in this study is considered realistic when comparing to the studies of e.g. Yongsiri et al. (2004) who applied similar experimental setup when determining the value of $R$ for the ratio between the mass transfer of oxygen and hydrogen sulfide. Yongsiri et al. (2004) found $n$ to be around 1.

Applying the described tracer gas method with propane as tracer for air–water mass transfer, Madsen et al. (submitted) were able to determine the air–water oxygen mass transfer of three wet detention ponds to lie in the range of 0.02–3.36 m$^2$ d$^{-1}$.

Conclusions

It is crucial for application of tracer gas methods in environmental systems, that a correct ratio between the mass transfer coefficients for oxygen and the applied tracer gas is determined. In this study procedures for determination of air–water mass transfer coefficients was reviewed and tested on oxygen and propane gas. The methodology recommended is based on direct measurements in the laboratory and does not include estimated parameters. An optimal data processing procedure was found based on a comparison of the results obtained using a number of methods described in the literature. The ratio between the mass transfer coefficients for oxygen and propane, respectively, was determined to 1.56 with a standard deviation of 0.12 based on 45 experiments. The methodology requires relatively simple laboratory techniques and is readily performed.

References


