Theoretical model for diffusive **greenhouse gas** fluxes estimation across water-air
interfaces measured with the static floating chamber method

Shangbin Xiao^{a,b,*}, Chenghao Wang^{a,c}, Richard Jeremy Wilkinson^d, Defu Liu^{a,e}, Cheng Zhang^a,
Wennian Xu^a, Zhengjian Yang^e, Yuchun Wang^f, Dan Lei^a

^a *College of Hydraulic & Environmental Engineering, China Three Gorges University, Yichang,
443002, China;*

^b *State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, China
Academy of Sciences, Xi'an, 710075, China;*

^c *School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe,
AZ 85287, USA;*

^d *Institute of Environmental Sciences, University of Koblenz-Landau, Landau, 76829, Germany*

^e *College of Resources and Environment Sciences, Hubei University of Technology, Wuhan,
430068, China;*

^f *Department of Water Environment, China Institute of Water Resources and Hydropower
Research, Beijing, 100038, China.*

***Corresponding Author:**

Email: shangbinx@163.com;

Tel.: +86-13545831849;

Fax: +86-717-6392318

Abstract:

Aquatic systems are sources of greenhouse gases on different scales, however the uncertainty of gas fluxes estimated using popular methods are not well defined. Here we show that greenhouse gas fluxes across the air-water interface of seas and inland waters are significantly underestimated by the currently used static floating chamber (SFC) method. We found that the SFC CH₄ flux calculated with the popular linear regression (LR) on changes of gas concentration over time only accounts for 54.75% and 35.77% of the corresponding real gas flux when the monitoring periods are 30 and 60 minutes respectively based on the theoretical model and experimental measurements. Our results do manifest that nonlinear regression models can improve gas flux estimations, while the exponential regression (ER) model can give the best estimations which are close to true values when compared to LR. However, the quadratic regression model is proved to be inappropriate for long time measurements and those aquatic systems with high gas emission rate. The greenhouse gases effluxes emitted from aquatic systems may be much more than those reported previously, and models on future scenarios of global climate changes should be adjusted accordingly.

Keywords: theoretical model; static floating chamber; gas flux estimation; linear regression; exponential regression

1. Introduction

Aquatic systems are sources of greenhouse gases over a wide range of degrees (Bange, 2006;

Bastviken et al., 2011; Bloom et al., 2010; Frankignoulle et al., 1998; Raymond et al., 2013; Wang et al., 2011), and the exchange of gases between aquatic systems and the atmosphere exerts an important influence on the global cycling and budget of greenhouse gases (Raymond et al., 2013). Inland waters (lakes, reservoirs, streams, and rivers) are generally supersaturated with carbon dioxide (CO_2) with respect to water in equilibrium with the atmosphere, and the latest estimated flux is 2.1 Pg C y^{-1} (Raymond et al., 2013). Inland waters are also substantial methane (CH_4) sources in the terrestrial landscape, and emit at least $103 \text{ Tg of CH}_4\text{y}^{-1}$, corresponding to $0.65 \text{ Pg of C as CO}_2\text{ equivalents y}^{-1}$ (Bastviken et al., 2011). CH_4 is also supersaturated in sea water (Ward et al., 1987), and the global oceanic source for atmospheric CH_4 is estimated to be 20 Tgy^{-1} (Conrad and Seiler, 1988). Data reported from some Arctic continental shelf areas, where the CH_4 in the surface water is supersaturated up to 2500% relative to the atmosphere (Shakhova et al., 2005), greatly increase the sea-air flux of CH_4 . The total budget, the rate of change, and the fraction of modern biogenic methane are well known, but how to apportion the individual sources is less certain (Reeburgh, 2007). Bange (2006) suggests that previous estimates of the oceanic nitrous oxide (N_2O) source strength are too low and that $7 \text{ Tg N}_2\text{O y}^{-1}$ is a conservative estimate. However, these flux estimations have a large uncertainty (Forster et al., 2009). A great deal of field work has been carried out to clarify gas fluxes across the air-water interface, which are commonly estimated with eddy correlation (eddy covariance, EC) (Blomquist et al., 2006), the boundary layer equation (BLE) (Liss and Slater, 1974) and static floating chambers (SFC) (Cole et al., 2010; Frankignoulle, 1988). The two former methods often lead to different results (Broecker et al., 1986; Cole et al., 2010; Frankignoulle, 1988; Matthews

et al., 2003; Vachon et al., 2010), and the BLE method underestimates the greenhouse gas fluxes from water bodies (Duchemin et al., 1999).

The SFC method is used by most researchers because of its convenience, low cost and direct measurement of diffusive fluxes at the surface. This method is favored by process studies (Denmead, 2008), and is often used to disclose small-scale spatial differences in gas fluxes (Hendriks et al., 2010). In heterogeneous environments such as reservoirs, the SFC method is thought to be better suited than the BLE technique to understand and evaluate greenhouse gas fluxes (Duchemin et al., 1999). EC is a direct measurement (Denmead, 2008), and is used to continuously quantify large-scale temporal variability of gases (Francis and Dodge, 1989), but is, however, complex and not applicable for small areas (Hu et al., 2014). At low wind speed, artificial turbulence resulted from the chamber walls not extending below the water surface can enhance gas exchange and increase gas fluxes (Matthews et al., 2003). Additionally, SFC method is also time-consuming. So, SFC and EC methods are usually combined for gas flux estimation of large areas with heterogeneous source strengths owing to their respective advantages (Denmead, 2008; Hendriks et al., 2010).

Diffusive process across the air-water interface results from the concentration (or partial pressure) difference of a specified gas between surface water and air. Thus, gas fluxes can also be calculated from the surface water and air concentrations if the gas transfer velocity (k) is known (Guérin et al., 2007). The diffusive gas flux across the air-water interface can be expressed as:

$$Flux = k \times (C_w - C_{sat}) \quad (1)$$

where C_w is the concentration of gas in the surface water, and C_{sat} is the concentration of gas in the surface water at equilibrium with the overlying atmosphere (Raymond and Cole, 2001). The factor k (gas transfer velocity) is primarily controlled by turbulent mixing on the water side of the air-water interface (Wanninkhof et al., 2009). Wind dominates turbulence and the gas transfer velocity at the air-water interface in lakes, reservoirs, and oceans (Gurin et al., 2007; Upstill-Goddard et al., 1990; Wanninkhof et al., 2009). Both sheer stresses at the riverbed and wind at the water surface result in turbulence at the air-water interface in large rivers (Beaulieu et al., 2012). Suppose k and C_w in equation (1) change little in a short measuring period, F is determined by C_{sat} . In equation (1), C_{sat} is calculated according to the Henry's law and defined as (Sander, 2015):

$$C_{sat} = k_H R T \times C_a \quad (2)$$

Here C_a is the corresponding gas concentration in the floating chamber at the beginning of sampling, R is the gas constant, T is the temperature and k_H is the Henry's law constant. If k_H refers to standard conditions ($T^\Theta = 298.15$ K) it will be denoted as k_H^Θ .

The SFC method consists of a closed chamber that floats at the water surface, which allows gas exchanging freely between the air within it and the underlying water. Flux is calculated according to the concentration change of the gas in the chamber over time (Goldenfum, 2010; Lambert and Frchette, 2005):

$$Flux = (V/A) \text{ slope} \quad (3)$$

where *slope* is the gas concentration gradient in the chamber, V is the volume of air in the floating chamber, and A is the area of the floating chamber covering the water surfa

ce. For a cylindrical chamber, V/A is its height.

Although it is so simple, directly determining the actual pre-deployment gas flux is impossible *in the field* (Livingston et al., 2006; Venterea, 2010). The core issue is how to quantify *slope*, which determines the gas flux of each measurements *using equation* (3). Most of previous floating chamber based gas fluxes are estimated *with linear regression* (LR). The *slope* value is either accepted or rejected according to the *coefficient of determination* (R^2) of the regression curve (Lambert and Fréchet, 2005). However, the continuously increasing or decreasing gas concentration in a chamber (C_a) results in changing C_{sat} accordingly over time. Thus, there are uncertainties in gas flux estimates if the LR method is used to calculate *slope* in equation (3).

The similar issue is well known that the gas concentration evolution over time in a closed chamber above soils is not linear, and the use of linear regression on gas concentrations seriously underestimate of gas fluxes between soils and atmosphere (Kutzbach et al., 2007). The reason is that placement of a chamber results in increasing gas concentration above the soil surface and decreasing vertical gas gradient (Rochette, 2011). Many studies focused on how to improve the gas flux estimation between soils and the overlying air in recent years (Hutchinson and Mosier, 1981; Kroon et al., 2008; Kutzbach et al., 2007; Pedersen et al., 2010). Matthias et al. showed that LR of closed chamber-based N_2O flux measurement in 20 minutes underestimated the value by about 55% and 10% for the smallest chamber ($V/A=5$ cm) and the largest chamber ($V/A=30$ cm) respectively (Matthias et al., 1978). According to the results of a grassland experiment, the N_2O flux estimate by LR on gas concentrations in the chamber used was only 44% of that by the exponential regression (ER) for closure times of twenty minutes (Kroon et al., 2008). Laboratory

comparisons of chamber based fluxes show that fluxes calculated with LR underestimated their reference by on average 33%, whereas fluxes calculated ER did not significantly differ from the responding reference (Pihlatie et al., 2013).

Livingston et al. (2006) deduced the gas concentration over time in the headspace of the chamber according to Fick's law and supposed uniform properties of the soil (one dimensional diffusion theory), and proposed a nonlinear diffusive flux estimator (NDFE) for gas flux-calculation. Based on the same theory, Venterea (2010) developed a more easily adaptable method, which requires knowing soil properties (texture, bulk density, water content, temperature, pH and so on), to determine the magnitude of theoretical flux bias. Now, more commercially available automated chamber systems are deployed for soil-air flux measuring, which can provide high temporal frequency soil gas fluxes (Görres et al., 2015). Sahoo and Mayya (2010) developed a two dimensional theory by considering both lateral and vertical diffusion in soil, which could provide a more reasonable explanation for the gas concentration in the deployed chambers over time. Venterea (2013) reviewed the most used schemes of chamber-based gas flux estimates across soil-air interface and compared their theoretical differences.

There is no lateral diffusion for gas transport across the water-air interface owing to mixed water, which is substantially suitable for one dimensional theory and different from that across the soil-air interface. For gas fluxes at air-water interfaces, Bastviken et al. (2004) also noticed that a simple calculation of the total gas amount that entered the floating chambers with the measurement time underestimated the instantaneous flux rate. More recently, Silva et al. (2015) presented that the application of LR model would lead to an underestimation of GHG fluxes by

10–50%, and recommended quadratic and exponential models should be used to replace the LR model. However, these reports are empirical and lacking in theoretical basis, which may reduce their credibility. Venterea (2013) pointed out that understanding the theoretical basis of chamber based flux estimates is favorable to cautious use of chambers and probing improved methods for accurate flux at the site- and global-scale. This paper aims to: 1) deduce the theoretical model of gas fluxes estimation measured with the SFC; 2) explain the inappropriateness of the quadratic regression model (QR) for gas flux estimates; and 3) further explore the uncertainty of flux estimates by LR model.

2 Materials and Methods

2.1 Theoretical model

The gas mass in the floating chamber at time $t+dt$ can be expressed as:

$$V C_a(t) + A \text{ Flux}(t)dt = V C_a(t+dt) \quad (4)$$

thus, we have

$$\text{Flux}(t) = (V/A)(C_a(t+dt) - C_a(t)) / dt \quad (5)$$

That is

$$\text{Flux}(t) = (V/A)C'_a(t) \quad (6)$$

From (2), (3) and (6), we then have

$$C_a(t) = C_w / f - (V/A)C'_a(t) / (k f) \quad (7)$$

where $f = R T k_H$.

We compute the integral for $C_a(t)$, then obtain

$$C_a(t) = C_w/f + b_1 e^{-t k f/(V/A)} \quad (8)$$

where b_1 is the integration constant. Next, from (7) and (8), we obtain

$$C_w/f + b_1 e^{-t k f/(V/A)} = C_w/f - (V/A) C'_a(t) / (k f) \quad (9)$$

that is

$$C'_a(t) = -k f b_1 e^{-t k f/(V/A)} / (V/A). \quad (10)$$

We compute the integral for $C_a(t)$ again, then obtain

$$C_a(t) = b_2 + b_1 e^{-t k f/(V/A)} \quad (11)$$

where b_2 is the integration constant and also the gas concentration in the chamber at equilibrium

with the underlying water; and $C_a(t)_{t=0} = b_2 + b_1$. From (6) and (10), we have

$$Flux(t) = -k f b_1 e^{-t k f/(V/A)} \quad (12)$$

next, from (1) and (11), we obtain

$$slope(t) = -k f b_1 / (V/A) e^{-t k f/(V/A)} \quad (13)$$

The initial $slope(t)$, i.e., $slope(0)$, which equals $Ca'(t)_{t=0}$, is the theoretical value to estimate the real gas flux. The equation (11) has the similar expression form to that derived for the soil-air interface (Kutzbach et al., 2007), and is also similar to the empirical model given by Silva et al (2015).

Instantaneous gas flux decreases with increasing V/A and over time according to Equation (12), which results in decreasing $slope$ by LR over time. This indicates that a large chamber with high V/A could improve the flux estimates fitted by LR. In fact, gas emission strength, V/A and measurement time have varying influence on flux estimates by linear regression according to

Equation (12) and (13).

2.2 Observation system in the field

The analysis of experiments data and model testing in this paper are based on our several thousand hours field campaigns for gas flux measurements in recent years (Wang et al., 2014; Xiao et al., 2013a; Xiao et al., 2013b; Xiao et al., 2014). We used a static closed floating chamber system to measure CH₄ and CO₂ fluxes across the air-water interface in rivers, reservoirs, and wetlands. The factor k is mainly dominated by winds in lakes, reservoirs, and oceans (Guérin et al., 2007; Musenze et al., 2014; Wanninkhof et al., 2009; Xiao et al., 2013a). Here we choose data acquired from a drinking reservoir (Guanzhuang Reservoir) when the weather was clear and the water was still. Guanzhuang Reservoir is about 30 km northeast of Yichang city, Hubei province, central China. It has a total capacity of 15.6 million m³ with a basin area of 31 km². Its dam height is 38.8 m. The reservoir is oligotrophic with total phosphorus below the analytical limit of detection (0.01 mg/ L) at our laboratory. This situation does not suit phytoplankton growth, but favors relatively stable dissolved gas concentrations. As is well known, phytoplankton can greatly change dissolved CO₂ and CH₄ in surface water due to its photosynthesis and respiration (Hamilton et al., 1995; Xiao et al., 2013a), hence the situations of this reservoirs are suitable for emission measurements.

The chambers we deployed comprise opaque, thermally insulated vertical tubes (diameter and height are 0.35 and 0.45 m respectively). Floats along the lower portion of the chambers, maintain an immersion depth of 5 cm during flux monitoring, i.e., the real height (V/A) for flux

calculation is 0.4 m. Two fans (12 V, 0.22 A) were fixed at the top within the chamber to properly mix the air inside within the headspace while not disturbing the water surface. When we measured the emission flux of CH₄ and CO₂ across the water-air interface, the chamber was connected to a DLT-100 Gas Analyzer (Los Gatos Research, USA) which could monitor the CH₄ and CO₂ concentrations inside the chamber continuously at a frequency of 1 Hz. The DLT-100 has been used and described in detail elsewhere (Hendriks et al., 2010; Herbst et al., 2011). Four diel field campaigns (one day and night for each season) covering spring, summer, autumn and winter were carried out from 2012 to 2013 to measure CO₂ and CH₄ fluxes across the air-water interface in the reservoir. A single flux measurement usually finished within 30 minutes. The monitoring site is around 120 m away from the reservoir dam, and its water depth was around 11-13 m during the measuring periods. We chose the site based on the considerations of its water depth and dynamic situation. Water depth is the dominant factor controlling bubble emissions and bubbling emissions occur only at water depths lower than 10 m (Abril et al., 2005; Rosa et al., 2003). Water near the dam is almost still, which can significantly reduce the possible impact on the gas emitting process. As stated above, gas emission strength goes up with increasing wind speed and water velocity. In fact, wind speeds were too low to be determined under most conditions. The background values of CO₂ and CH₄ in atmosphere were determined by the DLT-100 during the intervals of two neighboring flux measurements. All data of gas concentrations in the chamber monitored by the DLT-100 are averaged at intervals of 10, 20 or 60 seconds according to gas emission rate.

2.3 Distinguishing ebullition and diffusive fluxes

We can separate the bubble and diffusion flux using data acquired by the DLT-100 analyzer owing to its high sampling frequency. The method was described in detail elsewhere (Xiao et al., 2014). In fact, no obvious bubble emission was observed during the experiments reported in this paper.

3. Results and discussion

3.1 Goodness of fit of different methods

Three methods, i.e. LR, QR and ER are used to fit chamber gas concentrations ($C_a(t)$) over time to the experimental data. Goodness of fit of the LR, QR and ER curves was compared by F-test values, the coefficient of determination R^2 , and the residual sum of squares of all analyses. Féménias (2005) compared applications of the χ^2 test, the F test, the Durbin–Watson d test, and the f (or *Sign*) test, and pointed out the residual analysis method is faster, simpler, and often more accurate. It clearly shows that the ER function is best suited to describe the measured $C_a(t)$ evolution in the chamber according to our data (Table 1 and Figure 1B). The ER model can give the best estimates for around 72.4% of all measurements (Table 1). The main factor which prevents the ER from giving best estimates for all of the data is the gas exchange process across the air-water interface which is somewhat unstable. It is well known that wind dominates turbulence at the air-water interface in lakes, reservoirs, and oceans (Guérin et al., 2007; Upstill-Goddard et al., 1990; Wanninkhof et al., 2009), and the gas transfer velocity can change at different scales due to gusts and breezes, resulting in complicated gas diffusion patterns and a

correspondingly irregular growth pattern of gas concentrations in the chamber (Figure 1A). However, these episodes do not change the overall trend of the gas concentration in the chamber over time, i.e. the instantaneous flux should decrease over the long-term and the equilibrium of diffusion between the underlying water and the air in the chamber will be reached. The percentage of best estimates using ER increases at strong gas emission rates. For example, the percentage is 87.5% and 88.5% for the fit of CH₄ concentration in the chamber in spring and summer (Tables 1 and 2), when the gas emission is relatively strong and the influence of the wind variability on gas diffusion is relatively weak. Considering gas concentrations in the chamber should increase exponentially according to the theoretical model (Equation (11)), the ER function is expected to best approximate to true values among the three methods.

3.2 The effect of different regression models on flux estimates

The span of our measurements for flux analysis ranged from 5 to 25 minutes. The average flux values of CH₄ and CO₂ estimated by LR can only account for around 67.4% and 71.6% of those estimated by ER respectively (Table 3). QR gives much higher estimates than LR, and the average flux values of CH₄ and CO₂ estimated by QR can account for about 91.0% and 91.4% of those estimated by ER, respectively (Table 3 and Figure 2). The similar situation of quadratic regression (QR) results in estimates were much better than the linear values, and an exponential function gave the best estimation was also disclosed in air-soil interfaces (Matthias et al., 1978). This indicates that gas fluxes across the air-water interface, calculated using LR on gas concentrations over time in the chamber, are significantly underestimated. The situation was

more serious for a terrestrial ecosystem (Kroon et al., 2008; Kutzbach et al., 2007; Matthias et al., 1978). Kutzbach et al. (2007) showed that flux values estimated using QR were lower than those estimated from ER, especially for situations with strong gas uptake or release. Here, we also observe there is a significantly negative correlation between release intensity $f_{ER}'(t0)$ and $f_{LR}'(t0) / f_{ER}'(t0)$ for measurements with similar monitoring duration (Figure 3).

3.3 The effect of different regression models on flux estimates over time

Chamber gas concentrations over time are better fit by the ER function than by QR or LR functions for measurements with different time spans at Guanzhuang Reservoir (Table 4). For a single measurement, the initial slope values ($C'_a(t)_{t=0}$) estimated by LR and QR decrease over time, but the value estimated using ER changes little (Table 4). This indicates gas fluxes estimated by QR and especially LR decline gradually with extended measurement period (Figure 4).

It has been suggested that a single flux measurement should extend to around 30-60 minutes (Abril et al., 2005; Duchemin et al., 1999; Hirota et al., 2007; Lambert and Frchette, 2005; Zhang and Ding, 2011). However, the average flux estimates by LR can only account for around 54.75% and 35.77% of those by ER for CH₄ when the monitoring periods are 30 and 60 minutes respectively (Figure 4B). The result is in good agreement with the theoretical prediction.

Supposed k changes little during a flux measurement, the instantaneous $slope(t)$ decreases over time according to equation (13). Kutzbach et al. (2007) revealed that CO₂ flux estimates by LR were as low as 40% of those by ER for closure times of only two minutes, and increasing CO₂

flux strength increased the degree of underestimation. He also recommended replacing the LR with the nonlinear regression for closed chamber studies.

For the previous offline method to estimate gas fluxes, the gas samples are collected from the chamber and then analyzed using a gas chromatograph to determine their contents. The sampling interval is usually from 5 to 10 minutes (Chen et al., 2009; Huttunen et al., 2002) according to different gas emission strength considering both statistical significance and pressure in the chamber. With the technology development of On-Line instrumentation, measuring gas contents in the chamber in real-time is popular for flux estimates. The online method is also convenient, efficient and cheap. For the latter, a short deploying duration is enough to estimate gas fluxes and also helpful to improve the gas fluxes with LR. We suggest that a single measurement range of 5-10 minutes is qualified for gas flux estimates based on the average $f_{LR}'(t_0) / f_{ER}'(t_0)$ over time of 26 measurements (Figure 4B).

Our results show that SFC with LR underestimates gas fluxes, as shown elsewhere (Bastviken et al., 2004). In addition, the variability of $slope(t)$ is dependent on k (Figure 5), which is mainly dominated by wind in lakes, reservoirs, and oceans (Guérin et al., 2007; Upstill-Goddard et al., 1990; Wanninkhof et al., 2009). Some reported k values, determined by SFC (Guérin et al., 2007; Beaulieu et al., 2012; Borges et al., 2004), may be also substantially underestimated, because high winds are often expected in such environments, resulting in large k (Borges et al., 2004). Furthermore, gas emission strength is also up to the difference of partial pressure between the monitored water and the air. The gas emission strength of Guanzhuang Reservoir is very low according to the measurements, which resulted in relatively higher values of $f_{LR}'(t_0) / f_{ER}'(t_0)$.

Thus, we think previously reported greenhouse gas fluxes at the air-water interfaces of aquatic systems acquired by SFC may be greatly underestimate the real values.

3.4 The inappropriateness for QR model for gas flux estimates

Although the QR model can also give much better gas flux estimates than the LR model as it was suggested by Silva et al. (2015) (Figure 1 and Tables 2, 3 & 4), it is just an empirical model and unexplained in theory. The most important is that the fitted coefficients of the quadratic model have no physical significances (Livingston et al., 2006). In fact, the QR model can only fit well on the pre-existing data of gas concentrations in the chamber over time, and it cannot give a reasonable and realistic prediction for extending time (Figure 6). As mentioned above, according to our measurements from Guanzhuang Reservoir, the average flux values of CH₄ estimated by QR account for about 91.0% of those estimated by ER, while for CO₂ is 91.4%. Because the span of our measurements for flux analysis ranges only from 5 to 25 minutes and the gas emission intensity is very low, we think gas fluxes estimated by QR are also lower than the real values to some extent, especially for long time measurements and those aquatic systems with high gas emission rate.

4. Conclusions

A theoretical model for chamber based gas flux estimation across the water-air interface was developed in this paper. According to this model, the gas concentration process in the chamber increased exponentially over time. Our analyses show that SFC with LR underestimates gas

fluxes. QR model is inappropriate to gas flux estimation because both the fitted coefficients have no physical significances and it also underestimates the gas flux, especially for high gas emission intensity. Previous reports on chamber based gas fluxes across the air-water interface, which were mostly estimated with LR model, underestimated the real gas fluxes on different degrees. This is especially important to apportion the individual sources of greenhouse gases. The latter is also important for global climate models.

Acknowledgements This work was financially supported by the National Science Foundation of China (No. 41273110, 51079163), Natural Science Foundation of Hubei Province, China (2014CFB672) and China Three Gorges Corporation.

References

- Abril, G., Guérin, F., Richard, S., Delmas, R., Galy-Lacaux, C., Gosse, P., Tremblay, A., Varfalvy, L., dos Santos, M.A., Matvienko, B., 2005. Carbon dioxide and methane emissions and the carbon budget of a 10-years old tropical reservoir (Petit-Saut, French Guiana). *Global Biogeochem. Cycles* 19, GB4007.
- Bange, H.W., 2006. New Directions: The importance of oceanic nitrous oxide emissions.

357 Atmospheric Environment 40, 198-199.

358 Bastviken, D., Cole, J., Pace, M., Tranvik, L., 2004. Methane emissions from lakes: Dependence
359 of lake characteristics, two regional assessments, and a global estimate. *Global*
360 *Biogeochem. Cycles* 18, GB4009.

361 Bastviken, D., Tranvik, L.J., Downing, J.A., Crill, P.M., Enrich-Prast, A., 2011. Freshwater
362 Methane Emissions Offset the Continental Carbon Sink. *Science* 331, 50-50.

363 Beaulieu, J.J., Shuster, W.D., Rebholz, J.A., 2012. Controls on gas transfer velocities in a large
364 river. *Journal of Geophysical Research(Atmospheres)* 117, G02007,
365 doi:02010.01029/02011JG001794.

366 Blomquist, B.W., Fairall, C.W., Huebert, B.J., Kieber, D.J., Westby, G.R., 2006. DMS sea-air
367 transfer velocity: Direct measurements by eddy covariance and parameterization based on
368 the NOAA/COARE gas transfer model. *Phys. Rev. Lett.* 33, L07601.

369 Bloom, A.A., Palmer, P.I., Fraser, A., Reay, D.S., Frankenberg, C., 2010. Large-Scale Controls of
370 Methanogenesis Inferred from Methane and Gravity Spaceborne Data. *Science* 327, 322-
371 325.

372 Broecker, r.W., Ledwell, J., Takahashi, T., Weiss, L., Memer, y.L., 1986. Isotopic versus
373 micrometeorologic ocean CO₂ fluxes: a serious conflict. *J. Geophys. Res.* 91, 10517.

374 Cole, J.J., Bade, D.L., Bastviken, D., Pace, M.L., Van de Bogert, M., 2010. Multiple approaches
375 to estimating air-water gas exchange in small lakes. *Limnology and Oceanography:*
376 *Methods* 8, 285-293.

377 Conrad, R., Seiler, W., 1988. Methane and hydrogen in seawater (Atlantic Ocean). *Deep Sea*

378 Research Part A. Oceanographic Research Papers 35, 1903-1917.

379 Denmead, O.T., 2008. Approaches to measuring fluxes of methane and nitrous oxide between
380 landscapes and the atmosphere. *Plant and Soil* 309, 5-24.

381 Duchemin, E., Lucotte, M., Canuel, R., 1999. Comparison of static chamber and thin boundary
382 layer equation methods for measuring greenhouse gas emissions from large water bodies.
383 *Environ. Sci. Technol.* 33, 350-357.

384 Féménias, J.-L., 2005. Fitting models to correlated data III: A comparison between residual
385 analysis and other methods. *Journal of Molecular Spectroscopy* 232, 80-101.

386 Forster, G., Upstill-Goddard, R.C., Gist, N., Robinson, C., Uher, G., Woodward, E.M.S., 2009.
387 Nitrous oxide and methane in the Atlantic Ocean between 50°N and 52°S: Latitudinal
388 distribution and sea-to-air flux. *Deep Sea Research Part II: Topical Studies in Oceanography*
389 56, 964-976.

390 Francis, A.J., Dodge, C.J., 1989. Aerobic and anaerobic microbial dissolution of toxic metals
391 from coal wastes: mechanism of action. *Environ Sci Technol* 23, 435-441.

392 Frankignoulle, M., 1988. Field measurements of air-sea CO₂ exchange. *Limnology and*
393 *Oceanography* 33, 313-322.

394 Frankignoulle, M., Abril, G.B., Alberto, Bourge, I., Canon, C., Delille, B., Libert, E., Théate, J.-
395 M., 1998. Carbon Dioxide Emission from European Estuaries. *Science* 282, 434-436.

396 Görres, C., Kammann, C., Ceulemans, R., 2015. Automation of soil flux chamber measurements:
397 potentials and pitfalls. *BGD* 12.

398 Goldenfum, J.A., 2010. GHG Measurement Guidelines for Freshwater Reservoirs: Derived

From: The UNESCO/IHA Greenhouse Gas Emissions from Freshwater Reservoirs Research
Project. International Hydropower Association (IHA).

Guérin, F., Abril, G., Serça, D., Delon, C., Richard, S., Delmas, R., Tremblay, A., Varfalvy, L.,
2007. Gas transfer velocities of CO₂ and CH₄ in a tropical reservoir and its river
downstream. *Journal of Marine Systems* 66, 161-172.

Hamilton, S.K., Sippel, S.J., Melack, J.M., 1995. Oxygen depletion and carbon dioxide and
methane production in waters of the Pantanal wetland of Brazil. *Biogeochemistry* 30, 115-
141.

Hendriks, D.M.D., van Huissteden, J., Dolman, A.J., 2010. Multi-technique assessment of spatial
and temporal variability of methane fluxes in a peat meadow. *Agr Forest Meteorol* 150, 757-
774.

Herbst, M., Friborg, T., Ringgaard, R., Soegaard, H., 2011. Interpreting the variations in
atmospheric methane fluxes observed above a restored wetland. *Agr Forest Meteorol* 151,
841-853.

Hirota, M., Senga, Y., Seike, Y., Nohara, S., Kunii, H., 2007. Fluxes of carbon dioxide, methane
and nitrous oxide in two contrastive fringing zones of coastal lagoon, Lake Nakaumi, Japan.
Chemosphere 68, 597-603.

Hu, E., Babcock, E.L., Bialkowski, S.E., Jones, S.B., Tuller, M., 2014. Methods and Techniques
for Measuring Gas Emissions from Agricultural and Animal Feeding Operations. *Critical
Reviews in Analytical Chemistry* 44, 200-219.

Hutchinson, G.L., Mosier, A.R., 1981. Improved Soil Cover Method for Field Measurement of

Nitrous Oxide Fluxes. Soil Science Society of America Journal 45, 311-316.

Kroon, P.S., Hensen, A., van den Bulk, W.C.M., Jongejan, P.A.C., Vermeulen, A.T., 2008. The importance of reducing the systematic error due to non-linearity in N₂O flux measurements by static chambers. Nutr Cycl Agroecosys 82, 175-186.

Kutzbach, L., Schneider, J., Sachs, T., Giebels, M., Nykänen, H., Shurpali, N.J., Martikainen, P.J., Alm, J., Wilmking, M., 2007. CO₂ flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression. BGeo 4, 1005-1025.

Lambert, M., Fréchette, J., 2005. Analytical techniques for measuring fluxes of CO₂ and CH₄ from hydroelectric reservoirs and natural water bodies, in: Tremblay, A., Varfalvy, L., Roehm, C., Garneau, M. (Eds.), Greenhouse Gas Emissions—Fluxes and Processes: Hydroelectric Reservoirs and Natural Environments. Springer, Berlin, pp. 37-60.

Liss, P., Slater, P., 1974. Fluxes of gases across the air-sea interface. Nature 247, 181.

Livingston, G.P., Hutchinson, G.L., Spartalian, K., 2006. Trace gas emission in chambers: A non-steady-state diffusion model. Soil Sci Soc Am J 70, 1459-1469.

Matthews, C.J., St. Louis, V.L., Hesslein, R.H., 2003. Comparison of three techniques used to measure diffusive gas exchange from sheltered aquatic surfaces. Environmental science & technology 37, 772-780.

Matthias, A.D., Yarger, D.N., Weinbeck, R.S., 1978. A numerical evaluation of chamber methods for determining gas fluxes. Phys. Rev. Lett. 5, 765-768.

Musenze, R.S., Grinham, A., Werner, U., Gale, D., Sturm, K., Udy, J., Yuan, Z., 2014. Assessing the Spatial and Temporal Variability of Diffusive Methane and Nitrous Oxide Emissions

from Subtropical Freshwater Reservoirs. *Environmental Science & Technology* 48, 14499-14507.

Pedersen, A.R., Petersen, S.O., Schelde, K., 2010. A comprehensive approach to soil-atmosphere trace-gas flux estimation with static chambers. *European Journal of Soil Science* 61, 888-902.

Pihlatie, M.K., Christiansen, J.R., Aaltonen, H., Korhonen, J.F.J., Nordbo, A., Rasilo, T., Benanti, G., Giebels, M., Helmy, M., Sheehy, J., Jones, S., Juszczak, R., Klefoth, R., Lobo-do-Vale, R., Rosa, A.P., Schreiber, P., Serça, D., Vicca, S., Wolf, B., Pumpanen, J., 2013. Comparison of static chambers to measure CH₄ emissions from soils. *Agr Forest Meteorol* 171–172, 124-136.

Raymond, P., Cole, J., 2001. Gas exchange in rivers and estuaries: Choosing a gas transfer velocity. *Estuaries* 24, 312-317.

Raymond, P.A., Hartmann, J., Lauerwald, R., Sobek, S., McDonald, C., Hoover, M., Butman, D., Striegl, R., Mayorga, E., Humborg, C., Kortelainen, P., Durr, H., Meybeck, M., Ciais, P., Guth, P., 2013. Global carbon dioxide emissions from inland waters. *Nature* 503, 355-359.

Reeburgh, W.S., 2007. Oceanic Methane Biogeochemistry. *Chemical Reviews* 107, 486-513.

Rochette, P., 2011. Towards a standard non-steady-state chamber methodology for measuring soil N₂O emissions. *Anim Feed Sci Tech* 166–167, 141-146.

Rosa, L.P., Dos Santos, M.A., Matvienko, B., Sikar, E., Lourenço, R.S.M., Menezes, C.F., 2003. Biogenic gas production from major Amazon reservoirs, Brazil. *Hydrol. Process.* 17, 1443-1450.

462 Sahoo, B.K., Mayya, Y.S., 2010. Two dimensional diffusion theory of trace gas emission into soil
 463 chambers for flux measurements. *Agr Forest Meteorol* 150, 1211-1224.

464 Sander, R., 2015. Compilation of Henry's law constants (version 4.0) for water as solvent.
 465 *Atmos. Chem. Phys.* 15, 4399-4981.

466 Shakhova, N., Semiletov, I., Panteleev, G., 2005. The distribution of methane on the Siberian
 467 Arctic shelves: Implications for the marine methane cycle. *Geophysical Research Letters*
 468 32, L09601.

469 Upstill-Goddard, R.C., Watson, A.J., Lissi, P.S., Liddicoat, M.I., 1990. Gas transfer velocities in
 470 lakes measured with SF₆. *Tellus* 42B, 364-377.

471 Vachon, D., Prairie, Y.T., Cole, J.J., 2010. The relationship between near-surface turbulence and
 472 gas transfer velocity in freshwater systems and its implications for floating chamber
 473 measurements of gas exchange. *Limnology and Oceanography* 55, 1723.

474 Venterea, R.T., 2010. Simplified method for quantifying theoretical underestimation of chamber-
 475 based trace gas fluxes. *Journal of environmental quality* 39, 126-135.

476 Venterea, R.T., 2013. Theoretical Comparison of Advanced Methods for Calculating Nitrous
 477 Oxide Fluxes using Non-steady State Chambers. *Soil Sci Soc Am J* 77.

478 Wang, C., Xiao, S., Li, Y., Zhong, H., Li, X., Peng, F., 2014. Methane formation and
 479 consumption processes in Xiangxi Bay of the Three Gorges Reservoir. *Scientific Reports* 4.

480 Wang, F., Wang, B., Liu, C.-Q., Wang, Y., Guan, J., Liu, X., Yu, Y., 2011. Carbon dioxide
 481 emission from surface water in cascade reservoirs–river system on the Maotiao River,
 482 southwest of China. *Atmos. Environ.* 45, 3827-3834.

Wanninkhof, R., Asher, W.E., Ho, D.T., Sweeney, C., McGillis, W.R., 2009. Advances in Quantifying Air-Sea Gas Exchange and Environmental Forcing. *Annual Review of Marine Science* 1, 213-244.

Ward, B.B., Kilpatrick, K.A., Novelli, P.C., Scranton, M.I., 1987. Methane oxidation and methane fluxes in the ocean surface layer and deep anoxic waters. *Nature* 327, 226-229.

Xiao, S., Liu, D., Wang, Y., Yang, Z., Chen, W., 2013a. Temporal variation of methane flux from Xiangxi Bay of the Three Gorges Reservoir. *Scientific Reports* 3, doi:10.1038/srep02500.

Xiao, S., Wang, Y., Liu, D., Yang, Z., Lei, D., Zhang, C., 2013b. Diel and seasonal variation of methane and carbon dioxide fluxes at Site Guojiaba, the Three Gorges Reservoir. *Journal of Environmental Sciences* 25, 2065-2071.

Xiao, S., Yang, H., Liu, D., Zhang, C., Lei, D., Wang, Y., Peng, F., Li, Y., Wang, C., Li, X., Wu, G., Liu, L., 2014. Gas transfer velocities of methane and carbon dioxide in a subtropical shallow pond. *Tellus B* 66, 23795, <http://dx.doi.org/23710.23402/tellusb.v23766.23795>.

Zhang, Y., Ding, W., 2011. Diel methane emissions in stands of *Spartina alterniflora* and *Suaeda salsa* from a coastal salt marsh. *Aquat Bot* 95, 262-267.

Tables

Table 1. Summary of goodness-of-fit statistics for LR, QR and ER models applied to the measurements at Guanzhuang Reservoir

CH ₄	CO ₂	total
-----------------	-----------------	-------

measurements	spring	summer	autumn	winter	spring	summer	autumn	winter	
<i>n</i>	8	25	12	15	3	22	16	15	116
<i>n</i> -ER	7	22	8	10	2	16	9	10	84
%-ER	87.5%	88.0%	66.7%	66.7%	66.7%	72.7%	56.3%	66.7%	72.4%

502 *n*-ER: best estimated by ER; %-ER: percentage of best estimated by ER.

503

504 **Table 2. Comparison between the three different regressions used for flux estimations of**

505 **Guanzhuang Reservoir**

	CH ₄				CO ₂			
	spring	summer	autumn	winter	spring	summer	autumn	winter
$f_{ER}'(t0)$ (ppm/min)	0.007	0.033	0.001	0.001	0.334	0.513	0.385	0.248
$f_{LR}'(t0) / f_{ER}'(t0)$	0.771	0.596	0.673	0.728	0.837	0.740	0.708	0.648
$f_{QR}'(t0) / f_{ER}'(t0)$	0.957	0.887	0.897	0.922	0.957	0.907	0.912	0.889

506 The ratios of the initial slope $f_{LR}'(t0)/f_{ER}'(t0)$ and $f_{QR}'(t0)/f_{ER}'(t0)$ represent the degrees of flux

507 estimates accounted by LR and QR to ER respectively.

508

509 **Table 3. Summary of the LR, QR and ER methods applied to the measurements at**

510 **Guanzhuang Reservoir**

	CH ₄		CO ₂	
	$f_{LR}'(t0) / f_{ER}'(t0)$	$F_{QR}'(t0) / f_{ER}'(t0)$	$f_{LR}'(t0) / f_{ER}'(t0)$	$F_{QR}'(t0) / f_{ER}'(t0)$

minimum	0.424	0.683	0.374	0.511
maximum	0.989	1.085	0.986	1.042
average	0.674	0.910	0.716	0.914
standard deviation	0.16	0.07	0.15	0.09
coefficient of variation	0.23	0.08	0.21	0.10
<i>n</i>	59		57	

511

512

513

514

515

516

517

518

519

520

521

Table 4. An example of comparisons of initial slope ($C'_a(t)_{t=0}$) and goodness-of-fit of LR, QR

522

and ER models applied to a measurement for different time spans at Guanzhuang

523

Reservoir

time	$C'_a(t)_{t=0}$	goodness-of-fit statistics
------	-----------------	----------------------------

/min				F-test			Residual Sum of Squares		
	LR	QR	ER	LR	QR	ER	LR	QR	ER
10.0	0.0396	0.0463	0.0464	P<0.0001			0.005	0.003	0.003
15.1	0.0362	0.0460	0.0472	P<0.0001			0.016	0.005	0.004
20.0	0.0339	0.0446	0.0466	P<0.0001			0.038	0.007	0.007
25.0	0.0316	0.0440	0.0466	P<0.0001			0.088	0.008	0.008

Original data are averaged at an interval of 10 seconds.

Figure captions

Figure 1. Examples of CH₄ concentrations in the chamber over time and comparison of LR, QR and ER curves for two measurements at Guanzhuang Reservoir.

A: the monitored CH₄ concentration pattern in the chamber over time are concave upward, and

the ER model cannot give a higher coefficient of determination R^2 even than the LR model. This situation may result from increasing turbulence effect of wind on the surface water in the later period of the measurement. Original data are averaged at an interval of 60 seconds owing to the very low emission rates of CH_4 .

B: the monitored CH_4 concentration pattern in the chamber over time are concave downward, and the ER model can give a higher coefficient of determination R^2 even than the LR model and QR model.

+: the measured values of CH_4 in the chamber. (A) - the average value at an interval of 60 s; (B) - the raw value.

Figure 2. Comparison of initial slopes of LR, QR and ER functions for the measurements at Guanzhuang Reservoir.

Figure 3. The relation of CH_4 flux accounted by LR model with its different release intensity for measurements with monitoring duration of 23.9-25.0 minutes at Guanzhuang Reservoir.

Figure 4. CH_4 flux estimates accounted by LR model ($f_{LR}'(t0) / f_{ER}'(t0)$) over time of measurements at Guanzhuang Reservoir.

A: a single measurement; B: the average of 26 measurements

Figure 5. Curve patterns of gas fluxes estimation accounted by LR model ($f_{LR}'(t0) / f_{ER}'(t0)$) over

559 time with different k at 20°C.

560 Three gases fluxes estimations, (A) CO₂, (B) CH₄, and (C) N₂O, which are account by LR model

561 $(f_{LR}'(t0) / f_{ER}'(t0))$ over time at different k are shown here.

562

563 **Figure 6.** Comparison of CH₄ concentration in the chamber predicted by different regression

564 models

565 Note: although the QR model can give a much better fit result the measured data than the LR

566 model, we observe a decreasing gas concentration in the chamber over extending time, which is

567 not reasonable and natural. Measured data are the same as Fig. 1B.

568 +: the average value of measured CH₄ concentration in the chamber.

Fig. 3

Fig. 5