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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

HIGHLIGHTS

- The theoretical model of chamber based gas flux estimation is deduced.
- Quadratic regression model is inappropriate to estimate gas fluxes in theory.
- Gas fluxes estimated with exponential regression model are closer to real values.
- Reported gas fluxes based on floating static chambers underestimate the real values.

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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 CH_4 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 min 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.

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

* Corresponding author. College of Hydraulic & Environmental Engineering, China Three Gorges University, Yichang, 443002, China.
E-mail address: shangbinx@163.com (S. Xiao).

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(CH_4) sources in the terrestrial landscape, and emit at least 103 Tg of CH_4 y^{-1}, corresponding to 0.65 Pg of C as CO_2 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 Tg y^{-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 Tg N_2O 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 (Broecke 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 the 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:

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

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 (Guérin 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 Eq. (1) change little in a short measuring period, F is determined by C_{sat}. In Eq. (1), C_{sat} is calculated according to the Henry's law and defined as (Sander, 2015):

$$C_{sat} = k_H\, R\, T \times C_a \tag{2}$$

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 ($T^{\ominus} = 298.15$ K) it will be denoted as $k_H^{\ominus}$.

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 Fréchette, 2005):

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

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 surface. 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 Eq. (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 Fréchette, 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 Eq. (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 underestimates 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 min 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,