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# Biases in greenhouse gases static chambers measurements in stabilization ponds: Comparison of flux estimation using linear and non-linear models

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## HIGHLIGHTS

- There are uncertainties about greenhouse gas emissions from wastewater treatment.
- Static flux chambers are widely used for measure trace gases from stabilization ponds.
- There are biases on greenhouse gas flux measurements using static chambers technique.
- Using only linear models underestimate greenhouse gas flux measured by static chamber.

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## ABSTRACT

The closed static chamber technique is widely used to quantify greenhouse gases (GHG) i.e. $CH_4$, $CO_2$ and $N_2O$ from aquatic and wastewater treatment systems. However, chamber-measured fluxes over air–water interfaces appear to be subject to considerable uncertainty, depending on the chamber design, lack of air mixing in the chamber, concentration gradient changes during the deployment, and irregular eruptions of gas accumulated in the sediment. In this study, the closed static chamber technique was tested in an anaerobic pond operating under tropical conditions. The closed static chambers were found to be reliable to measure GHG, but an intrinsic limitation of using closed static chambers is that not all the data for gas concentrations measured within a chamber headspace can be used to estimate the flux due to gradient concentration curves with non-plausible and physical explanations. Based on the total data set, the percentage of curves accepted was 93.6, 87.2, and 73% for $CH_4$, $CO_2$ and $N_2O$, respectively. The statistical analyses demonstrated that only considering linear regression was inappropriate (i.e. approximately 40% of the data for $CH_4$, $CO_2$ and $N_2O$ were best fitted to a non-linear regression) for the determination of GHG flux from stabilization ponds by the closed static chamber technique. In this work, it is clear that when $R^2_{adj\text{-}non\text{-}lin} > R^2_{adj\text{-}lin}$, the application of linear regression models is not recommended, as it leads to an underestimation of GHG fluxes by 10–50%. This suggests that adopting only or mostly linear regression models will affect the GHG inventories obtained by using closed static chambers. According to our results, the misuse of the usual $R^2$ parameter and only the linear regression model to estimate the fluxes will lead to reporting erroneous information on the real contribution of GHG emissions from wastewater. Therefore, the $R^2_{adj}$ and non-linear regression model analysis should be used to reduce the biases in flux estimation by the inappropriate application of only linear regression models.



## 1. Introduction

Closed static flux chambers have been widely used for measuring greenhouse gas (GHG) emissions from aquatic ecosystems and wastewater treatment systems (Huttunen et al., 2003;

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Johansson et al., 2004; Singh et al., 2005; Lambert and Fréchette, 2005; Stadmark and Leonardson, 2005; Søvik et al., 2006; Yacob et al., 2006; Søvik and Kløve, 2007; Mander et al., 2008). This technique is widely applied because it has a high degree of adaptability and sensitivity, and is easy to use to simultaneously measure $CO_2$, $CH_4$ and $N_2O$ fluxes. Other techniques, such as the eddy co-variance method (Wille et al., 2008), are more complex and expensive and are difficult to use in multiple sites and field conditions (Kroon et al., 2008; Sachs et al., 2008). The closed static chamber technique also has its difficulties which may be associated with design aspects such as height of chamber, chamber area/perimeter ratio, insulation (Rochette and Eriksen-Hamel, 2008), disturbances during measurement, lack of air mixing in the chamber, temperature and under/over pressure within the chamber, as well as air sample handling and storage (Matthews et al., 2003; Vachon et al., 2010).

The closed static chamber technique consists of sealing off a certain volume of air immediately above the water or soil surface (headspace) for a period of time of typically 20–60 min (Smith and Conen, 2004). During this period the gas concentration in this space increases to a level that can be determined by gas chromatography or infrared analysis. The flux is then calculated from the rate of increase of gas concentration over time within the chamber headspace (Lambert and Fréchette, 2005). This calculation is based on the assumption of a linear increase in the concentration of the different gasses in the headspace (Anthony et al., 1995). However, this assumption has been widely applied to GHG emissions from soils with the conclusion that gas exchange may not be constant over time because of the non steady-state conditions of closed static chambers – and most likely of the natural processes occurring in the soil (Livingston et al., 2006; Kutzbach et al., 2007). The result of this inaccuracy in the basic assumption leads to an underestimation of GHG fluxes. A similar phenomenon may occur when the technique is used for GHG measurements in aquatic systems which may imply for example that studies reporting GHG emissions from wastewater treatment systems may equally be underestimating the GHG.

This study was therefore implemented to assess the validity of linear regression to estimate GHG emissions from stabilization ponds using the static chamber technique by comparing the fluxes obtained from linear and non-linear models. To do this, the analysis of the chamber headspace concentration data from static chambers was based on the comparison of $R^2$ and $R^2_{adjusted}$ coefficients to determine the goodness of fit for linear and non-linear models (i.e. linear, quadratic or exponential).

## 2. Material and methods

### 2.1. Field conditions

The experiments on GHG measurements were conducted at the anaerobic pond (AP) of a full-scale waste stabilization pond (WSP) system. The WSP is located in the experimental research station for wastewater treatment and reuse in for Ginebra, a small town of 10,000 inhabitants located in south-west Colombia (3°43′25.98 N, 76°15′59.45 W), at an altitude of 1040 MASL. The average ambient temperature at the site is 26 °C.

The AP influent is exclusively from domestic sources, and reaches the AP after passing through a fine screen to remove coarse material. The design characteristics of the AP are: flow rate 864 $m^3\ d^{-1}$, depth 4.0 m, and theoretical hydraulic retention time of 2 days. The effluent from the AP is transferred to a secondary facultative pond.

### 2.2. Closed chamber technique

The GHG measurements (i.e. $CO_2$, $CH_4$ and $N_2O$) in the AP were based on the closed static chamber technique (also called a transient or non-steady-state system). The criteria to standardize the methodology were similar to those for GHG measurements in soils (Anthony et al., 1995; Hutchinson et al., 2000; Kroon et al., 2008; Kutzbach et al., 2007) and aquatic systems (Huttunen et al., 2003; Matthews et al., 2003; Johansson et al., 2004; Lambert and Fréchette, 2005; Mander et al., 2008; Vachon et al., 2010).

Two similar closed static chambers modified with an air circulation pump (Fig. 1) were constructed to measure $CH_4$, $CO_2$, and $N_2O$ fluxes at the pond's surface. The chambers were cylindrical (0.3 m × 0.3 m: diameter × height) and were constructed using 4.5 mm-thick transparent acrylic sheets. The chamber dimensions had an area/perimeter ratio of 75. On top of the chambers two holes were drilled to insert two gas-tight butyl rubber stoppers. One stopper was used to set a thermometer while the other was the sampling port. On the sampling port a 0.30 m plastic tube (PVC, i.d. 3 mm) was attached. The free end of each plastic tube was connected to a three-way stopcock that was used to take samples. A peristaltic pump (Cole Parmer, Masterflex Model Nr. 77521-57, and Barrington, Illinois, U.S.A.) with a flow rate of 75 ml $min^{-1}$ (4.5 l $h^{-1}$) was connected to establish the circulation of air within the chamber's headspace.

### 2.3. Sampling protocol

At the beginning of sampling a 70 mm-thick Styrofoam block was added to the rim of the chamber to keep the device floating. Then the chambers were installed gently on the water surface of the AP. The chambers were partially submerged verifying that the edges were about 50 mm beneath the water surface to prevent gas leakage from the chamber. The chambers were anchored with lines to the banks of the pond, to prevent movement and disturbances during the sampling. A boat was used to fix the chambers at the measurement points and the sampling only started once disturbances and turbulence had stopped.

The measurement time was taken as 12 min due to frequent random gas bubbling events and high productivity of $CH_4$ and $CO_2$ as can be expected in AP. This relatively short time provides an adequate balance to detect concentration changes in the chamber

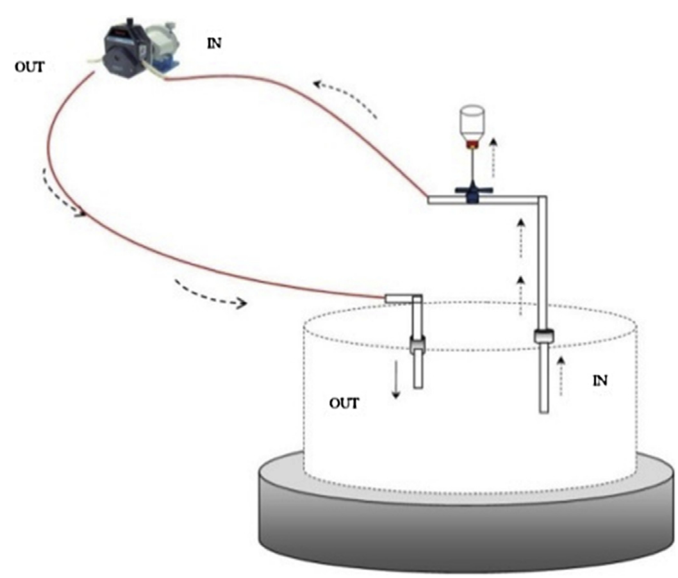


**Fig. 1.** Closed static chamber fitted with an air pump to improve air mixing.