# Theoretical Comparison of Advanced Methods for Calculating Nitrous Oxide Fluxes using Non-steady State Chambers

**Rodney T. Venterea***
USDA-ARS
Soil and Water Management Unit
1991 Upper Buford Circle
St. Paul, MN 55108

**Non-steady state (NSS) chambers provide much of the data used in bottom-up assessments of global nitrous oxide ($N_2O$) emissions. Due to inherent limitations in NSS chambers and flux calculation (FC) methods, it is likely that these assessments are negatively biased. Potentially more accurate FC schemes have been developed recently. However, there is little consensus regarding optimum FC methods and they are often selected without critical evaluation of their theoretical basis. This study used diffusion modeling to assess the accuracy of several advanced and conventional FC methods under conditions that both adhered to and violated theoretical assumptions on which the methods are based. Two methods (non-steady-state diffusive flux estimator [NDFE] and chamber bias correction [CBC]) having the same theoretical basis but differing computational approaches displayed contrasting behavior. The NDFE tended to overestimate the actual pre-deployment flux ($f_0$) to an increasing degree as assumptions were increasingly violated. In contrast, CBC was most accurate over the broadest range of conditions and relatively insensitive to assumption violation, except when unaccounted-for processes increased above certain levels. Modified R-based Hutchinson and Mosier method (HMR) underestimated $f_0$ under all conditions but became more accurate relative to NDFE and CBC as lateral gas diffusion and soil biological $N_2O$ uptake increased. This analysis offers new insight into the behavior of FC schemes under varying conditions and provides additional evidence that the most commonly used schemes tend to substantially underestimate $f_0$. Improved understanding of the theoretical basis and limitations of FC schemes should promote more prudent use of chambers, development of improved methods, and more accurate $N_2O$ flux estimates at the site- and global-scale.**

**Abbreviations**: 1D, one-dimensional; A1,A2,A3,A4, assumptions 1 through 4; CBC, chamber bias correction; DP, deployment period; FC, flux-calculation; FEB, flux-estimate bias; *H*, chamber height; HM, Hutchinson and Mosier method; HMR, modified R-based Hutchinson and Mosier method; LR, linear regression; MAE, mean absolute error; NDFE, non-steady-state diffusive flux estimator; NSS, non-steady-state; ODE, ordinary differential equation; PDE, partial differential equation; Pr, production rate; QR, quadratic regression.

Non-steady state chambers are widely used for measuring soil-to-atmosphere fluxes of $N_2O$ and other biogenic trace gases. Site-level chamber measurements provide much of the data used in "bottom-up" assessments of regional and global $N_2O$ emissions, and are used to calibrate emissions models that also contribute to these assessments (USEPA, 2012; Del Grosso et al., 2005). Several FC schemes are available for use with NSS gas flux chambers, and different methods can produce substantially different results. Venterea et al. (2010) found that selection of a FC method altered growing season $N_2O$ emissions esti-

Soil Sci. Soc. Am. J. 77:709–720
doi:10.2136/sssaj2013.01.0010
Mention of trade names or commercial products is solely for the purpose of providing specific information and does not imply recommendation or endorsement by the USDA.
Received date 27 Feb. 2013.
*Corresponding author (rod.venterea@ars.usda.gov).

mates by up to 35% averaged over 3 yr. Levy et al. (2011) concluded that FC method selection was the largest source of uncertainty in $N_2O$ flux estimates. While linear regression (LR) is commonly used (Rochette and Eriksen-Hamel, 2008), LR tends to underestimate $f_0$ (Matthias et al., 1978; Anthony et al., 1995). Furthermore, Livingston et al. (2006) showed that commonly used alternatives to LR, including quadratic regression (QR) (Wagner et al., 1997) and the method of Hutchinson and Mosier (HM) (1981), are also likely to underestimate $f_0$. Thus, $N_2O$ emissions assessments based on extrapolation of NSS chamber data are likely to be negatively biased.

Flux-calculation methods developed since 2006 claim to provide more accuracy in estimating $f_0$ than existing methods and therefore may alleviate problems with flux underestimation. At least three "advanced" FC schemes have been developed that are based on a more rigorous theory compared with previous methods, each of which employs different underlying assumptions and/or implementation techniques. Livingston et al. (2006) developed the NDFE method that uses an exact solution to a partial differential equation (PDE) describing non-steady state gas diffusion. The NDFE theory assumes vertical uniformity of soil–gas diffusivity, restriction to one-dimensional (1D) diffusion, and no soil biological uptake. An analytical solution to the PDE was derived by Livingston et al. (2006) that could be solved for fo using a nonlinear regression solver. Venterea and Baker (2008) showed that the NDFE method did not always accurately predict $f_0$ when soils were not vertically uniform and that it often generated more than one $f_0$ estimate for a given data set. Venterea (2010) developed the CBC method based on the same theory as NDFE but which delivers a single flux estimate and avoids nonlinear regression. The CBC method must be combined with a direct calculation FC scheme and also requires soil property data and parameter estimation. Kutzbach et al. (2007) and Levy et al. (2011) found that the NDFE method tended to generate extraneously high flux estimates which Kutzbach et al. (2007) attributed to physical conditions that violated the NDFE restriction to 1D diffusion or to leakage resulting from imperfectly sealed chambers. Pedersen et al. (2010) developed the HMR method that attempts to account for lateral subsurface gas diffusion as well as chamber leakage by extending the theory originally used to develop the HM method. The HM and HMR methods make assumptions about the nature of soil–gas concentration profiles.

Use of experimental data to evaluate FC method accuracy is problematic because the true $f_0$ value under field conditions is not known (Anthony et al., 1995) and development of laboratory devices that simulate field conditions has proven to be difficult (Martin et al., 2004; Widen and Lindroth, 2003). In addition, field data are subject to measurement error which further complicates the assessment of FC method accuracy (Venterea et al., 2009). Thus, numerical modeling using generally accepted diffusion theory has been used to evaluate FC accuracy by comparing known (model-simulated) $f_0$ values to fluxes estimated using the various FC methods. Previous studies have not compared the performance of the NDFE, CBC, and HMR methods. In addition to vertical gas diffusion, previous modeling studies have accounted for zero-order trace gas production (Conen and Smith, 2000), first-order gas consumption (Hutchinson et al., 2000), and lateral gas diffusion occurring beneath the chamber walls (Matthias et al., 1978; Healy et al., 1996). These studies have all assumed that soil physical properties and therefore soil–gas diffusivity were constant over the depth of the soil profile, which is an unlikely condition (Venterea and Baker, 2008). The current study employed a diffusion-reaction model that simulates a wider range of biophysical conditions than previously used models. The main objectives of this analysis were to use the model to quantify the bias of several advanced and conventional FC methods, and to assess the sensitivity of flux estimates to violation of specific assumptions on which each of the methods are based. The analysis was designed to evaluate the theoretical, best-case performance of each method under each set of conditions, that is, in the absence of errors in measurement of chamber $N_2O$ concentration or other required input variables.

# METHODS

## Model Generation of Non-steady State Chamber Data

The model used by Venterea and Baker (2008) to account for soil non-uniformity was expanded to account for 2D diffusion, Michaelis–Menten biological kinetics, and chamber leakage. The basic elements of the model are described below with additional details supplied as Supplemental material. The governing equation for gas transport was

$$S(z)\frac{\partial C}{\partial t}=\frac{\partial}{\partial z}\left[D_s(z)\frac{\partial C}{\partial z}\right]+\frac{\partial}{\partial y}\left[D_s(z)\frac{\partial C}{\partial y}\right]+\rho(z)\mathrm{Pr}-\theta(z)U \quad [1]$$

where $S$ is a mass storage coefficient, $C$ is the gas-phase $N_2O$ concentration, $t$ is time, $D_s$ is the soil–gas diffusion coefficient, $z$ is depth, $y$ is horizontal distance, ρ is bulk density, Pr is the $N_2O$ production rate, θ is volumetric water content, and $U$ is the $N_2O$ uptake rate. Soil physical properties (i.e., ρ and θ) and therefore $D_s$ were allowed to vary with depth but were assumed to be uniform in the lateral ($y$) dimension and constant over time.

For each simulation, a specific vertical distribution of ρ and θ was assumed across the depth of the profile which was then used to calculate $S$ and $D_s$ as functions of $z$. Equation [1] was discretized using the Crank–Nicolson method for the spatially-variable diffusion terms (Beu, 2007) and Taylor-series expansion of nonlinear reaction terms (Wu et al., 1990) to generate a tri-diagonal matrix that was solved in two-spatial dimensions using the alternating implicit finite difference algorithm written in FORTRAN (Lapidus and Pinder, 1982). At each time step, gas concentrations in the soil profile at 1-mm increments were calculated and $N_2O$ flux at the soil-atmosphere interface was determined by applying Fick's law across the upper 1 mm. For each set of conditions, solutions to Eq. [1] were first obtained with a free-atmosphere upper boundary until the system evolved to steady state with unchanging soil–gas $N_2O$ concentrations and a constant soil-to-atmosphere $N_2O$ flux. The upper boundary condition was then changed to account for $N_2O$ accumulating in a homogeneously mixed chamber having a specific chamber volume-to-area ratio (*H*, also referred to as chamber height). Model-calculated chamber $N_2O$ concentrations and surface $N_2O$ fluxes were recorded at specific times after deployment. Chamber deployment altered the upper boundary condition and therefore affected gas diffusion within the soil and across the soil-atmosphere interface but was assumed to not affect soil temperature or other factors regulating gross $N_2O$ production or consumption. For all simulations, values of Pr in Eq. [1] were selected so that resulting $f_0$ values occurring at steady state before chamber deployment would be 100 mg N $m^{-2}$ $h^{-1}$. Previous analysis using similar procedures showed that FC method error expressed as a proportion of $f_0$ is independent of $f_0$ and the vertical distribution of Pr (Hutchinson et al., 2000; Venterea and Baker, 2008; Conen and Smith, 2000); this result was confirmed here in preliminary simulations.

## Selection of Biophysical Conditions

Flux-calculation method performance was evaluated across a range of conditions including those that violated assumptions on which the FC methods were based. Assumptions evaluated were: (A1) $N_2O$ gas transport is limited to 1D diffusion; (A2) no biological uptake of $N_2O$ occurs in the soil; (A3) no leakage of $N_2O$ occurs from the chamber; and (A4) soil–gas diffusivity is constant with depth. The NDFE and CBC methods assume all four conditions, while the HMR method assumes A2 and A4 but claims to account for lateral diffusion (A1) and chamber leakage (A3). Additional assumptions of the HM and HMR methods were also examined (described below). Fourteen "series" of simulations were used for the evaluation, with each series consisting of seven different biophysical conditions. Within each series, one condition served as a "baseline condition" where assumptions A1, A2, A3, and (in some cases) A4 were met. In the other six conditions in each series, one model parameter corresponding to one of the assumptions was allowed to vary in a manner that increasingly violated that assumption while all other parameters were held constant. Model parameters used to evaluate each assumption are shown in Table 1. Series 1 to 6 assumed that soil physical properties were uniform with depth, while Series 7 to 14 assumed that θ and ρ varied with depth. Series 6 to 12 assumed vertical profiles for θ and ρ based on measured values in three different soils that were used as input in previous model simulations (see Fig. 1 of Venterea and Baker, 2008) while Series 13 to 14 assumed hypothetical layered soils with varying thickness of the upper soil layer. The baseline conditions in Series 1 to 6 and Series 13 to 14 adhered to all four assumptions, while the baseline conditions in Series 7 to 12 adhered to A1, A2, and A3, but violated A4.

Series 1 to 4 and 7 to 9 examined assumption A1 as controlled by chamber wall insertion depth ($D_{ch}$) (Table 1). Decreasing $D_{ch}$ allowed for increasing amounts of lateral gas diffusion occurring beneath the chamber walls. All other simulations assumed $D_{ch}$ was sufficient to prevent lateral diffusion by setting $D_{ch}$ equal to the full depth of the soil profile. Series 5 and 6 examined assump-

**Table 1. Values of key parameters used in each series of simulations.**

| Series | Assumption evaluated | Fixed parameters† | | | | | Varying parameters‡ |
|---|---|---|---|---|---|---|---|
| | | ***H*** | ρ | θ | WFPS | ε | |
| | | m | Mg $m^{-3}$ | $m^3$ $m^{-3}$ | % | $m^3$ $m^{-3}$ | |
| | | | | Uniform soils | | | |
| 1 | No lateral diffusion (A1) | 0.05 | 1100 | 0.06 | 9.4 | 0.53 | $D_{ch}$, mm (1000), 160, 80, 40, 20, 10, 5 |
| 2 | | 0.10 | 1100 | 0.06 | 9.4 | 0.53 | |
| 3 | | 0.20 | 1100 | 0.06 | 9.4 | 0.53 | |
| 4 | | 0.10 | 1100 | 0.28 | 47 | 0.31 | |
| 5 | No biological uptake (A2) | 0.05 | 1100 | 0.24 | 40 | 0.34 | $V_m$, mg N $m^{-3}$ $H_2O$ $h^{-1}$ (0), 30, 60, 90, 120, 150, 180 |
| 6 | | 0.05 | 1100 | 0.35 | 60 | 0.23 | |
| | | | | Non-uniform soils§ | | | |
| 7 | No lateral diffusion (A1) | 0.10 | 1190 | 0.14 | 25 | 0.41 | $D_{ch}$, mm (1000), 160, 80, 40, 20, 10, 5 |
| 8 | | 0.10 | 1380 | 0.26 | 54 | 0.22 | |
| 9 | | 0.10 | 200 | 0.09 | 11 | 0.72 | |
| 10 | No chamber leakage (A3) | same as Series 7 | | | | | $\alpha_L$, $m^{-2}$ (0), 1, 2, 4, 10, 20, 40 |
| 11 | | same as Series 8 | | | | | |
| 12 | | same as Series 9 | | | | | |
| 13 | Soil uniformity (A4) | 0.10 | 800¶<br>1200 | 0.04<br>0.36 | 6<br>66 | 0.66<br>0.19 | *d*, mm (0), 10, 30, 50, 75, 100, 150 |
| 14 | | 0.10 | 800<br>1200 | 0.04<br>0.53 | 6<br>97 | 0.66<br>0.02 | |

† Variables held constant for all conditions within each series: *H* is chamber height, ρ is bulk density, θ is water content, WFPS is water-filled pore space, ε is air-filled porosity.

‡ Values in parentheses were used for baseline conditions and other values were used in non-baseline conditions. $D_{ch}$ is chamber insertion depth, $V_m$ is maximum $N_2O$ uptake rate, $\alpha_L$ is leakage coefficient, d is thickness of upper soil layer. Unless indicated $D_{ch}$ = 1000 mm, $V_m$ = 0, $\alpha_L$ = 0, *d* = 0.

§ Soil physical properties for Series 7 to 12 are average values over the upper 0.10 m of soil. Series 7 and 10 used the moldboard plowed (MB) profile; Series 8 and 11 used the no-till (NT) profile; Series 9 and 12 used the temperate forest (TF) profile (per Fig. 1 of Venterea and Baker, 2008);

¶ Smaller values of ρ, θ, and WFPS, and larger values of e for Series 13 to 14 are for the upper soil layer above the depth d and other values are for the soil layer below the depth *d*.

tion A2 as controlled by the maximum substrate utilization rate ($V_m$) which was used to calculate $U$ in Eq. [1] based on Michaelis–Menten kinetics for biological reduction of $N_2O$ to $N_2$. All other simulations assumed $V_m$ and $U$ equal to zero. Series 10 to 12 examined assumption A3 as controlled by the rate of chamber leakage which was controlled by a leakage coefficient ($\alpha_L$) based on Fickian diffusion through a hole in the chamber.

Series 13 to 14 were designed to simulate a specific set of soil biophysical conditions assumed by Hutchinson and Mosier (1981) in their original formulation of the HM method, that is, where "the zone of $N_2O$ production lies somewhat below the surface and is overlain by a layer of relatively dry, loosely packed soil" (p. 312). Accordingly, hypothetical soil profiles with uniform θ and ρ values in each of two layers were simulated (Table 1). The thickness ($d$) of the upper (drier and less dense) soil layer was allowed to vary from 0 to 150 mm. Production of $N_2O$ was assumed to be negligible in the upper layer but constant (zero-order) in the underlying layer which was assumed to be moderately wet for Series 13 and close to fully saturated for Series 14 (Table 1). Series 13 to 14 were the only series in which soil physical properties differed for the varying conditions; for this reason the results were analyzed separately from Series 1 to 12.

Each biophysical condition described above was simulated over three different chamber deployment periods (DP) periods (25, 50, and 100 min). In each case, chamber $N_2O$ concentrations were recorded at five equally-spaced time points (including time zero). A total of 284 unique chamber data sets were generated and evaluated by each FC method.

## Flux Calculations

Each set of simulated chamber data was used to calculate an estimated flux ($f_{est}$) using each advanced scheme (NDFE, CBC, and HMR) and three conventional schemes (LR, QR, and HM). For LR, the rate of change in chamber $N_2O$ concentration was estimated using the SLOPE function, and for QR, the slope at time zero was estimated using the LINEST function in Microsoft Excel. For HM, the first, middle, and final time points were used to calculate the slope per Hutchinson and Mosier (1981). For LR, QR, and HM, slope values were multiplied by $H$ to determine $f_{est}$. For HMR and NDFE, flux-estimates were obtained using nonlinear regression solvers (available for HMR at http://cran.opensourceresources.org/and for NDFE at http://arsagsoftware.ars.usda.gov). The HMR solver allows the user to select LR or HMR and also provides a recommendation. In all cases, the HMR solver recommended the HMR method. In cases where the NDFE solver generated more than one $f_{est}$ value, the value that was closest to $f_0$ while also generating non-zero estimates of other model parameters was selected.

The CBC method involves first using a conventional "base" method to obtain an initial flux estimate and then applying a correction factor that depends on soil properties, $H$, and DP (Venterea, 2010; Venterea and Parkin, 2012) (an example calculation spreadsheet is available on-line at http://www.ars.usda.gov/pandp/people/people.htm?personid=31831). For the majority of this analysis, QR was used as the base method (referred to as CBC–QR). Selected comparisons were made using LR as the base method (referred to as CBC–LR). Because the CBC method relies on soil physical properties, correction factors for the uniform soils (Series 1–6) and non-uniform soils (Series 7–14) were handled differently. Correction factors for uniform soils were calculated using θ and ρ values input to the model which were constant across the soil profile. Correction factors for non-uniform soils were calculated using θ and ρ values representative of a soil sample collected over the upper 0.10 m (Table 1) as recommended by Venterea and Parkin (2012). Flux-estimate bias (FEB) for each method was calculated as a percentage of $f_0$ using $\mathrm{FEB} = \frac{f_{est} - f_0}{f_0} \times 100$ (Livingston et al., 2006). The absolute accuracy of flux estimates was evaluated over multiple ($n$) comparisons using the mean absolute error (MAE) = $\frac{1}{n}\sum_n |f_{est} - f_0|$ (Willmott and Matsuura, 2005).

## Sensitivity to Violation of Theoretical Assumptions

Violation of assumptions A1 to A3 in Series 1 to 12 was expected to result in increasing nonlinearity in chamber data, because each process reduces the amount of $N_2O$ that accumulates in the chamber during a given time period relative to the baseline condition. Preliminary analysis indicated that a simplified curvature index could be used as a proxy for the decrease in cumulative $N_2O$ flux into the chamber. This quantity was therefore used to represent the extent to which each assumption was violated in Series 1 to 12. Each simulated chamber data set was first characterized with respect to its curvature using the index (β) given by

$$\beta = \frac{C_f - C_m}{C_m - C_0} \quad [2]$$

where $C$ is the simulated chamber $N_2O$ concentration and the subscripts 0, $m$, and $f$ refer to the first (time zero), middle (third), and final (fifth) time points following chamber deployment. The β value varies inversely with the degree of curvature, varying from a value of 0 (maximum curvature) to 1 (no curvature, i.e., perfect linearity). In addition to the actual curvature (β) for each chamber data set, the degree of curvature expected when assumptions A1, A2, and A3 were met was determined for each simulation. This was done using the NDFE theory in reverse, that is, Eq. [11] of Livingston et al. (2006) was used together with soil properties (θ and ρ) and chamber conditions ($H$ and DP) to calculate the chamber data predicted by the NDFE model (see Appendix). These chamber data were used in Eq. [2] to determine the theoretical curvature ($\beta_{th}$) which was then used to determine percent deviation of observed from theoretical curvature using

$$\beta_{dev} = \frac{\beta_{th} - \beta}{\beta_{th}} \times 100 \quad [3]$$

Values of $\beta_{dev}$ different than 0% indicate more ($\beta_{dev} > 0\%$) or less ($\beta_{dev} < 0\%$) data curvature than predicted by NDFE model assumptions. For each baseline condition in Series 1 to 6, it was expected that the model-simulated chamber data would display $\beta_{dev}$ values close to zero (this was confirmed in results). Because assumption A4 was not adhered to in Series 7 to 12, interpretation of $\beta_{dev}$ values for these series is somewhat different than for Series 1 to 6; that is, for each baseline condition in Series 7 to 12, $\beta_{dev}$ values different from zero can be attributed entirely to violation of assumption A4. However, for all series (1–12), increasing $\beta_{dev}$ values relative to the baseline condition can be interpreted in the same way, that is, as representing increasing violation of assumption A1, A2, or A3. The $\beta_{dev}$ index was found to be well-correlated ($r^2$ = 0.99) with the decrease in $N_2O$ mass accumulating in the chamber in the non-baseline conditions relative to the respective baseline condition for each series. It was also found that FEB varied in a consistent manner with $\beta_{dev}$. Thus, the sensitivity of FEB to deviation from each assumption was evaluated from the slope of FEB vs. $\beta_{dev}$ using linear regression.

# RESULTS

## Baseline Conditions

For baseline conditions with uniform soils (Series 1–6 and 13–14), where biophysical conditions were in agreement with all NDFE and CBC assumptions, $\beta_{dev}$ values were close to zero (<1%) and FEB for NDFE– and CBC–QR was within 2.1% of $f_o$ (Table 2). For baseline conditions with non-uniform soils (Series 7–12), $\beta_{dev}$ values diverged from zero to varying degrees, and FEB for NDFE and CBC–QR ranged from –26 to –6% and from –11 to –6%, respectively. The temperate forest soil profile (Series 9 and 12) which had the greatest vertical variation in soil properties with depth (Venterea and Baker, 2008) also had the greatest deviation from theoretical curvature in its baseline condition and resulted in the greatest FEB. The HMR method was consistently less accurate than NDFE or CBC–QR for all baseline conditions, underestimating $f_o$ by up to 43% in uniform soils and 45% in non-uniform soils (Table 2). All FC methods were highly accurate for the baseline condition for Series 14 which had the highest degree of linearity in chamber data of all simulations ($r^2$ > 0.999) and where even LR estimated $f_o$ within 1.2%.

## Series 1 to 12

As expected, as the magnitude of lateral diffusion (Series 1–4, 7–9), biological uptake (Series 5–6), or chamber leakage (Series 10–12) increased, increasing nonlinearity in chamber $N_2O$ concentrations vs. time was exhibited (Fig. 1).

## Non-steady-state Diffusive Flux Estimator

Flux-estimates bias with NDFE was highly sensitive to deviation from theoretical assumptions, regardless of the source of the deviation, and tended to overestimate $f_0$ for most conditions (Fig. 2). Maximum FEB values within each series ranged from 50 to 125%. The relationship between FEB and $\beta_{dev}$ displayed similar patterns for all series, that is, for $\beta_{dev}$ below approximately 40%, FEB increased with increasing $\beta_{dev}$. In contrast, for $\beta_{dev}$ > 40%, FEB tended to decrease with increasing $\beta_{dev}$. Except for some cases (Series 1, 2, 7, and 9), FEB at a given value of $\beta_{dev}$ was similar or identical for different DP values (Fig. 2). The NDFE-based flux estimates displayed a greater range of variation in FEB than CBC–QR or HMR (Fig. 2 and 3) and had the greatest MAE of all methods at intermediate values of $\beta_{dev}$ (Fig. 4). The NDFE was more sensitive than CBC or HMR to deviation from theoretical assumptions for all sources of deviation (Table 3).

## Chamber Bias Correction

The CBC–QR method displayed greater accuracy than NDFE across the majority of conditions (Fig. 2) and was substantially less sensitive to violation of assumptions A1, A2, and A3 than NDFE or CBC–LR (Table 3). Sensitivity of CBC–QR to lateral diffusion effects was similar to that of HMR for $\beta_{dev} \leq 40\%$ but greater than HMR for $\beta_{dev}$ > 40% (Table 3). The CBC–QR was insensitive to uptake effects, but more sensitive to leakage ef-

**Table 2. Deviation of observed from theoretical curvature ($\beta_{dev}$) and flux-estimate bias (FEB) for baseline conditions in each series of simulations calculated for the non-steady-state diffusive flux estimator (NDFE), chamber bias correction–quadratic regression (CBC–QR), and modified R-based Hutchinson and Mosier (HMR) methods.**

| Series | Deployment period, min | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 25 | 50 | 100 | 25 | 50 | 100 | 25 | 50 | 100 | 25 | 50 | 100 |
| | $\beta_{dev}$, % | | | NDFE | | | CBC–QR | | | HMR | | |
| | | | | FEB, % | | | | | | | | |
| | Uniform soils | | | | | | | | | | | |
| 1 | 0.45 | 0.47 | 0.44 | 2.03 | 2.09 | 2.09 | 0.95 | 1.63 | 3.14 | –26.16 | –34.05 | –42.85 |
| 2 | 0.16 | 0.19 | 0.21 | 1.05 | 1.11 | 1.13 | 0.65 | 0.35 | 0.33 | –14.71 | –20.04 | –26.64 |
| 3 | 0.05 | 0.07 | 0.08 | 0.56 | 0.62 | 0.65 | 0.75 | 0.59 | 0.29 | –7.78 | –10.89 | –15.02 |
| 4 | 0.05 | 0.06 | 0.07 | 0.53 | 0.59 | 0.62 | 0.74 | 0.59 | 0.31 | –7.85 | –10.97 | –15.11 |
| 5 | 0.15 | 0.12 | 0.10 | 0.10 | 0.65 | 0.68 | –0.37 | –0.53 | –0.16 | –19.96 | –23.07 | –30.18 |
| 6 | 0.17 | 0.06 | 0.09 | 0.10 | 0.61 | 0.64 | 0.05 | 0.34 | 0.08 | –12.76 | –14.97 | –20.25 |
| 13† | 0.02 | 0.02 | 0.03 | 0.36 | 0.42 | 0.45 | 0.60 | 0.68 | 0.64 | –4.15 | –5.91 | –8.33 |
| 14† | –0.02 | –0.01 | –0.01 | 0.17 | 0.24 | 0.28 | –0.87 | –0.68 | –0.50 | –0.08 | –0.16 | –0.32 |
| | Non-uniform soils | | | | | | | | | | | |
| 7, 10 | –2.29 | –5.46 | –9.54 | –7.95 | –10.91 | –14.06 | –6.25 | –6.53 | –5.65 | –17.08 | –21.25 | –25.78 |
| 8, 11 | 0.16 | –1.61 | –4.01 | –6.28 | –8.38 | –10.52 | –6.38 | –7.12 | –7.37 | –11.50 | –14.19 | –17.08 |
| 9, 12 | –8.95 | –16.31 | –22.67 | –12.72 | –20.32 | –26.42 | –10.80 | –10.78 | –7.28 | –31.01 | –38.18 | –44.67 |

† In Series 13 to14, baseline conditions assumed uniform soil properties but non-baseline conditions assumed non-uniform (i.e., layered) soil properties.

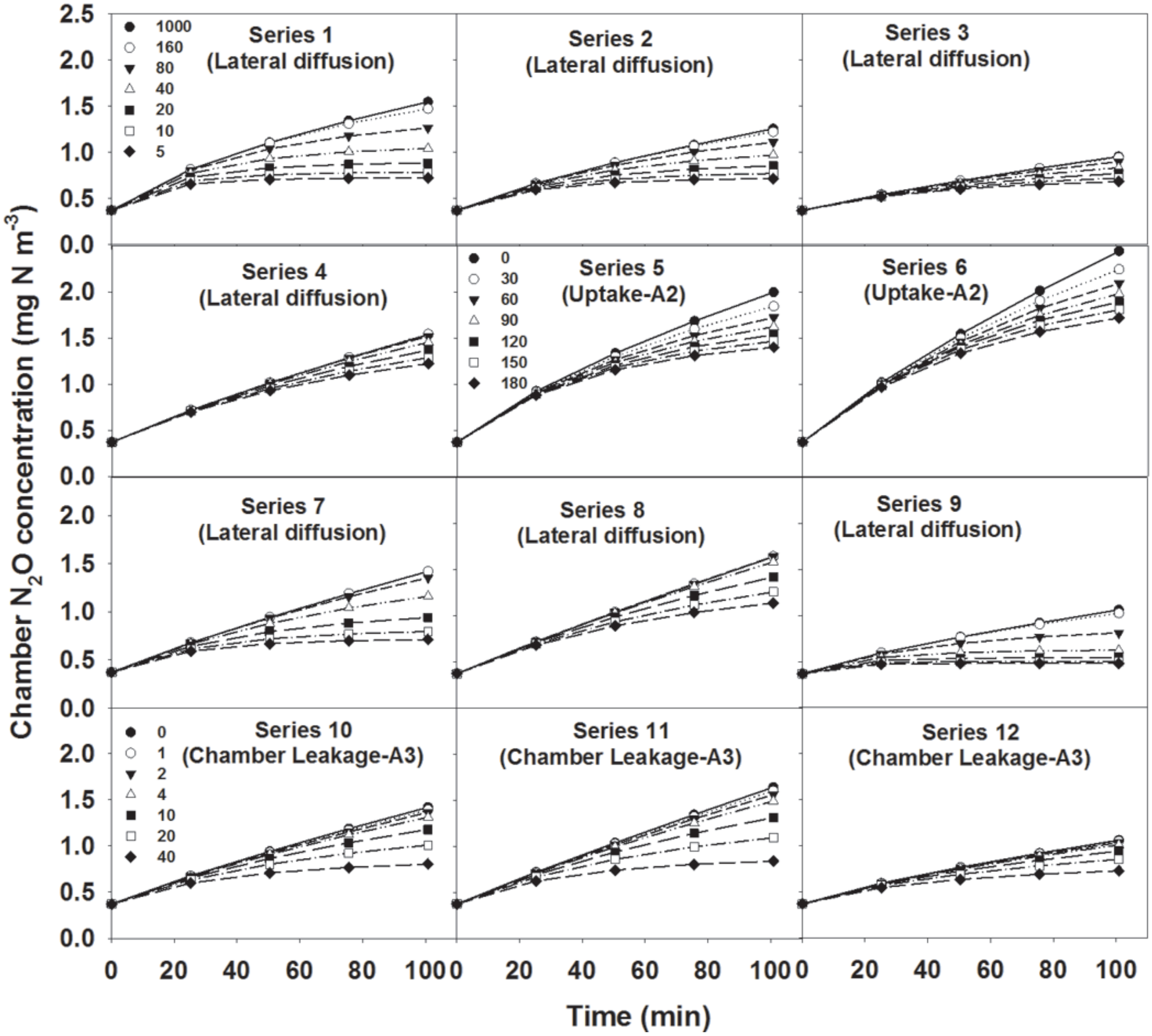


**Fig. 1. Simulated chamber $N_2O$ data for Series 1 to 12. Legends in Series 1 are wall insertion depths ($D_{ch}$, mm) which apply to Series 1 to 4 and 7 to 9. Legends in Series 5 are maximum $N_2O$ uptake rates ($V_m$, mg N $m^{-3}$ $H_2O$ $h^{-1}$) which apply to Series 5 to 6. Legends in Series 10 are leakage coefficients ($\alpha_L$, $m^{-2}$) which apply to Series 10 to 12. Results using chamber deployment period (DP) of 100 min are shown.**

fects compared to HMR (Table 3). For a given value of $\beta_{dev}$ within each series, FEB did not change with DP. The CBC–QR method displayed the lowest MAE of all methods for 5% < $\beta_{dev} \leq$ 65%.

## Modified R-based Hutchinson and Mosier Method

The HMR method underestimated $f_0$ across all biophysical conditions by 4.4 to 46% (Fig. 3). The HMR was increasingly accurate as DP decreased in all cases. In contrast to other methods, HMR-based flux estimates tended to not change or became slightly more accurate as $\beta_{dev}$ increased with each DP. The HMR-based flux estimates were least sensitive to chamber leakage across all conditions and less sensitive than NDFE and CBC to lateral diffusion for $\beta_{dev} \geq$ 40% (Table 3).

## Hutchinson and Mosier Method, Quadratic Regression, and Linear Regression

Fluxes estimated by HM were nearly identical to HMR estimates for $\beta_{dev} \leq$ 55%, but HM became increasingly less accurate than HMR as $\beta_{dev}$ increased above 55% (Fig. 4). Similar to HM and HMR, QR was consistently more accurate as DP decreased (Fig. 3). Except for $\beta_{dev}$ < 5%, QR was less accurate than HMR or HM, and in contrast to HMR became increasingly less accurate as $\beta_{dev}$ increased within each DP. The difference in MAE between QR and HMR or HM increased as $\beta_{dev}$ increased above 5% (Fig. 4). Linear regression consistently underestimated $f_0$ (results not shown) and had the greatest MAE of all conventional methods (Fig. 4). However, LR had lower MAE than NDFE for $\beta_{dev}$ in the range of 30 to 70%. None of the conventional methods (LR, QR, or HM) achieved the same accuracy as NDFE for $\beta_{dev}$ < 15%, CBC–QR for $\beta_{dev}$ < 65%, or HMR for $\beta_{dev}$ > 65%.

## Series 13 to 14

As the thickness ($d$) of the drier, more porous soil layer increased from 0 to 150 mm, chamber $N_2O$ concentrations became increasingly nonlinear in time (Fig. 5a). Fluxes estimated by CBC–QR were consistently more accurate than NDFE and HMR for $d$ > 0 at all DPs (Fig. 5b). The HMR and HM flux-

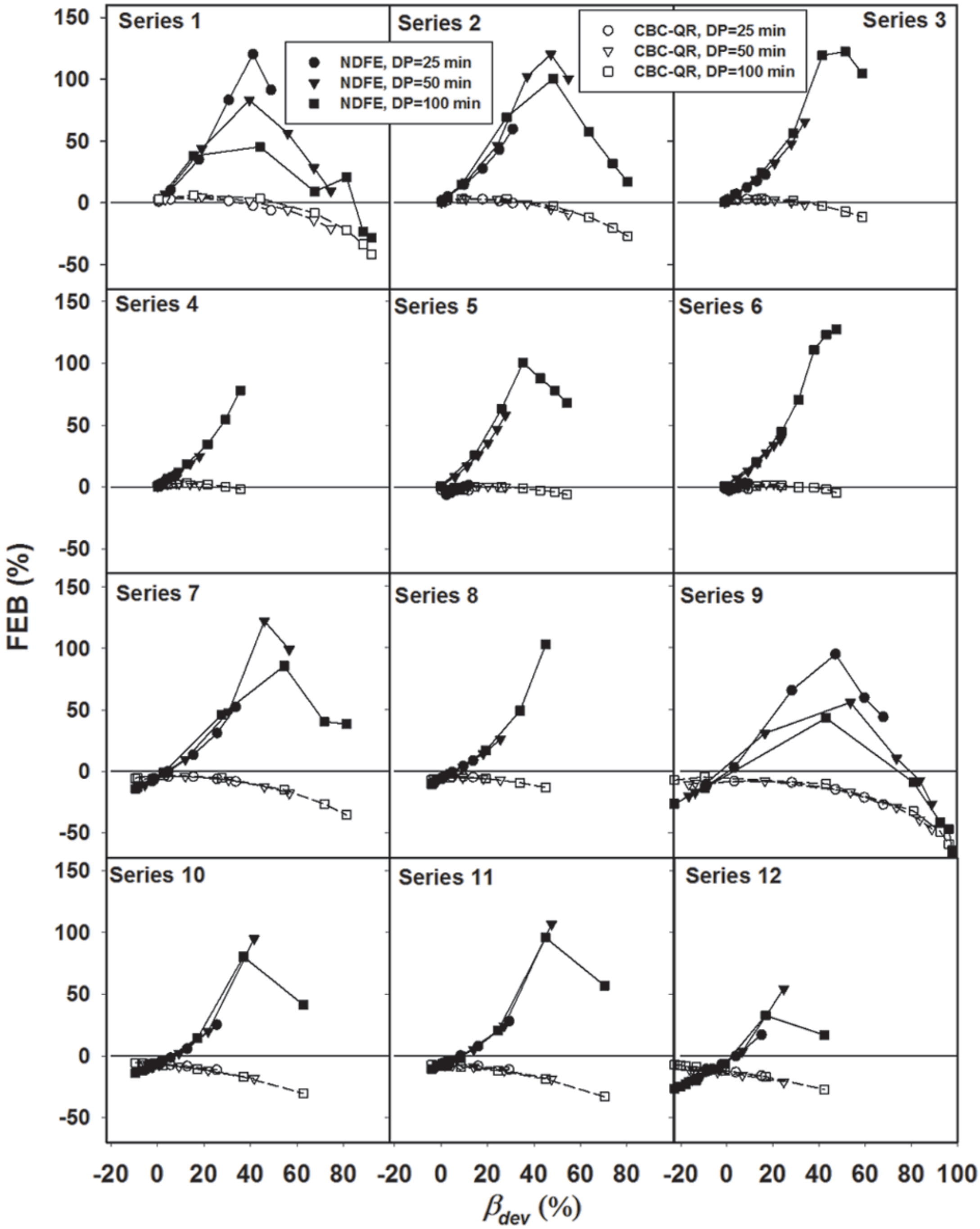


**Fig. 2. Flux-estimate bias (FEB) using the non-steady-state diffusive flux estimator (NDFE) (solid symbols) and chamber bias correction–quadratic regression (CBC–QR) (open symbols) methods vs. percent deviation from theoretical curvature ($\beta_{dev}$) for varying chamber deployment periods (DP).**

estimates were nearly identical except for $d$ = 150 mm and DP = 100 min, where HMR was substantially more accurate in both Series 13 and 14 (Fig. 5b). Series 13 to 14 and the baseline conditions in Series 7 to 12 also evaluated the CBC assumption that average soil properties across the upper 10 mm can be used to calculate correction factors in layered and otherwise physically non-uniform soils. This assumption by itself was relatively robust for CBC–QR, resulting in FEB in the range of −12 to 4.5% (mean = −4.4%) for cases in which A4 was the only assumption violated. A greater range of error was found for CBC–LR, with FEB ranging from −9 to 40% (mean = 3.7%).

## DISCUSSION

The NDFE, CBC, and HMR methods respond very differently to changing biophysical conditions and have very different sensitivities to violation of the theoretical assumptions on which the methods are based. For all sources of deviation from the underlying assumptions, the NDFE method was substantially more sensitive than CBC–QR or HMR and, in contrast to all other FC methods, tended to overestimate $f_0$ under most conditions. These results are consistent with Kutzbach et al. (2007) who proposed that violation of the NDFE restriction to no lateral diffusion and/or no chamber leakage contributed to extraneously high fluxes estimated by NDFE compared with other methods. The current

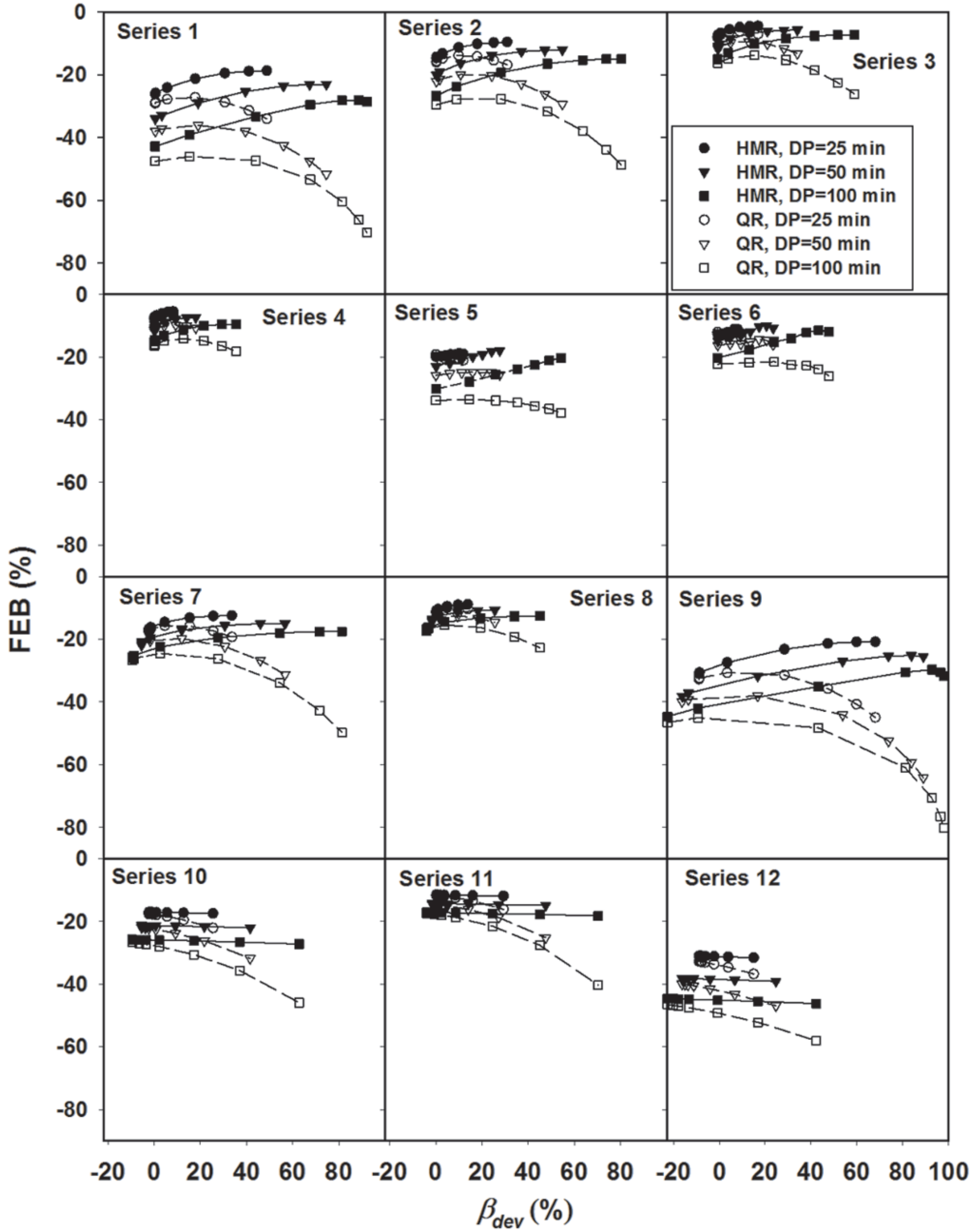


**Fig. 3. Flux-estimate bias (FEB) using the modified R-based Hutchinson and Mosier method (HMR) (solid symbols) and quadratic regression (QR) (open symbols) methods vs. percent deviation from theoretical curvature ($\beta_{dev}$) for varying chamber deployment periods (DP).**

results show that the NDFE method is similarly sensitive to violation of the assumption regarding biological uptake.

Even though the CBC method is based on the same theory as NDFE, its differing computation procedures were substantially more robust than NDFE in maintaining accuracy under conditions that violated theoretical assumptions. The NDFE method relies on nonlinear regression to estimate a model parameter ($\tau$), while the CBC method uses a correction factor based on an empirical estimate of $\tau$. The greater theoretical robustness of CBC–QR results from the relative insensitivity of the QR method to changing biophysical conditions and the stability of the CBC estimate of $\tau$ compared to NDFE. However, in practice the accuracy of CBC flux estimates will also depend on the accuracy of determining the CBC correction factors and further analysis is needed in this regard, as discussed further below.

The results found here can be used as an initial guide for FC method selection particularly when the extent of lateral diffusion or other effects is not known. When accurate estimates of soil water content, bulk density, and temperature are available, $\beta_{dev}$ can be estimated using spreadsheet-based calculations (see Appendix and example spreadsheet). Relationships between FEB and $\beta_{dev}$ (Fig. 4) can then be used to determine the optimum FC scheme to minimize FEB for a given set of conditions. However, in practice, measurement error as well as the biophysical conditions examined in this analysis will contribute to flux-estimation error. Measurement error was neglected here so that FC method bias could be examined solely in response to violation of theoretical assumptions. Previous studies have found that HM and HMR are more sensitive to errors in determining chamber $N_2O$ concentrations than QR or LR (Venterea et al., 2009; Parkin et al., 2012). Effects of measurement error may also be influenced by the number of sampling points taken during the deployment period. Five points, which is more than is commonly used, was selected here for the same reason, that is, to minimize measurement effects to that theoretical performance could be better compared.

Sensitivity of flux estimates to errors in determining correction factors used for the CBC method also needs to be evaluated. Using results obtained here combined with Monte Carlo analysis, Venterea and Parkin (unpublished results) found that CBC–QR was less sensitive to random analytical errors in determining chamber $N_2O$ concentrations than HMR or NDFE, and that CBC correction factors were mainly sensitive to estimation of soil bulk density and much less sensitive to water content, temperature, or use of alternative soil–gas diffusivity models (e.g., Deepagoda et al., 2011) that are also used to determine correction factors. Additional analysis is required to generate FC method selection criteria that consider the degree of measurement error as well as biophysical conditions examined here.

Other studies provide guidance regarding chamber insertions depths, design of vent tubes and chamber seals and other considerations that increase the likelihood that assumptions regarding no lateral diffusion or chamber leakage are valid (e.g., Hutchinson and Livingston, 2001, 2002; Xu et al., 2006). The current results support these recommendations. All methods (except HMR) had increasing bias as lateral diffusion and chamber leakage increased. The accuracy observed with HMR at higher lateral diffusion rates did not reach the level of accuracy achieved with other methods at lower lateral diffusion rates. However, avoidance of lateral diffusion may be problematic in highly porous soil and/or in irregular, rocky terrain where optimum chamber insertion depths are not feasible. While the extent of lateral diffusion and chamber leakage can be least partly controlled, the extent of soil non-uniformity and soil $N_2O$ uptake generally cannot be. Previous analysis based on denitrification kinetics indicated that soil biological uptake is not likely to affect NSS chamber data (Venterea et al., 2009). Recent findings regarding the $N_2O$-reducing capacity of a wider range of soil microbes (Sanford et al., 2012) suggest that soil $N_2O$ uptake may be more generally important.

The HMR method consistently underestimated $f_0$ but displayed better accuracy than NDFE or CBC under more extreme conditions where lateral diffusion, biological uptake, or chamber leakage suppressed the amounts of $N_2O$ accumulating in the chamber (i.e., for $\beta_{dev} \geq 65\%$). In these cases, all methods in-

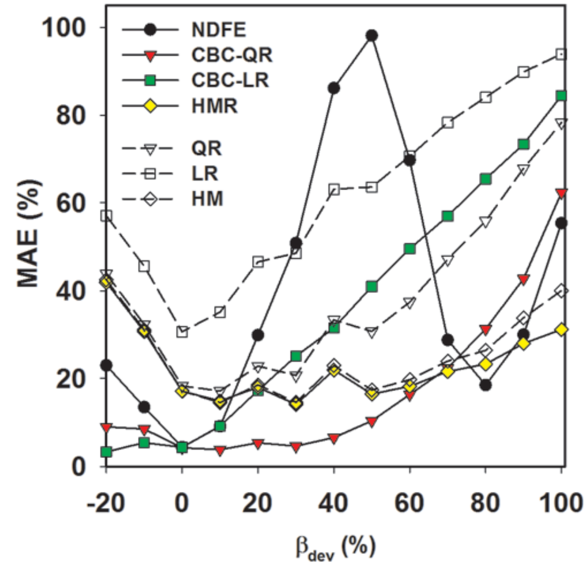


**Fig. 4. Mean absolute error (MAE) of flux estimates using the various flux-calculation (FC) methods vs. percent deviation from theoretical curvature ($\beta_{dev}$). Each symbol represents MAE calculated over a range of $\beta_{dev}$ corresponding to ±5% of the $\beta_{dev}$ indicated on the horizontal axis (for example, the value indicated for $\beta_{dev}$ = 0% was calculated over range of –5% to +5%).**

**Table 3. Sensitivity of flux-estimate bias (FEB) to deviation from theoretical curvature ($\beta_{dev}$) for each source of deviation for the non-steady-state diffusive flux estimator (NDFE), chamber bias correction (CBC), and modified R-based Hutchinson and Mosier (HMR) methods. Mean values (with standard error) are shown across all simulations.**

| Source of deviation | $\beta_{dev} \leq 40\%$ | | | | $\beta_{dev} > 40\%$ | | | |
|---|---|---|---|---|---|---|---|---|
| | NDFE | CBC–QR† | CBC–LR | HMR | NDFE | CBC–QR | CBC–LR | HMR |
| | Percent change in FEB per percent change in $\beta_{dev}$ | | | | | | | |
| | % | | | | | | | |
| Lateral diffusion (A1) | 1.75 (0.11) | 0.14 (0.05) | –0.71 (0.02) | 0.18 (0.01) | –2.18 (0.20) | –0.76 (0.05) | –0.90 (0.03) | 0.08 (0.02) |
| Biological uptake (A2) | 1.94 (0.42) | ‡ns | –0.67 (0.01) | 0.18 (0.02) | –1.72 (-)§ | ‡ns | –0.75 (-)§ | 0.19 (-)§ |
| Chamber leakage (A3) | 1.34 (0.10) | –0.20 (0.01) | –0.86 (0.01) | –0.02 (0.002) | ¶ | ¶ | ¶ | ¶ |

† QR, quadratic regression; LR, linear regression.

‡ ns = sensitivity not significantly different than zero ($P > 0.1$).

§ Insufficient data to determine standard error.

¶ Insufficient data to determine sensitivity.

cluding HMR had MAE ≥ 20%. In no cases did HMR achieve the same levels of accuracy that NDFE achieved when $\beta_{dev}$ was <5%, or the same levels of accuracy that CBC–QR achieved when $\beta_{dev}$ < 65%. Even though FEB with HMR improved or did not change as $\beta_{dev}$ increased within each DP (Fig. 3), when data from all DPs were aggregated FEB increased with $b_{dev}$ (Fig. 4). This resulted from substantially greater FEB at higher DP within each series and because greater DPs had a higher upper range of $\beta_{dev}$ values.

Although the HM method is commonly applied to NSS chamber measurements, it is seldom mentioned that the method was developed with specific conditions in mind, that is, as mentioned above where "the zone of $N_2O$ production lies somewhat below the surface and is overlain by a layer of relatively dry, loosely packed soil". Furthermore, the HM (and HMR) methods make two assumptions that were postulated to apply to these conditions: (i) at some fixed depth ($d$) in the soil, the $N_2O$ soil–gas concentration ($C_d$) remains constant throughout the chamber deployment period, and (ii) vertical diffusion into the chamber is controlled by a *linear* soil–gas concentration gradient between the depth $d$ and the soil surface. Thus, the concentration gradient is assumed to be $(C_d - C_{ch})/d$ where $C_{ch}$ is the concentration at the soil surface which also represents the concentration inside the chamber. These simplifying assumptions were used by Hutchinson and Mosier (1981) to convert the transport equation from a PDE having two variables ($z$ and $t$) to an ordinary differential equation (ODE) having an exponential solution in a single variable ($t$). However, it is known that transient (non-steady) solutions of the diffusion equation with altered boundary conditions tend to generate nonlinear gradients even in uniform media (e.g., Carslaw and Jaeger, 1946). In media such as soil that tend to have varying diffusivity, nonlinear gradients are expected even at steady state because greater diffusivity at one point in the soil must be balanced by a lower gradient to maintain a uniform and steady flux. This is illustrated by simulation results for the case of 1D diffusion in non-uniform (but non-layered) soil, where nonlinear vertical gradients in the upper 100 mm are predicted before and following chamber placement (Fig. 6a). Livingston et al. (2006) and Venterea and Baker (2008) showed that these assumptions lead to substantial flux underestimation by HM for the case of 1D diffusion in uniform and non-uniform soil, respectively.

Series 13 and 14 were designed to further test the HM assumptions under conditions consistent with the original description of Hutchinson and Mosier (1981). The HM assumptions are ostensibly consistent with model-calculated soil–gas concentrations for Series 14. As shown in Fig. 6b, the gradients appear highly linear with depth across the entire upper layer ($r^2$ > 0.998) at all times. However, closer inspection shows that the diffusion model predicts large variation in gradients at the millimeter scale.

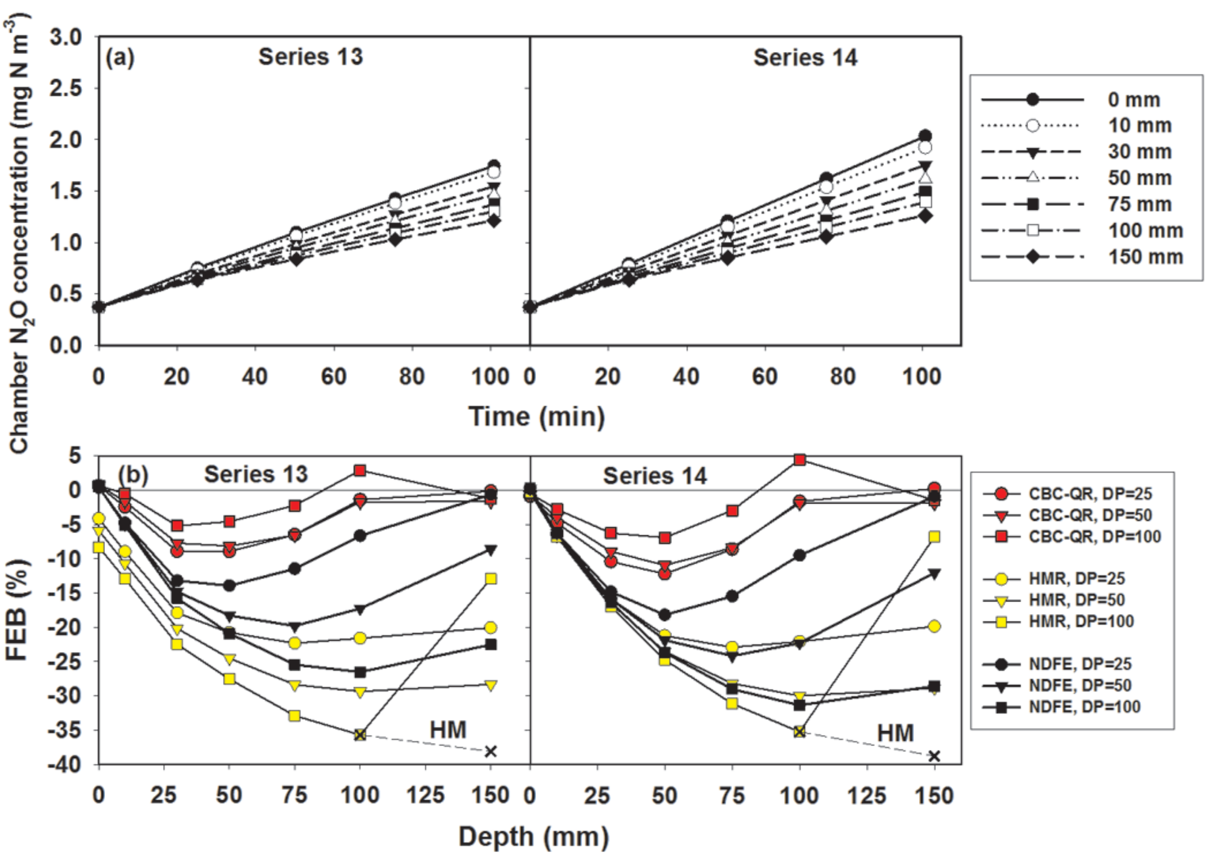


**Fig. 5. Results of Series 13 to 14: (a) Simulated chamber $N_2O$ data, and (b) flux-estimate bias (FEB) using the non-steady-state diffusive flux estimator (NDFE), chamber bias correction–quadratic regression (CBC–QR), and modified R-based Hutchinson and Mosier method (HMR) methods at varying thicknesses of upper soil layer (*d*, mm) and for varying chamber deployment periods (DP). In (b), results for the HM method are also shown in cases where they did not agree with the HMR method.**

Following deployment, the gradient (and correspondingly the vertical flux) across the upper 2 mm was 25% less than the gradient and flux across the 2 mm closest to the interface of the two soil layers. The model also predicts a nearly constant soil–gas $N_2O$ concentration of 18 mg N $m^{-3}$ occurring in the upper 1 mm of the more dense layer ($z$ = 51 mm) that changed by only 5% after 100 min. This result is also ostensibly consistent with the second HM assumption regarding constant concentration at depth. However, the HM theory assumes that the gradient between the depth of constant concentration and the surface is linear, and does not account for the abrupt change in the gradient occurring at $z$ = 50 mm (Fig. 6b). We conducted additional simulations assuming different types of soil layering including transition zones between layers with similar results to those shown for Series 13 to 14. Hutchinson et al. (2000) also showed that when a constant gas concentration at a specific depth was *imposed* as a boundary condition, flux suppression following chamber deployment did not change compared with a no-flux lower boundary condition as used here. Thus, the HM and HMR assumptions regarding vertical gas diffusion in soil have yet to be replicated by any theoretically-based modeling.

The HMR model extended the HM theory by adding a term to the ODE intended to account for lateral diffusion and chamber leakage which assumes that both effects are driven by gradients proportional to ($C_{ch}$– $C_o$) where $C_o$ is the ambient atmospheric concentration (Pedersen et al., 2010). Thus, the assumption regarding linear gradients that was used to describe vertical diffusion in the original HM method was assumed by HMR to describe lateral diffusion. Results of the current simulations predict nonlinear lateral gradients that evolve following chamber deployment in laterally uniform soil (Fig. 6c) which are at odds with HMR assumptions. These results suggest that the simplifying assumptions of the HM and HMR methods are not likely to occur in soil even when chambers are deployed for short periods (e.g., 12 min).

Coefficient of correlation ($r^2$) values obtained by comparing actual chamber data to FC model-fits are commonly reported in $N_2O$ studies even though $r^2$ values are not generally reliable indicators of model accuracy (Spiess and Neumeyer, 2010). Findings from the current analysis provide additional evidence of the limited value of the $r^2$ criterion. For all simulations, $r^2$ values adjusted for degrees of freedom for HMR-model fits to data were always $^3$0.995, even though fluxes were underestimated by up to 46%. In 47% of cases where $r^2$ with HMR was greater than $r^2$ with NDFE, HMR was *less* accurate than NDFE. Also, LR yielded $r^2 \geq 0.99$ in 46% of all simulations even though LR underestimated $f_0$ by up to 60% in these cases. Thus, as previously shown by Livingston et al. (2006) and Conen and Smith (2000), even though a given FC model may appear to match data very well based on $r^2$ values, this agreement does not provide assurance of its accuracy.

## CONCLUSIONS

This analysis provides new insight into the behavior of FC schemes under varying conditions. As shown here and in previous studies, FC method selection can have large effects on $N_2O$ flux estimates. The current results provide more evidence that the most commonly used FC schemes tend to substantially underestimate the actual $N_2O$ flux by 20 to more than 50%. More informed selection and use of FC methods will minimize biases and can only serve to improve the accuracy of regional and global $N_2O$ emissions assessments. Reducing chamber DPs can reduce bias for some FC methods but also reduces precision (Venterea et al., 2009). For other trace gases (e.g., $CO_2$) where high-precision, real-time analytical instrumentation is available, DP*s* <10 min are frequently used (Davidson et al., 2002). For $N_2O$, similar analyzers exist (e.g., Iqbal et al., 2013) but are not as widely available, and DPs <20 min are seldom used. Logistical constraints associated with sampling multiple chambers within limited time windows in replicated experiments may still present challenges for real-time analyzers. Micrometeorological techniques for measuring soil-to-atmosphere $N_2O$ fluxes (e.g., Wagner-Riddle et al., 2007) and

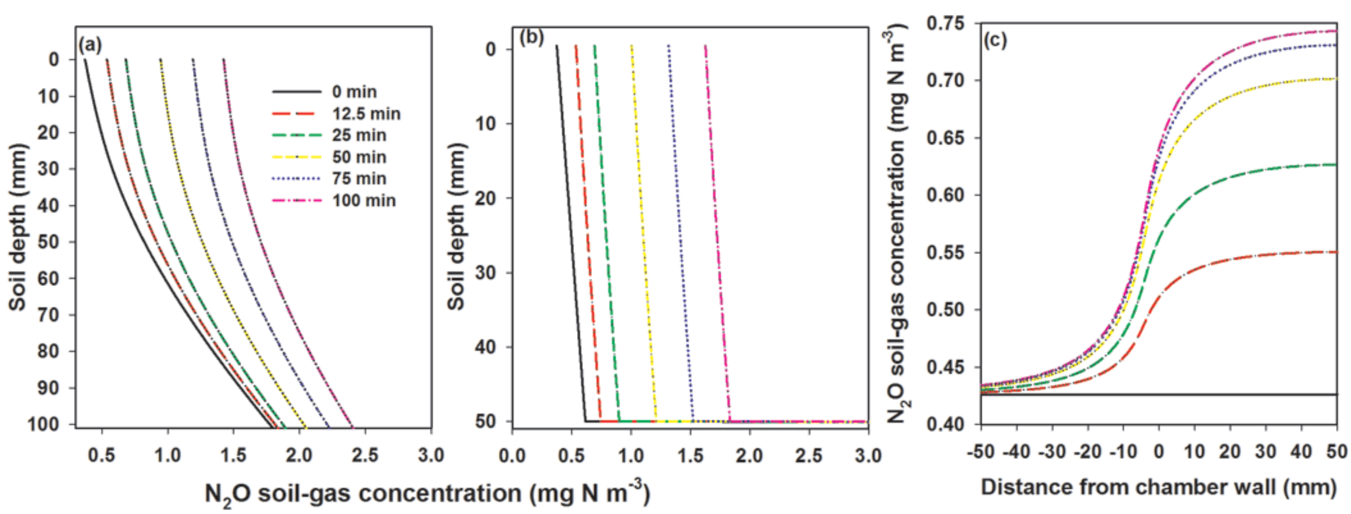


**Fig. 6. Model-simulated soil–gas $N_2O$ concentration profiles at varying times after chamber deployment: (a) vertical profiles for Series 7 with chamber insertion depth ($D_{ch}$) of 1000 mm, (b) vertical profiles for Series 14 with thickness of upper soil layer (d) of 50 mm, and (c) lateral profiles for Series 7 with $D_{ch}$ of 5 mm.**

inverse modeling approaches (Jeong et al., 2012) eliminate these concerns and provide additional information not available from NSS chambers. However, these approaches have their own limitations particularly for replicated plot-scale treatment comparisons (Denmead, 2008). Thus, it is likely that NSS chambers will continue to be widely used and therefore more careful consideration of FC method selection is warranted.


## ACKNOWLEDGMENTS

This work was supported in part by the National Research Initiative Competitive Grant no. 2009-55112-05216 from the USDA CSREES/NIFA Air Quality Program, and the Agricultural Research Service of the USDA as part of the GRACEnet Project.


## REFERENCES


Anthony, W.H., G.L. Hutchinson, and G.P. Livingston. 1995. Chamber measurement of soil-atmosphere gas exchange: Linear vs. diffusion-based flux models. Soil Sci. Soc. Am. J. 59:1308–1310. doi:10.2136/sssaj1995.03615995005900050015x

Beu, T.A. 2007. Numerical solutions of the diffusion equation. In: O.-G. Piringer and A.L. Baner, editors, Plastic packaging materials for food: Barrier function, mass transport, quality assurance, and legislation. Wiley-VCH Verlag GmbH, Weinheim, Germany.

Carslaw, H.S., and J.C. Jaeger. 1946. Conduction of heat in solids. 2nd ed. Oxford Univ. Press, New York.

Conen, F., and K.A. Smith. 2000. An explanation of linear increases in gas concentration under closed chambers used to measure gas exchange between soil and the atmosphere. Eur. J. Soil Sci. 51:111–117. doi:10.1046/j.1365-2389.2000.00292.x

Davidson, E.A., K. Savage, L.V. Verchot, and R. Navarro. 2002. Minimizing artifacts and biases in chamber-based measurements of soil respiration. Agric. For. Meteorol. 113:21–37. doi:10.1016/S0168-1923(02)00100-4

Deepagoda, T.K.C., P. Moldrup, P. Schjønning, K. Kawamoto, T. Komatsuc, and L. Wollesen de Jonge. 2011. Generalized density-corrected model for gas diffusivity in variably saturated soils. Soil Sci. Soc. Am. J. 75:1315–1329. doi:10.2136/sssaj2010.0405

Del Grosso, S.J., A.R. Mosier, W.J. Parton, and D.S. Ojima. 2005. DAYCENT model analysis of past and contemporary soil $N_2O$ and net greenhouse gas flux for major crops in the USA. Soil Tillage Res. 83:9–24. doi:10.1016/j.still.2005.02.007

Denmead, T.O. 2008. Approaches to measuring fluxes of methane and nitrous oxide between landscapes and the atmosphere. Plant Soil 309:5–24. doi:10.1007/s11104-008-9599-z

Healy, R.W., R.G. Striegl, T.F. Russell, G.L. Hutchinson, and G.P. Livingston. 1996. Numerical evaluation of static-chamber measurements of soil–atmosphere gas exchange: Identification of physical processes. Soil Sci. Soc. Am. J. 60:740–747. doi:10.2136/sssaj1996.03615995006000030009x

Hutchinson, G.L., and G.P. Livingston. 2001. Vents and seals in nonsteady-state chambers used for measuring gas exchange between soil and the atmosphere. Eur. J. Soil Sci. 52:675–682. doi:10.1046/j.1365-2389.2001.00415.x

Hutchinson, G.L., and G.P. Livingston. 2002. Soil-atmosphere gas exchange. In: J.H. Dane and G.C. Topp, editors, Methods of soil analysis. Part 4. SSSA Book Ser. 5. SSSA, Madison, WI. p. 1159–1182.

Hutchinson, G.L., G.P. Livingston, R.W. Healy, and R.G. Striegl. 2000. Chamber measurement of surface-atmosphere trace gas exchange: Numerical evaluation of dependence on soil, interfacial layer, and source/sink properties. J. Geophys. Res. Atm. 105:8865–8875. doi:10.1029/1999JD901204

Hutchinson, G.L., and A.R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Sci. Soc. Am. J. 45:311–316. doi:10.2136/sssaj1981.03615995004500020017x

Iqbal, J.M., J.Castellano, and T.B. Parkin. 2013. Evaluation of photoacoustic infrared spectroscopy for simultaneous measurement of $N_2O$ and $CO_2$ gas concentrations and fluxes at the soil surface. Global Change Biol. 19:327–336. doi:10.1111/gcb.12021

Jeong, S., Z. Chuanfeng, A.E. Andrews, E.J. Dlugokencky, C. Sweeney, L. Bianco et al. 2012. Seasonal variations in $N_2O$ emissions from central California. Geophys. Res. Lett. 39:L16805. doi:10.1029/2012GL052307

Kutzbach, L., J. Schneider, T. Sachs, M. Giebels, H. Nykänen, N.J. Shurpali et al. 2007. $CO_2$ flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression. Biogeoscience 4:1005–1025. doi:10.5194/bg-4-1005-2007

Lapidus, L., and G.F. Pinder. 1982. Numerical solution of partial differential equations in science and engineering. John Wiley & Sons, New York.

Levy, P.E., A. Gray, S.R. Leeson, J. Gaiawyn, M.P.C. Kelly, M.D.A. Cooper et al. 2011. Quantification of uncertainty in trace gas fluxes measured by the static chamber method. Eur. J. Soil Sci. 62:811–821. doi:10.1111/j.1365-2389.2011.01403.x

Livingston, G.P., G.L. Hutchinson, and K. Spartalian. 2006. Trace gas emission in chambers: A non-steady-state diffusion model. Soil Sci. Soc. Am. J. 70:1459–1469. doi:10.2136/sssaj2005.0322

Martin, J.G., P.V. Bolstad, and J.M. Norman. 2004. A carbon dioxide flux generator for testing infrared gas analyzer-based soil respiration systems. Soil Sci. Soc. Am. J. 68:514–518. doi:10.2136/sssaj2004.0514

Matthias, A.D., D.N. Yarger, and R.S. Weinback. 1978. A numerical evaluation of chamber methods for determining gas fluxes. Geophys. Res. Lett. 5:765–768. doi:10.1029/GL005i009p00765

Parkin, T.B., R.T. Venterea, and S.K. Hargreaves. 2012. Calculating the detection limits of chamber-based soil greenhouse gas flux measurements. J. Environ. Qual. 41:705–715. doi:10.2134/jeq2011.0394

Pedersen, A.R., S.O. Petersen, and K. Schelde. 2010. A comprehensive approach to soil atmosphere trace-gas flux estimation with static chambers. Eur. J. Soil Sci. 61:888–902. doi:10.1111/j.1365-2389.2010.01291.x

Rochette, P., and N.S. Eriksen-Hamel. 2008. Chamber measurements of soil nitrous oxide flux: Are absolute values reliable? Soil Sci. Soc. Am. J. 72:331–342. doi:10.2136/sssaj2007.0215

Sanford, R.A., D.D. Wagner, Q. Wu, J.C. Chee-Sanford, S.H. Thomas, C. Cruz-Garcia et al. 2012. Unexpected nondenitrifier nitrous oxide reductase gene diversity and abundance in soils. P. Natl. Acad. Sci. 109:19709–19714. doi:10.1073/pnas.1211238109

Spiess, A.N., and N. Neumeyer. 2010. An evaluation of $R^2$ as an inadequate measure for nonlinear models in pharmacological and biochemical research: A Monte Carlo approach. BMC Pharmacol. 10(6):1–11.

USEPA. 2012. Inventory of U.S. greenhouse gas emissions and sinks: 1990–2010. EPA 430-R-12-001. U.S. Environmental Protection Agency, Washington, DC. http://www.epa.gov/climatechange/ghgemissions/usinventoryreport.html (accessed 13 Mar. 2013).

Venterea, R.T. 2010. Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. J. Environ. Qual. 39:126–135. doi:10.2134/jeq2009.0231

Venterea, R.T., and J.M. Baker. 2008. Effects of soil physical nonuniformity on chamber-based gas flux estimates. Soil Sci. Soc. Am. J. 72:1410–1417. doi:10.2136/sssaj2008.0019

Venterea, R.T., M. Dolan, and T.E. Ochsner. 2010. Urea decreases nitrous oxide emissions compared with anhydrous ammonia in a Minnesota corn cropping system. Soil Sci. Soc. Am. J. 74:407–418. doi:10.2136/sssaj2009.0078

Venterea, R.T., and T.B. Parkin. 2012. Quantifying biases in non-steady state chamber measurements of soil-atmosphere gas exchange. In: M. Liebig et al., editors, Managing agricultural greenhouse gases. Elsevier, Maryland Heights, MO.

Venterea, R.T., K.A. Spokas, and J.M. Baker. 2009. Accuracy and precision analysis of chamber-based nitrous oxide gas flux estimates. Soil Sci. Soc. Am. J. 73:1087–1093. doi:10.2136/sssaj2008.0307

Wagner, S.W., D.C. Reicosky, and R.S. Alessi. 1997. Regression models for calculating gas fluxes measured with a closed chamber. Agron. J. 89:279–284. doi:10.2134/agronj1997.00021962008900020021x

Wagner-Riddle, C., A. Furon, N.L. Mclaughlin, I. Lee, J. Barbeau, S. Jayasundara et al. 2007. Intensive measurement of nitrous oxide emissions from a corn-soybean-wheat rotation under two contrasting management systems over 5 years. Global Change Biol. 13:1722–1736. doi:10.1111/j.1365-2486.2007.01388.x

Widen, B., and A. Lindroth. 2003. A calibration system for soil carbon dioxide-efflux measurement chambers: Description and application. Soil Sci. Soc. Am. J. 67:327–334. doi:10.2136/sssaj2003.0327

Willmott, C.J., and K. Matsuura. 2005. Advantages of the mean absolute error (MAE) over the root mean square error (RMSE) in assessing average model performance. Clim. Res. 30:79–82. doi:10.3354/cr030079

Wu, J.C., L.T. Fan, and L.E. Erickson. 1990. Three-point backward finite-difference method for solving a system of mixed hyperbolic-parabolic partial equations. Comput. Chem. Eng. 14:679–685. doi:10.1016/0098-1354(90)87036-O

Xu, L., M.D. Furtaw, R.A. Madsen, R.L. Garcia, D.J. Anderson, and D.K. McDermitt. 2006. On maintaining pressure equilibrium between a soil CO2 flux chamber and the ambient air. J. Geophys. Res. Atm. 111(D08S10). doi:10.1029/2005JD006435