

Simplified Method for Quantifying Theoretical Underestimation of Chamber-Based Trace Gas Fluxes

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Closed chambers used to measure soil-atmosphere exchange of trace gases including nitrous oxide (N_2O) and carbon dioxide (CO_2) generate errors due to suppression of the gas concentration gradient at the soil-atmosphere interface. A method is described here for estimating the magnitude of flux underestimation arising from chamber deployment. The technique is based on previously established gas transport theory and has been simplified to facilitate application while preserving the fundamental physical relationships. The method avoids the use of nonlinear regression but requires knowledge of soil properties including texture, bulk density, water content, temperature, and pH. Two options are presented: a numerical technique which is easily adapted to spreadsheet application, and a graphical method requiring minimal calculation. In both cases, the magnitude of theoretical flux underestimation (TFU) is determined, taking into account effects of chamber geometry and deployment time, the flux-calculation scheme, and properties of the soil and gas under consideration. Application to actual data and recent studies confirmed that TFU can vary widely within and across sites. The analysis also revealed a highly linear correlation between soil water content and TFU, suggesting that previously observed relationships between water content and trace gas flux may in part reflect artifacts of chamber methodology. The method described here provides a practical means of improving the absolute accuracy of flux estimates and normalizing data obtained using different chamber designs in different soils.

THE vast majority of studies examining soil-atmosphere exchange of N_2O have used chambers placed on the soil surface (Stehfest and Bouwman, 2006). Chamber methods are also commonly used to measure soil respiration and exchange of CO_2 (Davidson et al., 2002). It is widely recognized that chamber methods for determining trace gas fluxes suffer from the so-called “chamber effect” due to suppression of the gas concentration gradient at the soil surface following chamber deployment, resulting in an underestimation of the actual predeployment flux (Hutchinson and Mosier, 1981; Healy et al., 1996; Rochette and Bertrand, 2007). Livingston et al. (2006) demonstrated that even chamber data that appear to be highly linear in time can result in substantial underestimation when linear regression (LR) is used to calculate the flux. Livingston et al. (2006) and Venterea and Baker (2008) also demonstrated that widely used nonlinear flux-calculation methods that attempt to account for the chamber effect, including the models of Hutchinson and Mosier (1981) and Wagner et al. (1997), also result in negatively biased flux estimates.

The magnitude of the chamber-induced errors is known to increase with increased chamber deployment time, decreased chamber height, greater soil air-filled porosity, and when LR is used to determine flux (Hutchinson et al., 2000; Venterea et al., 2009b). There is wide variation in the application of chamber types and techniques, and therefore the magnitude of flux underestimation is also expected to vary widely across studies (Rochette and Eriksen-Hamel, 2008). Within a given study, the sensitivity of the chamber effect to variations in soil properties may also confound the interpretation of treatment effects (Venterea and Baker, 2008).

Given this uncertainty and variation, a technique for estimating the magnitude of flux underestimation should be considered to improve the design of chamber measurement systems and to normalize data obtained using different protocols. Methods for evaluating chamber-induced errors which rely on detailed numerical techniques have been developed, but have not seen much application (Healy et al., 1996; Perera et al., 2002; Senevirathna et al., 2007; Venterea and Baker, 2008). Livingston et al. (2006) developed a flux-calculation scheme, termed the nonlinear diffusive flux estimator (NDFE), based on fundamental gas transport theory. The NDFE has also not seen much application, perhaps due

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Abbreviations: H_c , chamber height; LR, linear regression; NDFE, nonlinear diffusive flux estimator; Quad, quadratic; T_d , chamber deployment time; T_s , soil temperature; TFU, theoretical flux underestimation.

to the fact that it requires the implementation of a nonlinear regression solver which is not easily adaptable to spreadsheet application when processing large data sets. Another drawback of the NDFE solver is the potential for multiple solutions for a given data set, which requires additional decision-making by the user (Livingston et al., 2006; Venterea and Baker, 2008).

The method described here attempts to simplify the application of gas transport theory toward determining the magnitude of flux underestimation under specific soil and measurement conditions. The techniques for applying the method are described followed by application to actual data, a discussion of its theoretical basis, assumptions, limitations, and potential implications.

Materials and Methods

Method Description

Numerical and graphical options for applying the method are described below. Each option is aimed at calculating the TFU (%), defined as

$$\text{TFU} \equiv 100 \frac{f_o - f}{f_o} \quad [1]$$

where f_o is the actual predeployment flux and f is the flux calculated from chamber data. Thus, f_o can be estimated from

$$f_o = \frac{f}{1 - \text{TFU}/100} \quad [2]$$

Both options involve the determination of two error parameters (E_1 and E_2) before determining TFU. The E_1 parameter accounts for the effects of soil and trace gas physical properties on chamber dynamics. The E_2 parameter accounts for these factors together with chamber geometry and deployment time. The error parameters are derived from gas transport theory, and their mathematical definitions are given in sections below.

Numerical Option

The numerical option uses direct computation of E_1 , E_2 , and TFU and therefore can be applied to individual flux measurements where factors such as water content, bulk density, or temperature may be varying. The calculations are relatively straightforward and adaptable to spreadsheet applications. An example spreadsheet using the numerical option is provided as supplemental information, available with the online version of this article.

Step 1: Determine E_1 by Calculation

The E_1 parameter is computed from:

$$E_1 = \left[\phi + \theta(\beta K - 1) \right] D \phi^2 (1 - \theta/\phi)^{(2+3/b)} \quad [3]$$

where ϕ is the total soil porosity (cm^3 pores cm^{-3} soil) determined from $(1 - \rho/\rho_p)$ where ρ and ρ_p are the soil bulk density and particle density, respectively, θ is the volumetric water content ($\text{cm}^3 \text{H}_2\text{O cm}^{-3}$ soil), β is a correction factor for pH (applicable to CO_2 only), K is the trace gas Henry's Law gas-liquid partitioning coefficient (cm^3 gas cm^{-3} H_2O), D is the trace gas diffusivity

in free air (cm^2 gas h^{-1}), and b is the Campbell soil pore-size distribution parameter, which can be estimated from $b = 13.6 \text{CF} + 3.5$ where CF is the clay fraction ($0 < \text{CF} < 1$) (Rolston and Moldrup, 2002). Note that for soils with clay content $> 40\%$ or organic matter $> 5\%$, the final terms in Eq. [3] may need to be modified for greater accuracy (see Theory section). Using the units specified above for each term in Eq. [3] results in E_1 having units of cm^6 gas cm^{-4} soil h^{-1} .

The temperature dependency of D can be estimated from:

$$D_T = D_{25} \left[\frac{273.15 + T_s}{298.15} \right]^{1.72} \quad [4]$$

where D is the diffusivity at a given soil temperature (T_s , °C) and D_{25} is the diffusivity at 25°C (Rolston and Moldrup, 2002). The temperature dependency of K can be estimated from:

$$K = K_{25} \exp \left[\chi \left(\frac{1}{T_s + 273.15} - \frac{1}{298.15} \right) \right] \quad [5]$$

where K is the Henry's constant at a given T_s , K_{25} is the Henry's constant at 25°C, and χ (K) is a temperature response factor (Sander, 1999). Values used for D_{25} , K_{25} , and χ were $652.3 \text{ cm}^2 \text{ h}^{-1}$, 0.8318 cm^3 gas cm^{-3} H_2O , and 2400 K for CO_2 , and $511.7 \text{ cm}^2 \text{ h}^{-1}$, 0.6116 cm^3 gas cm^{-3} H_2O , and 2600 K for N_2O , respectively (Fuller et al., 1966; Healy et al., 1996; Sander, 1999).

The β term in Eq. [3] accounts for the formation of soluble carbonate species from dissolved CO_2 which will also influence chamber CO_2 dynamics (Hutchinson and Rochette, 2003). This effect can be accounted for using equilibrium constants for dissociation of carbonic acid and bicarbonate, $\text{p}K_a = 6.42$ and $\text{p}K_b = 10.43$, respectively, (values at 25°C per Snoeyink and Jenkins, 1980) in the following relation

$$\beta = 1 + 10^{(\text{pH} - \text{p}K_a)} + 10^{(2\text{pH} - \text{p}K_a - \text{p}K_b)} \quad [6]$$

Values of $\text{p}K_a$ and $\text{p}K_b$ at varying temperature can be found in Tables 4 through 7 of Snoeyink and Jenkins (1980). Since pH is not expected to affect N_2O gas-liquid partitioning, β should be set equal to 1 for N_2O . For CO_2 , β reduces to 1 for pH less than approximately 5.0.

Step 2: Determine E_2 by Calculation

The value of E_2 is then determined from

$$E_2 = \ln \left[\frac{H_c^2}{E_1 T_d} \right] \quad [7]$$

where H_c is the chamber height, or more precisely, the ratio of the chamber internal volume to surface area in contact with the soil, and where T_d is the total chamber deployment time. Since H_c values are commonly expressed in units of cm^3 gas cm^{-2} soil (which are commonly simplified to centimeters), use of h as the time units for T_d and cm^6 gas cm^{-4} soil h^{-1} as the units for E_1 results in E_2 being a dimensionless quantity.

Step 3: Determine Theoretical Flux Underestimation by Calculation

Values of TFU for a given flux-calculation scheme can be determined as a function of E_2 using the relation:

$$TFU = \frac{a + bE_2}{1 + cE_2 + dE_2^2} \quad [8]$$

where a , b , c , and d are regression functions specific to each scheme (Table 1). Estimation of the flux value corrected for the effect of chamber deployment can then be made using Eq. [2].

Graphical Option

The graphical option can be used to efficiently estimate the magnitude of flux underestimation for a given chamber technique and range of soil conditions without the need for extensive calculations. This option can be useful for evaluating or designing chamber protocols for a specific application.

Step 1: Determine E_1 Graphically

Using the relations described above for the numerical option, the E_1 parameter has been determined and plotted for a range of soil bulk density, volumetric water content, and clay content values for N_2O and CO_2 , respectively, in Fig. 1 and 2. The E_1 value for a particular soil and trace gas can be determined visually from these plots. If the exact bulk density or clay content values for a given soil are not shown in the graphs, E_1 can be approximated by linear interpolation of the plotted values. The plotted values assume a particle density of 2.65 g cm^{-3} used to calculate total porosity from bulk density, and also assume a soil temperature of 20°C , and $\text{pH} = 6.5$ (for CO_2). More precise values of E_1 corresponding to specific bulk density, clay content, particle density, pH , or soil temperature values can be determined using the numerical option described above.

Step 2: Determine E_2 by Calculation

The value of E_2 is determined using Eq. [7] as described above for the numerical option. Again, a consistent set of units must be used for E_1 , H_c , and T_d so that E_2 remains a dimensionless quantity.

Step 3: Determine Theoretical Flux Underestimation Graphically

The TFU is then estimated graphically by visual interpolation of the curves in Fig. 3, and estimation of the flux value corrected for the effect of chamber deployment can then be made using Eq. [2].

Theoretical Basis

The theory on which this method is based has been described by Livingston et al. (2006) and Venterea and Baker (2008) and will not be addressed in thorough detail here. The method is based on the exact solution to a partial differential equation describing trace gas transport from the soil into a closed chamber derived by Livingston et al. (2006) and given by

$$C_c(t) = C_c(0) + \frac{f_o \tau}{H_c} \left[\frac{2}{\sqrt{\pi}} \sqrt{t/\tau} + \exp(t/\tau) \text{erfc}(\sqrt{t/\tau}) - 1 \right] \quad [9]$$

where $C_c(t)$ is the chamber trace gas concentration at time (t) following deployment, $C_c(0)$ is the initial time-zero chamber trace gas concentration, erfc is the complementary error function, and H_c and f_o are as defined above. The term τ is further defined as:

$$\tau = \frac{H_c^2}{SD_p} \quad [10]$$

In Eq. [10], S is a storage coefficient given by Venterea and Baker (2008)

$$S = \phi + \theta(\beta K - 1) \quad [11]$$

and D_p is the soil-gas diffusivity which can be estimated from the Rolston and Moldrup (2002) model

$$D_p = D\phi^2(1 - \theta/\phi)^{(2+3/b)} \quad [12]$$

where ϕ , θ , K , D , β , and b are as defined above. It should be noted that Eq. [12] is an empirically-obtained relation which may not be highly accurate in soils with high clay content ($> 40\%$) or organic matter ($> 5\%$) (Rolston and Moldrup, 2002). For these cases, the reader is referred to Rolston and Moldrup (2002) for discussion of options for estimating D_p as a function of soil properties. If alternative expressions are used for D_p in Eq. [12], then the form of Eq. [3] will change accordingly (see Eq. [13–14] below regarding the derivation of Eq. [3]).

For a given chamber deployment time (T_d) and any value of H_c , f_o , and τ , Eq. [9] can be used to generate hypothetical chamber time series data. These data can then be subjected to any flux-calculation scheme to calculate f values that in turn can be used to calculate TFU using Eq. [1]. Analyses by Livingston et al. (2006) and Venterea and Baker (2008) have shown two important characteristics of Eq. [9] which make the current method possible: (i) for given values of T_d and τ , and for a given flux-calculation scheme, TFU is independent of f_o and H_c , and (ii) for a given flux-calculation scheme, TFU plots as a smooth function of τ/T_d or other quantities derived from this ratio. For the current analysis, it was found that functions relating TFU to $\ln(\tau/T_d)$ generated coefficients of determination (r^2) values > 0.999 .

The method consists of first determining $\ln(\tau/T_d)$ for a given set of conditions, and then using regression functions relating $\ln(\tau/T_d)$ to TFU for each flux-calculation scheme. The $\ln(\tau/T_d)$ term is obtained in two steps, first by determining

$$E_1 \equiv SD_p \quad [13]$$

which can be expressed by Eq. [3] after substituting Eq. [11] and [12] into [13]. Equations [13] and [10] can be substituted in Eq. [7] to yield the critical parameter

$$E_2 = \ln \left[\frac{\tau}{T_d} \right] \quad [14]$$

Table 1. Regression coefficients describing relationships between the theoretical flux underestimation and error parameter 2 (E_2) using Eq. [8] for flux-calculation using linear regression (LR) and the nonlinear models of Hutchinson and Mosier (1981) (HM) and Wagner et al. (1997) (Quad) ($r^2 > 0.999$).

Flux-calculation scheme	Regression coefficient			
	a	b	c	d
Linear regression	44.3456	-5.5105	0.1799	0.0363
HM	25.0140	-3.2561	0.2772	0.0439
Quad	26.8575	-3.5666	0.2814	0.0471

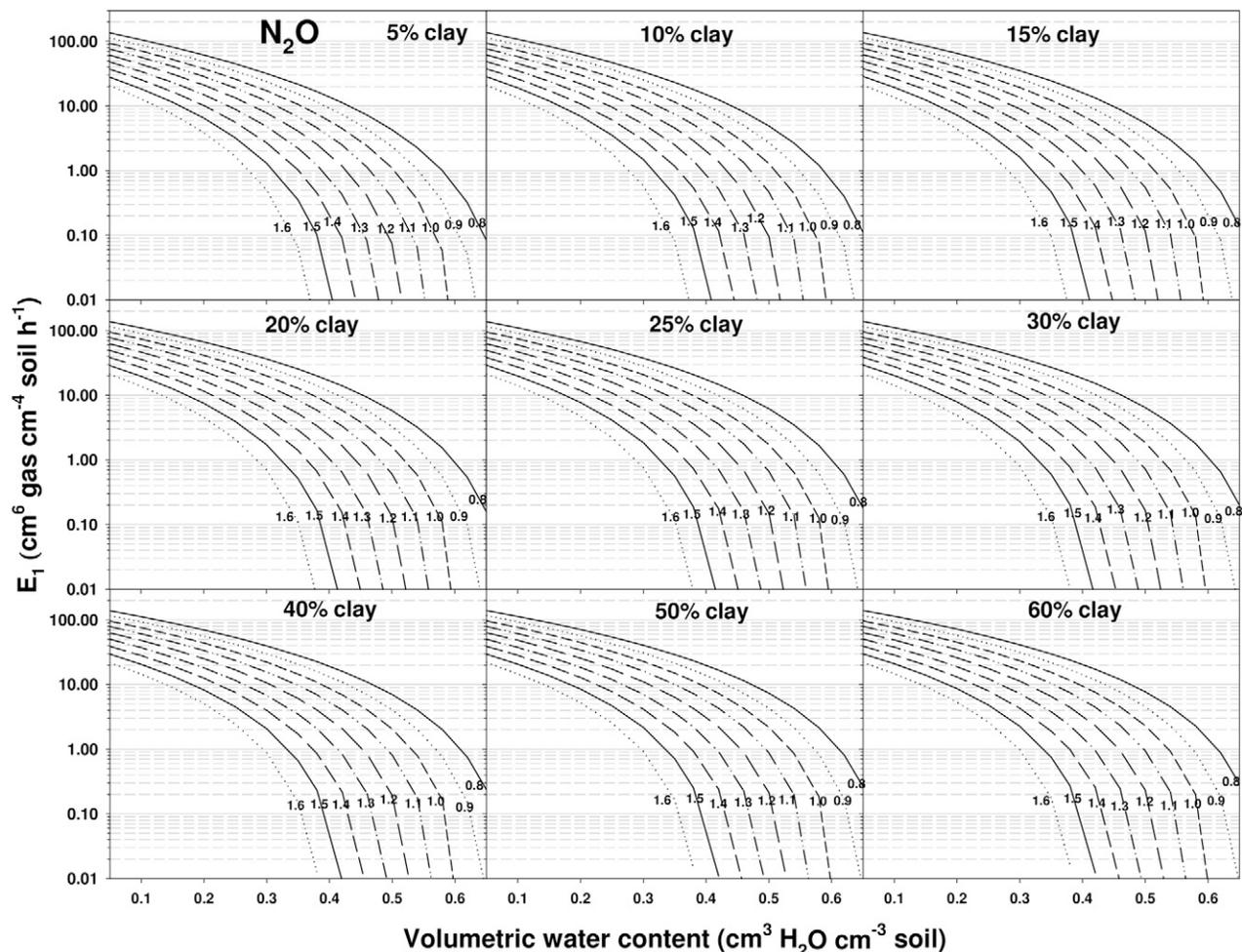


Fig. 1. Values of the error parameter E_1 at varying soil volumetric water content, bulk density, and clay content for calculating theoretical underestimation of N_2O flux. Values were calculated using Eq. [3] to [5] assuming particle density of 2.65 g cm^{-3} and soil temperature of 20°C . Values ranging from 0.8 to 1.6 indicate varying bulk density values in units of g cm^{-3} .

Relationships between $\ln(\tau/T_d)$ (or E_2) and TFU given by Eq. [8] and shown in Fig. 3 were obtained by first generating 231 sets of chamber time series data using Eq. [9] over a range of values of τ (0.1–1000 h) and T_d (0.25–2.0 h). For each combination of τ and T_d , separate chamber time series data sets were generated for the case of 3, 4, or 5 equally spaced sampling events (including an initial time zero sample) during chamber deployment. Each of these time series data sets were then used to calculate f using each of the three flux-calculation schemes, and TFU values for each data set were then computed directly from Eq. [1] since f_o was known. For each data set, calculated TFU values differed by $<1.5\%$ depending on whether 3, 4, or 5 sampling points were used (only three sampling points could be used for the Hutchinson and Mosier (1981) model). Nonlinear regression using SigmaPlot v. 10.0 (Systat Software Inc., Chicago) was used to obtain the coefficients in Table 1 using Eq. [8]. The resulting regression functions had r^2 values > 0.999 . The data used to generate the regression functions are not plotted in Fig. 3 to facilitate determination of TFU by visual inspection.

Application to Actual Flux Calculations

The numerical option was applied to chamber data collected during mid-summer from two different sites in central Minnesota, both under corn (*Zea mays* L.) production. Soil at Site 1 was a Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed, superactive, mesic Typic Hapludoll) with 23% clay and 25 g C kg^{-1} in the upper 10 cm, described in greater detail by Venterea et al. (2005, 2009a). Soil at Site 2 was a Hubbard loamy sand (sandy, mixed, frigid Entic Hapludoll) with 8% clay and 18 g C kg^{-1} in the upper 10 cm, described in greater detail by Zvomuya et al. (2003). At each site, soil CO_2 and N_2O fluxes were measured using vented and insulated stainless steel chambers measuring approximately 0.50 m long by 0.29 m wide by 0.086 m high placed in interrow locations using methods described by Venterea et al. (2005, 2009a). The actual internal volume of each chamber was determined by measuring and accounting for variation in the height of the soil surface at 20 locations within each chamber area. At Site 1, gas samples were withdrawn from chambers by syringe at 0, 10, 20, 30, 40, and 60 min after deployment. At Site 2, gas samples were withdrawn at 0, 15, 30, 45, and 60 min after deployment, and ad-

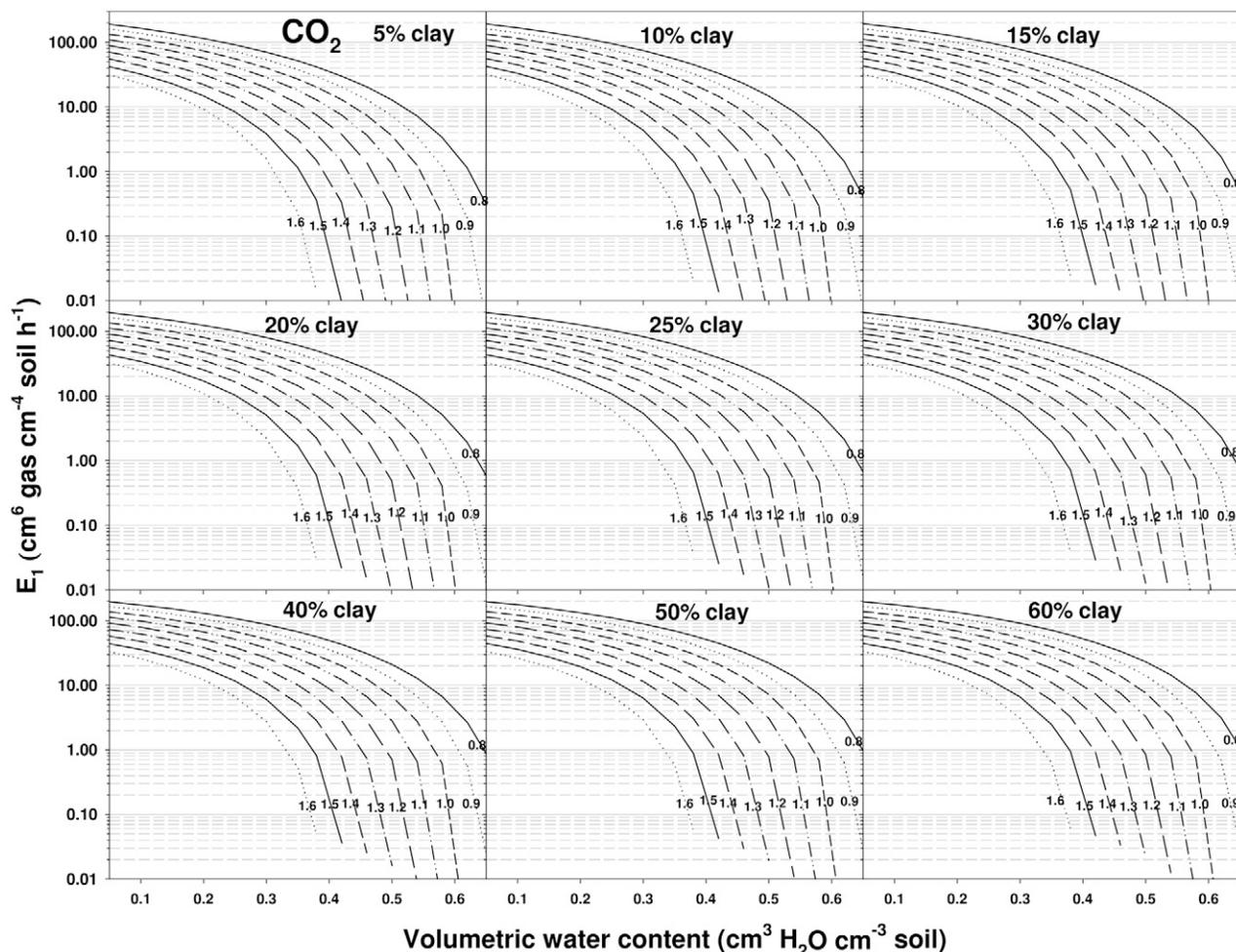


Fig. 2. Values of the error parameter E_1 at varying soil volumetric water content, bulk density, and clay content for calculating theoretical underestimation of CO_2 flux. Values were calculated using Eq. [3] to [5] assuming particle density of 2.65 g cm^{-3} , soil temperature of 20°C , and pH 6.5. Values ranging from 0.8 to 1.6 indicate varying bulk density values in units of g cm^{-3} .

ditional samples were taken (from Chamber 3 only) at 75 and 90 min after deployment. For all chambers, 12-cm^3 samples were taken at each time point and immediately transferred to 9-cm^3 glass vials which were analyzed within 48 h by gas chromatography with a thermal conductivity detector for CO_2 and an electron capture detector for N_2O (Venterea et al., 2005, 2006). At Site 1, N_2O fluxes were close to or below detectable limits ($< 1 \mu\text{g N m}^{-2} \text{ h}^{-1}$) and are therefore not reported.

During each flux measurement, soil temperature was determined using a portable temperature probe (Fisher, Hampton, NH) inserted to the 5-cm depth. Within 1 h after each flux measurement, three core samples (5-cm ID by 5-cm deep) were taken from within 5 m of each chamber for gravimetric determination of bulk density and water content by drying at 105°C . Soil pH was also measured after mixing 5 g of soil with 5 mL of $1 \text{ mol L}^{-1} \text{ KCl}$. The soil data were used to calculate E_1 using Eq. [3] to [5] (Table 2). Fluxes of CO_2 were calculated using LR and the quadratic (Quad) model of Wagner et al. (1997), each with and without adjustments for TFU using the numerical option described above. As is commonly practiced, if the nonlinear model generated a flux estimate lower than LR, the LR result was reported. The NDFE

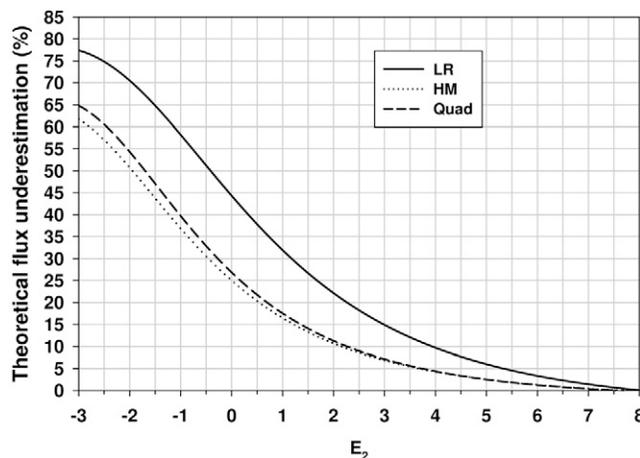


Fig. 3. Theoretical flux underestimation as a function of error parameter E_2 for flux-calculation using linear regression (LR) and the nonlinear models of Hutchinson and Mosier (1981) (HM) and Wagner et al. (1997) (Quad). Curves are described by Eq. [8] using regression coefficients in Table 1.

Table 2. Soil bulk density (ρ), water content (θ), temperature (T_s), pH, and error coefficients (E_1) for individual chamber measurement locations.

Site	Chamber	ρ	θ	T_s	pH	E_1	
						CO_2	$\text{N}_2\text{O}^\dagger$
		g cm^{-3}	$\text{cm}^3 \text{cm}^{-3}$	$^\circ\text{C}$		$-\text{cm}^6 \text{cm}^{-2} \text{h}^{-1}-$	
1	1	1.33	0.22	18.6	5.36	20.3	–
	2	1.42	0.22	17.0	5.24	14.1	–
	3	1.41	0.24	17.2	5.30	11.9	–
2	1	1.12	0.12	20.3	4.17	65.8	49.0
	2	1.06	0.11	24.5	4.80	80.5	60.2
	3	1.15	0.04	24.0	4.90	99.1	76.6

† N_2O data are not reported for Site 1, so these values are not shown.

model of Livingston et al. (2006) was also used to calculate flux using the nonlinear regression solver available at <http://arsagsoft-ware.ars.usda.gov/>. For each data set, fluxes were calculated using the first 3, 4, 5, or more (if available) sampling points.

Results and Discussion

Application to Actual Flux Calculations

Due to instantaneous feedback of chamber gas concentrations on soil-gas diffusion, the actual predeployment flux is nearly impossible to determine directly under field conditions (Livingston et al., 2006). Given this inherent limitation, the reliability of the current method was assessed by evaluating: (i) the stability of flux values determined using different numbers of sampling points obtained over varying times for each chamber deployment, and (ii) the degree of agreement among different flux-calculation schemes, that is, the TFU-corrected LR and Quad schemes and the NDFE.

Chamber CO_2 and N_2O concentrations increased in a manner consistent with the “chamber effect”, that is, the rate of increase tended to decrease over time (Fig. 4). Thus, fluxes estimated by LR without adjustment for TFU (open symbols in Fig. 5) also tended to decrease with increasing T_d . One exception was in Chamber 2 at Site 1, where the measured CO_2 concentration at 0.33 h was not consistent with the trend exhibited by the five other sampling points (Fig. 4a), resulting in a lower flux as determined by LR using the first three sampling points (Fig. 5a). A similar result occurred in Chamber 2 at Site 2 for N_2O (Fig. 5c).

Soil properties varied both across and within sites (Table 2). The lower bulk density and water content at Site 2 resulted in higher E_1 values (Table 2), corresponding to lower E_2 and thus higher TFU values. Fluxes determined by LR and Quad with adjustment for TFU (open and hatched bars in Fig. 5) were relatively stable. With the exception of the one anomalous measurement in Chamber 2 at Site 1, coefficients of variation (CV) determined from fluxes obtained at varying T_d were $\leq 7.0\%$ for LR and Quad (Table 3). The TFU-adjusted fluxes determined by LR and Quad applied to the entire data set from each chamber also agreed with each other fairly well, yielding relative errors (RE) ranging from -6.6% to $+4.8\%$ (Table 3).

Evaluation of the NDFE and comparison to the current method was complicated due to the fact that in nearly all cases

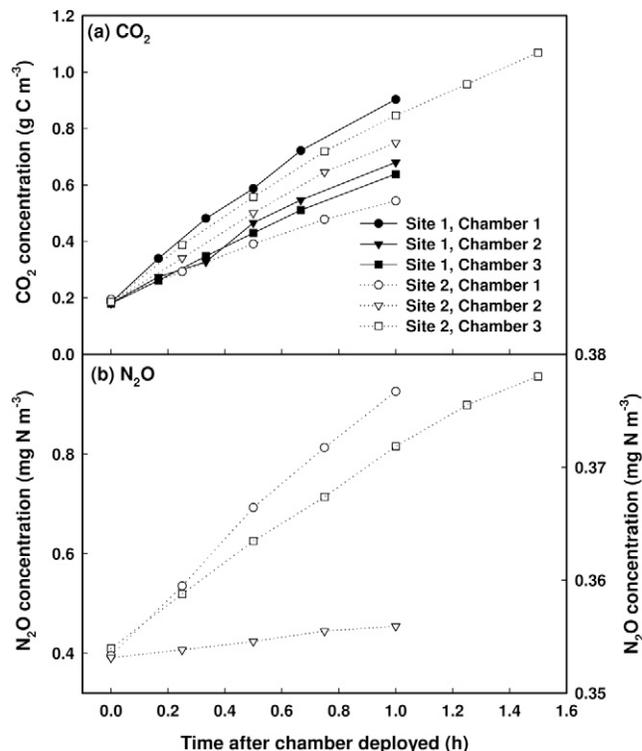


Fig. 4. Measured chamber concentrations of (a) carbon dioxide (CO_2) and (b) nitrous oxide (N_2O) vs. time after chamber deployed at Site 1 (CO_2 only) and Site 2. Note that in (b), the right-hand vertical axis applies to Chamber 3 only.

the NDFE solver generated two or three different solutions for each data set. The potential for multiple solutions arising from the NDFE has been previously noted by Livingston et al. (2006) and Venterea and Baker (2008). The NDFE nonlinear regression solver is designed to simultaneously solve for three parameters in Eq. [9]: $C_i(0)$, f_p , and τ . More than one set of these parameter values may be obtained by the solver, due to convergence of the solver to local as well as global minima in sums of squares (Livingston et al., 2006). The current method, while based on the same theory as the NDFE, avoids the practical complications of multiple nonlinear regression analysis.

For the current analysis, the NDFE solver was run 100 times for each data set. The value of each solution was reported together with its frequency, that is, the number of times out of 100 runs that each solution was obtained (solid bars and corresponding numbers in Fig. 5). The NDFE analysis is further complicated because increased frequency of a solution does not appear to correlate with increased confidence in that solution. In several instances, the more frequently obtained solutions agreed very well with fluxes determined by LR without adjustment for TFU and were lower than fluxes determined by Quad without adjustment for TFU (Fig. 5). In contrast, the less frequently obtained solutions agreed more closely with TFU-adjusted fluxes (Fig. 5).

For example, using all five sampling points collected over 1 h in Chamber 1 from Site 2, 70 out of 100 runs of the NDFE solver generated a CO_2 flux value of $49 \text{ mg C m}^{-2} \text{ h}^{-1}$ which was nearly identical to the flux calculated from nonadjusted

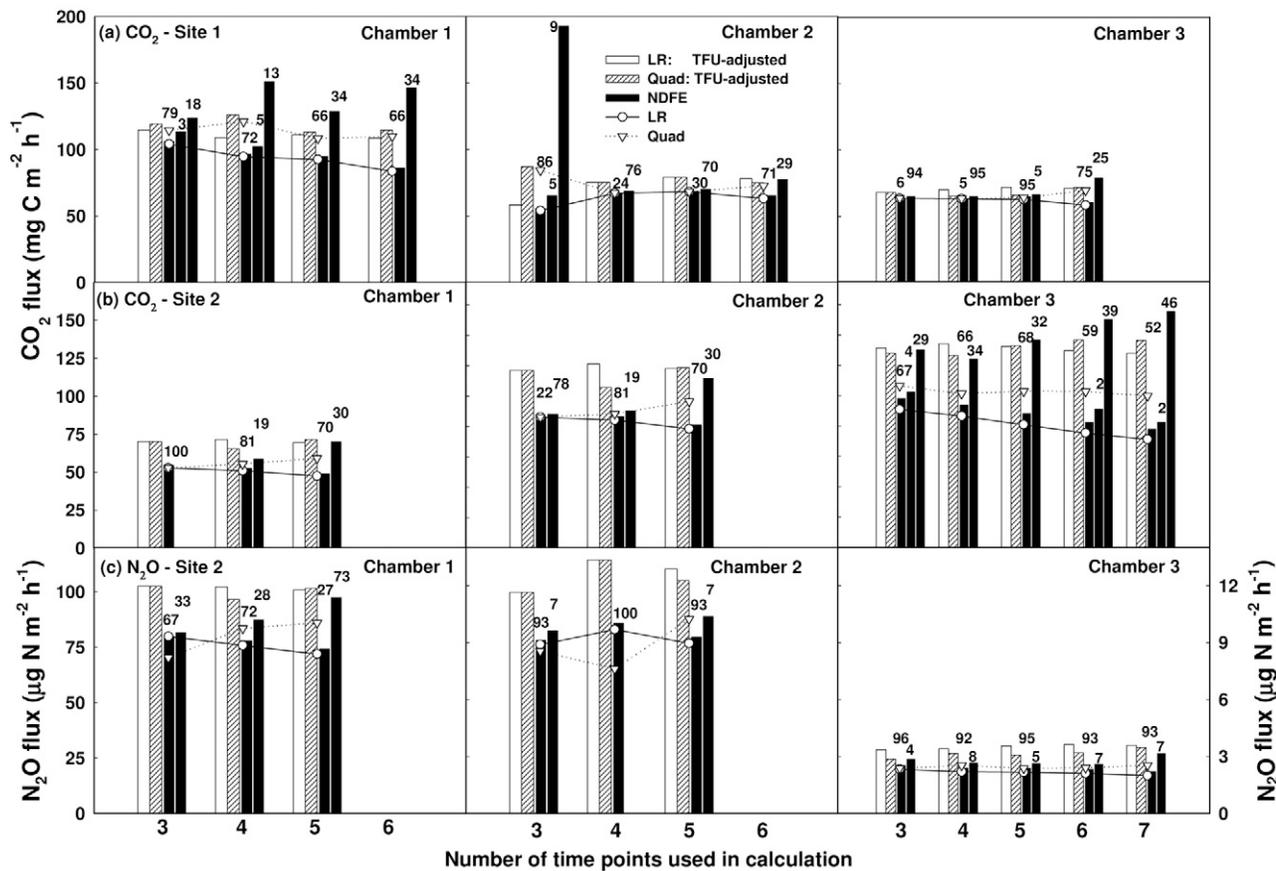


Fig. 5. Carbon dioxide (CO_2) fluxes at (a) Site 1 and (b) Site 2, and (c) nitrous oxide (N_2O) fluxes at Site 2 calculated using varying number of sampling points. In (a), 3, 4, 5, or 6 sampling points correspond to chamber deployment times (T_d) of 0.33, 0.50, 0.67, or 1.0 h, respectively. In (b) and (c), 3, 4, 5, 6, or 7 sampling points correspond to $T_d = 0.50, 0.75, 1.0, 1.25, \text{ or } 1.5$ h, respectively. Symbols connected by lines are fluxes determined from linear regression (LR) and quadratic (Quad) calculation schemes with no adjustment for theoretical flux underestimation (TFU). Open and hatched bars represent TFU-adjusted fluxes, and solid bars represent fluxes determined using the nonlinear diffusive flux estimator (NDFE). Values above solid bars are percentage of solutions yielding the corresponding flux values based on 100 runs of the NDFE solver. In (c), the right-hand vertical axis applies to Chambers 2 and 3.

Table 3. Coefficients of variation (CV) and relative errors (RE) of fluxes calculated by linear regression (LR) and quadratic (Quad) schemes adjusted for theoretical flux underestimation using the current method compared to the nonlinear diffusive flux estimator (NDFE).

Site	Chamber	CV†			RE‡		
		LR	Quad	NDFE§	Quad vs. LR	NDFE vs. LR§	NDFE vs. Quad§
%							
CO_2							
1	1	2.5	5.0	9.7	-5.5	-35	-28
	2	13	7.1	59	3.7	0.86	-3.0
	3	2.3	4.2	9.7	-0.82	-11	-10
2	1	1.4	4.6	13	-2.9	-0.58	2.3
	2	1.8	6.2	13	-0.41	5.6	6.0
	3	1.9	3.6	9.5	-6.6	-22	-14
N_2O							
2	1	0.91	3.3	9.0	-0.74	3.4	4.1
	2	7.0	7.0	5.4	4.8	19	15
	3	2.6	6.5	8.4	0.95	6.6	5.8

† The CV values were determined from fluxes calculated at varying deployment times (T_d).

‡ The RE values (expressed as %) were determined from $(f_{LR} - f_{Quad})/f_{LR}$, $(f_{LR} - f_{NDFE})/f_{LR}$, and $(f_{Quad} - f_{NDFE})/f_{Quad}$ respectively, where f is flux calculated over the entire deployment period and the subscripts refer to the flux-calculation scheme.

§ For NDFE, CV, and RE values were determined using highest flux values obtained at each T_d .

LR. However, 30 out of 100 NDFE solutions were nearly identical to the higher flux ($70 \text{ mg C m}^{-2} \text{ h}^{-1}$) calculated from TFU-adjusted LR (Fig. 5). To address the question of which of the two NDFE-generated values is “correct”, the τ values re-

turned by the NDFE solver were examined. NDFE-generated τ values were > 200 h for the lower flux estimate and 2.82 h for the higher estimate, which compares to a value of 2.75 h determined using the numerical option together with Eq. [10].

The close agreement between the independently calculated and NDFE-obtained values of τ lends more confidence to the higher of the two NDFE flux estimates, which was obtained by only 30% of the NDFE solver runs.

The above analysis of τ values was applied to all of the chamber data sets. The analysis indicated that the NDFE solutions yielding the highest flux values also consistently yielded τ values most similar to those determined from the numerical option and Eq. [10]. Therefore, CV and RE values for the NDFE-generated fluxes were calculated using the highest flux value obtained for each data set. The CV values for NDFE were consistently higher than for TFU-adjusted LR and Quad (Table 3). In five of nine cases, agreement between fluxes generated by NDFE and LR or Quad was relatively good, with RE values ranging from -3% to $+6.6\%$, while in the other four cases, RE ranged from -35% to $+19\%$ (Table 3).

Assumptions and Limitations

The flux-correction method described here is theoretically based and therefore must be employed with some caution and recognition of its key assumptions and limitations, which follow directly from the assumptions used in deriving Eq. [9]. These assumptions include: (i) gas transport in the soil profile is driven by one-dimensional vertical diffusion, (ii) the chamber atmosphere is homogeneously mixed, (iii) irreversible consumption of the trace gas in the soil (e.g., biological uptake) or in the chamber (e.g., gas-phase or surface reaction) is negligible, and (iv) the soil is vertically uniform with respect to physical properties (Livingston et al., 2006; Venterea and Baker, 2008). Each of these assumptions are discussed below.

Livingston et al. (2006) examined assumption (i) using numerical modeling and concluded that one-dimensional vertical diffusion is a valid assumption only if chambers are equipped with an adequately designed vent tube to minimize pressure perturbations, and if chamber base insertion depth is sufficient to minimize lateral diffusion. Guidelines for designing vent tubes and determining adequate insertion depths are given by Xu et al. (2006), Hutchinson and Livingston (2001, 2002), and Hutchinson and Mosier (1981).

Livingston et al. (2006) also examined assumption (ii) and concluded that in cases where forced mechanical mixing (e.g., a fan or recirculation system) is not provided, temperature gradients within the chamber and pressure fluctuations resulting from a properly designed vent tube are likely to provide sufficient mixing. Livingston et al. (2006) cautioned, however, that under calm conditions and particularly for taller chambers, some means of mechanical mixing may be required to avoid trace gas concentration gradients within the chamber, and they further cautioned that mechanical mixing systems must be designed to minimize pressure-induced transport within the soil profile (also see Davidson et al., 2002). In cases where pressure-driven transport within the profile is known to be important and cannot be overcome by vented chamber designs, other more numerically intensive methods of estimating chamber-induced errors may be useful (Perera et al., 2002; Livingston et al., 2006; Senevirathna et al., 2007).

Regarding assumption (iii), Venterea et al. (2009b) showed that biological consumption of N_2O in the soil profile is not likely to affect chamber N_2O concentration dynamics except under a combination of extreme conditions. These conditions included the coexistence water-filled pore space values less than approximately 65%, nearly complete anaerobic conditions within the upper 5 cm of soil, N_2O uptake kinetics higher than most if not all reported data, and for $H_c \leq 10$ cm and $T_d \geq 1$ h. However, this analysis did not address situations where chamber N_2O concentrations decrease during the deployment period, that is, where the direction of N_2O flux appears to be from atmosphere to soil, as has been observed in some cases (Chapuis-Lardy et al., 2007). The flux-correction method described here is based on theory which does not account for gas consumption and therefore should not be used in these cases, or for other biogenic trace gases like methane which are known to undergo substantial uptake in the soil profile. In these cases, other approaches may be useful (Senevirathna et al., 2007; Perera et al., 2002). Additionally, the method is not applicable for trace gases which may react with other gaseous constituents in the chamber headspace (e.g., nitric oxide) or with chamber surfaces (e.g., ammonia).

Venterea and Baker (2008) examined the assumption of vertically uniform soil physical properties (assumption iv) and demonstrated that Eq. [9] did not exactly apply to soil profiles with very large near-surface vertical gradients in bulk density and water content. In these cases, the method described here should be applied with some caution, since selection of a sampling depth interval for these properties could greatly affect the resulting TFU estimate. Analysis based on the method of Venterea and Baker (2008) indicates that using soil physical data for the near-surface layer (i.e., the upper 0–5 cm) should provide a reasonably accurate estimate of E_1 for most non-uniform soils. Alternatively, more exact TFU estimates can be made using numerical techniques described by Venterea and Baker (2008), provided that highly resolved ρ and θ vs. depth data are available, to determine the optimum sampling interval for a particular soil.

The above limitations relate to evaluating the accuracy of chamber-based flux estimates. Additional considerations relate to the precision of these estimates. Venterea et al. (2009b) developed a spreadsheet method using Monte Carlo simulation techniques to calculate the variances in flux estimates resulting from specific variances in measurement systems used to determine chamber trace gas concentrations. Venterea et al. (2009b) showed that measures taken to increase the absolute accuracy of flux estimates, including shorter deployment times and taller chambers, and use of nonlinear flux-calculation schemes, will also increase the variance in flux estimates to an extent that depends on errors associated with sampling techniques and analytical instrument performance.

Implications

A review by Rochette and Eriksen-Hamel (2008) found that LR is commonly used for determining soil N_2O emissions, which implies that a majority of reported data substan-

tially underestimate actual N₂O emissions. To demonstrate the potential range of flux underestimation, TFU values were calculated for several recent studies where sufficient information was reported or obtained from the authors. This analysis was done under the assumption of a fixed ρ and varying θ (Fig. 6). For $\theta = 0.10$, TFU ranged from 7 to 35% and for $\theta = 0.40$, TFU ranged from 1.8 to 12% across the studies. These results point out the potential danger in comparing or aggregating flux magnitudes across studies where different methods, and different soils, were used. Thus, attempts to develop accurate large-scale emissions estimates or to validate emissions models based on a collection of studies may be hindered in the absence of corrections for these effects, such as that provided by the current method.

Soil property effects can also confound data analysis within an individual study or experimental site where the same chamber methods and flux-calculation schemes are employed. Venterea and Baker (2008) showed that soil profiles having identical pre-deployment fluxes but differing in ρ and θ generated substantially different flux chamber data and TFU values. The effects of soil physical properties alone on chamber dynamics, which are quantified here by the E_1 term, have been well-documented theoretically and empirically (Healy et al., 1996; Hutchinson et al., 2000; Conen and Smith, 2000; Butnor et al., 2005). Interpretation of experimental data comparing gas fluxes among treatments that vary in soil properties as the result of tillage or organic amendment may be confounded by these effects.

Another important result of the current analysis is the highly linear relationship ($r^2 \geq 0.99$) between TFU and θ shown in Fig. 6. This strong relationship implies that uncorrected chamber flux data collected from a given soil over a range of θ values will appear to exhibit increased flux at higher water content in the absence of any actual variation. This results from the fact that increased θ results in decreased TFU. For example, if the actual flux is assumed constant over a range of θ values, the uncorrected flux will increase linearly with θ , and the relationships will exhibit the same r^2 values (≥ 0.99) as shown in Fig. 6 for each set of conditions. This has potentially important implications, since correlation with θ has been observed in many chamber-based studies, particularly for N₂O emissions (e.g., Flechard et al., 2007; Smith et al., 1998; Davidson et al., 1993). The current result therefore raises the possibility that observed relationships between N₂O (and possibly CO₂) fluxes and soil moisture indices have been influenced to some extent by artifacts of the chamber method. Laboratory studies of N₂O production rates, which generally do not use chambers and therefore would not suffer from the chamber effect, have also shown correlation with moisture content (e.g., Linn and Doran, 1984; Maag and Vinther, 1996). Thus, further investigation, including the application of flux-correction techniques, is needed to address this issue.

The sensitivity of TFU to soil physical properties as illustrated in Fig. 6 also has important implications for method application. It is well known that θ , and also under some circumstances ρ , can be highly variable in both time and space within a given experimental site. Thus, the most ideal applica-

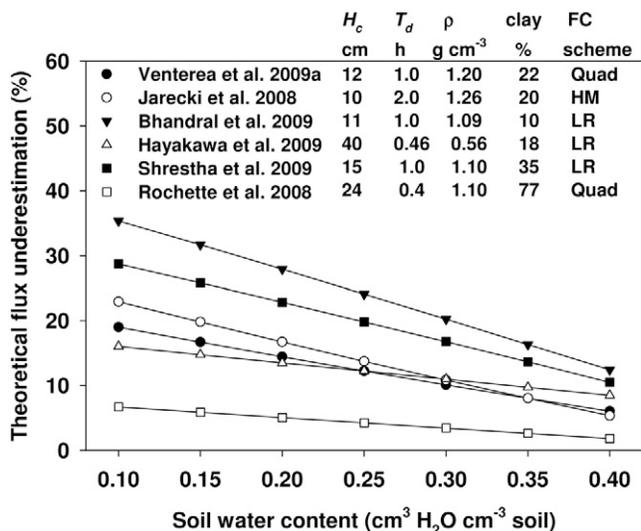


Fig. 6. Theoretical flux underestimation calculated using Eq. [3] to [8] as a function of soil volumetric water content (θ) based on published chamber volume to surface area ratio (H_c), deployment time (T_d), flux-calculation (FC) schemes, and soil physical properties for several recent studies assuming a fixed soil bulk density (ρ) and varying θ within each site. The FC schemes included linear regression (LR), the quadratic (Quad) model of Wagner et al. (1997), and the nonlinear (HM) model of Hutchinson and Mosier (1981).

tion would utilize robust soil data that can account for this variability. Venterea et al. (2009a) used the numerical option described here to calculate TFU for more than 3000 individual chamber measurements collected over three growing seasons, relying on regular measurement of soil physical properties. Total growing season N₂O emissions based on TFU-corrected nonlinear flux-calculation scheme were on average 28 and 8% higher, respectively, than emissions based on uncorrected LR and nonlinear schemes.

Conclusions

The method described here can be used to increase the absolute accuracy of fluxes obtained using chambers, and thereby provide a means of improving emissions assessments across studies and scales. The main advantage of the method compared to the NDFE technique of Livingston et al. (2006) is that the current technique is more easily adaptable to spreadsheet application without the use of nonlinear regression solvers. While the current method and the NDFE are based on the same theory, reliance of the NDFE on nonlinear regression leads to practical complications, including the need to select from multiple solutions. The current method can be applied in a standard spreadsheet and returns a single solution. An example calculation spreadsheet is available with the online version of this article. The main disadvantage of the current method is that information regarding soil physical properties is required for accurate application. However, similar information may be required as criteria for selecting among multiple solutions generated by the NDFE solver. Thus, the requirement of soils data may not be a real practical disadvantage of the current method compared to the NDFE.

Supplemental Information Available

An example calculation spreadsheet is available online in Microsoft Excel format at <http://jeq.scijournals.org>. The file uses actual data (from Site 2, Chambers 1 and 2) to calculate TFU using three, four, and five sampling points.

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