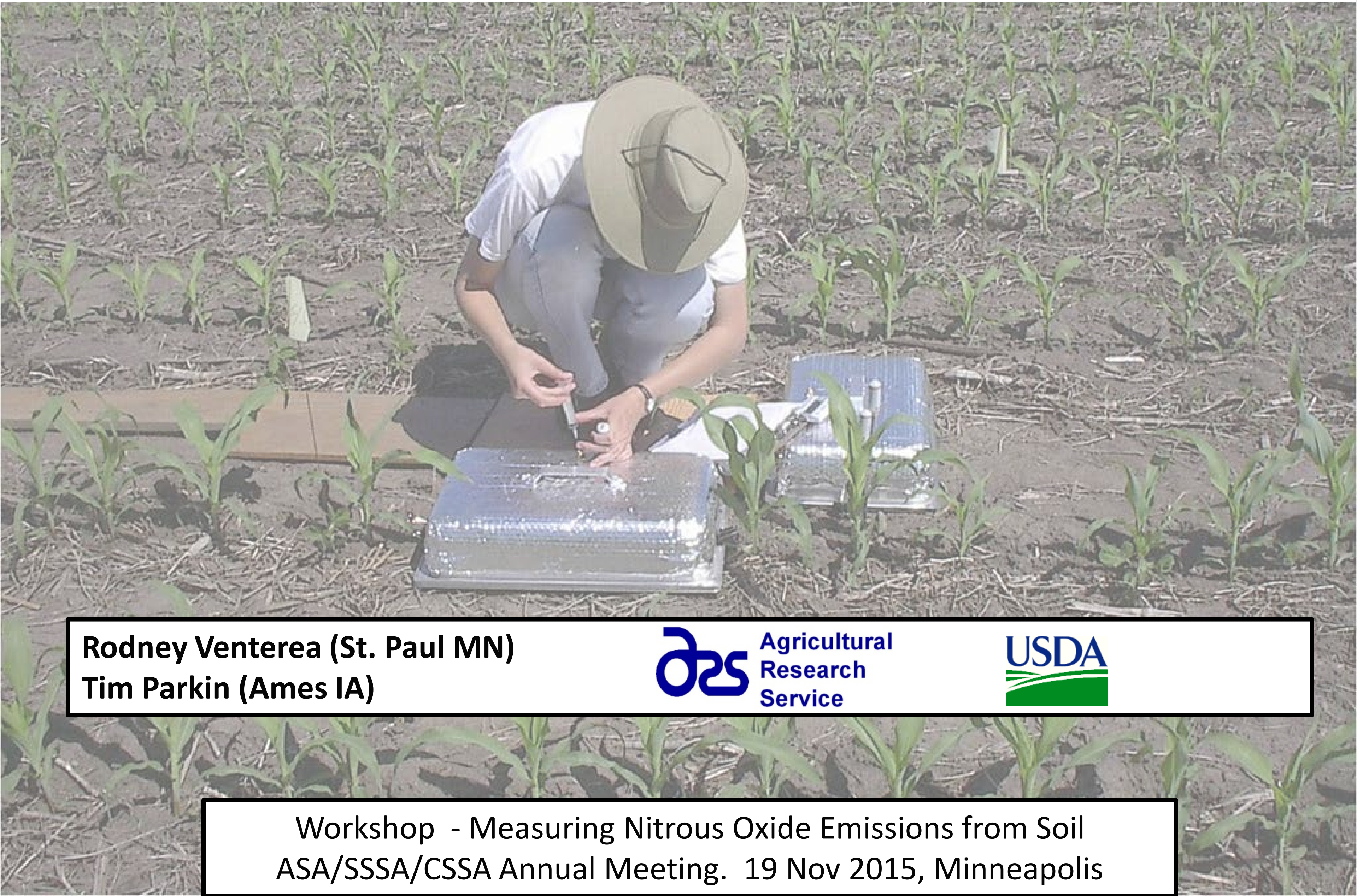
Intuitive and Non-Intuitive Implications of Gas Diffusion Theory on Chamber-Based Flux Measurements



Rodney Venterea (St. Paul MN)
Tim Parkin (Ames IA)

Agricultural Research Service

USDA

Workshop - Measuring Nitrous Oxide Emissions from Soil
ASA/SSSA/CSSA Annual Meeting. 19 Nov 2015, Minneapolis

Outline

- What do diffusion theory and statistics tell us about selection of a flux-calculation (FC) method?

- What tools are available to evaluate FC methods & options:
  - Accuracy (bias)
  - Precision
  - The balance of Accuracy and Precision

- General recommendations & considerations

What is the best flux-calculation (FC) method?

Does it matter?

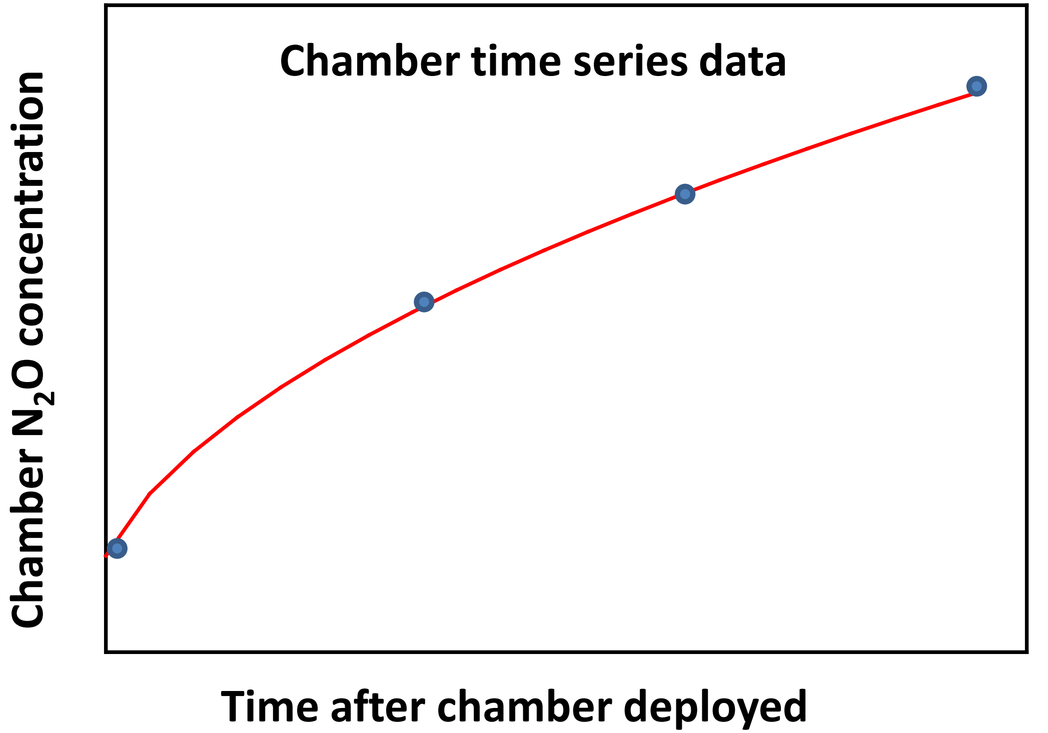
1. **Chamber data used to validate models which in turn are used for large-scale emissions assessments. If measurements are wrong, then the assessments will be wrong.**

2. **Meta-analyses can be confounded if different methods are used.**

3. **Choice of method can affect not only absolute estimates, but also relative differences over time or among treatments.**

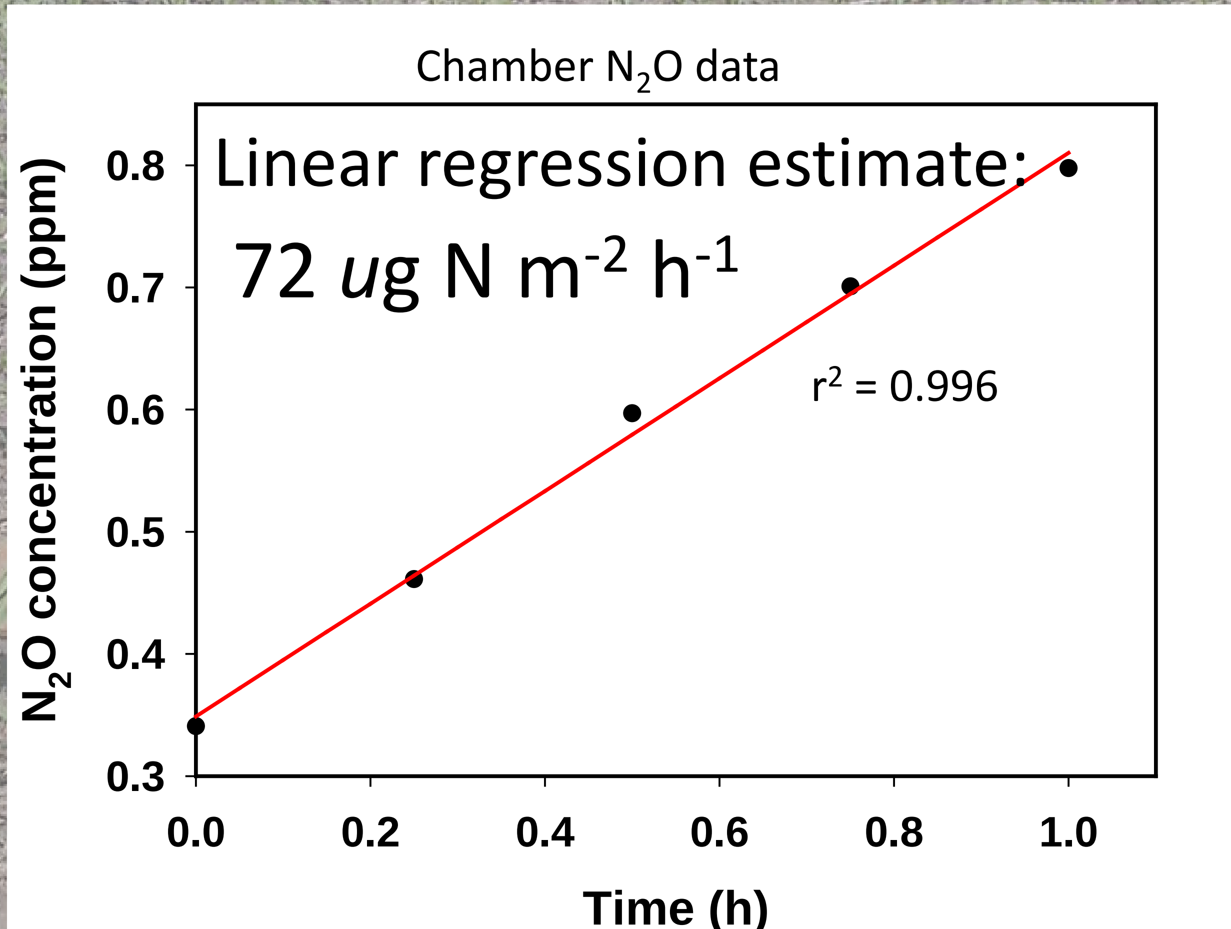
The "Chamber Effect"

- Gas accumulation suppresses diffusion, leads to non-linearity
- Flux at time zero will be underestimated using Linear Regression (LR)
- Non-linear models have been developed to overcome this problem



- Rochette & Eriksen-Hamel 2008: Only ¼ of studies used a non-linear scheme
- Levy et al 2011: choice of FC method was largest source of uncertainty
- No consensus regarding calculation methods, wide variety in approaches.

Sensitivity of flux estimate to FC method selection: Example



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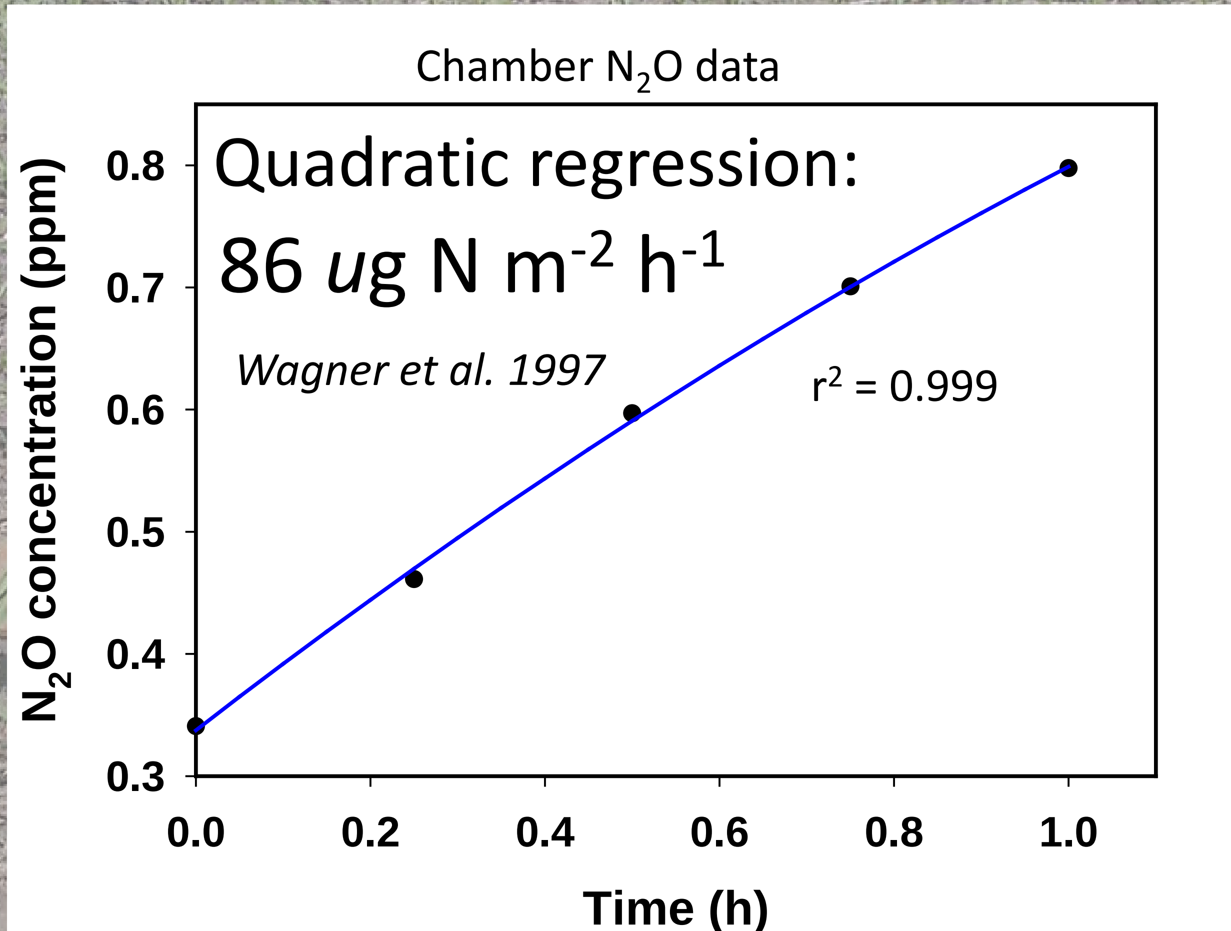
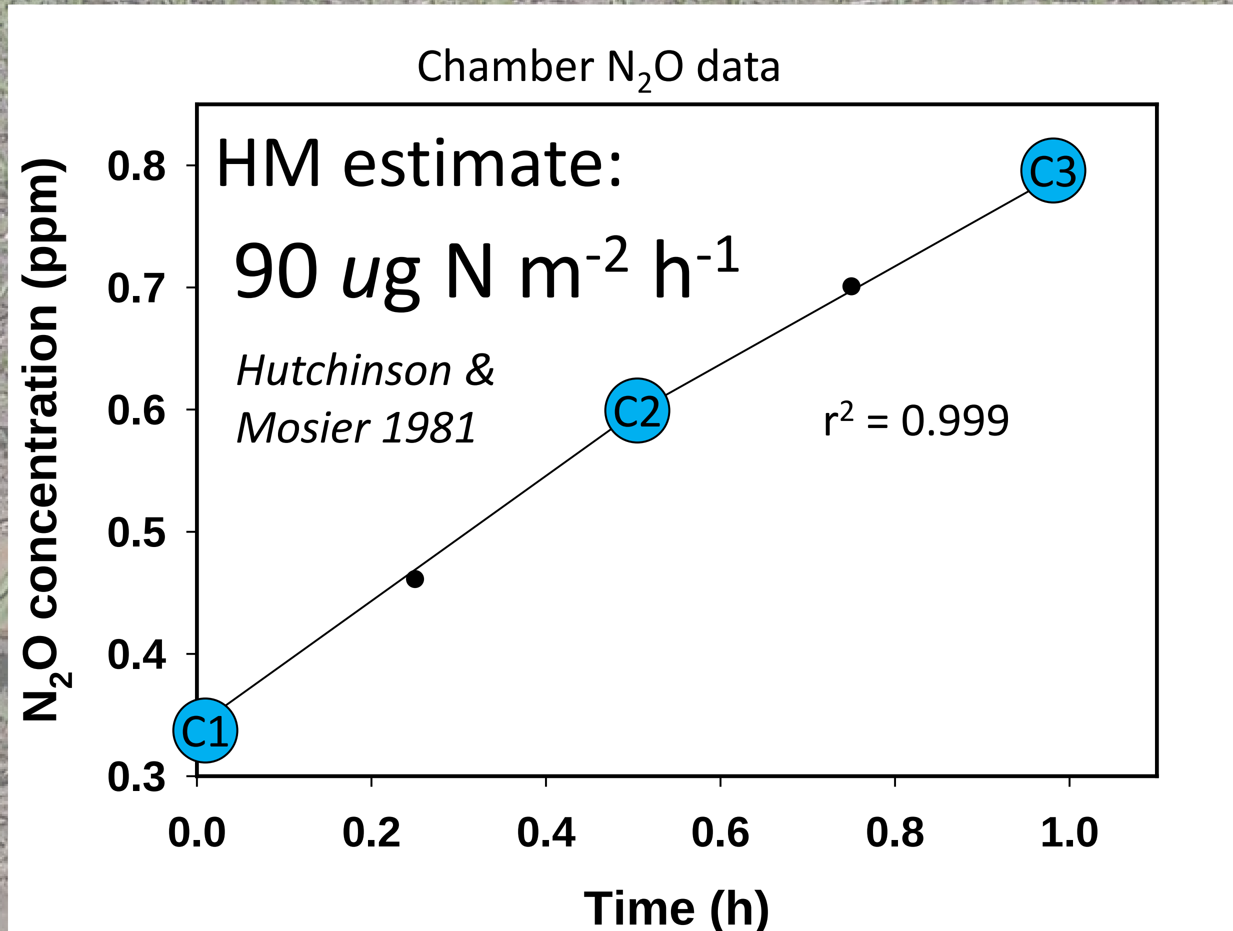
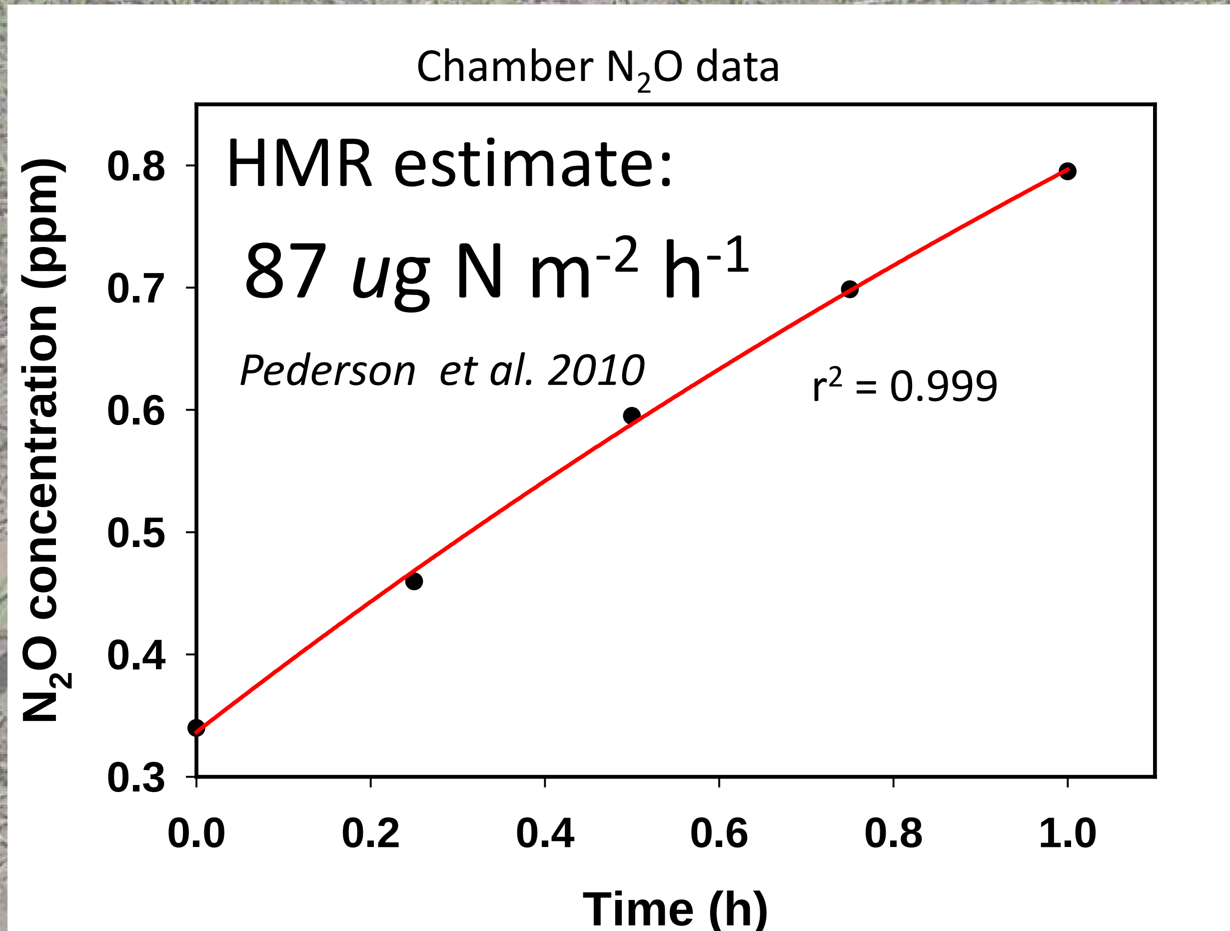


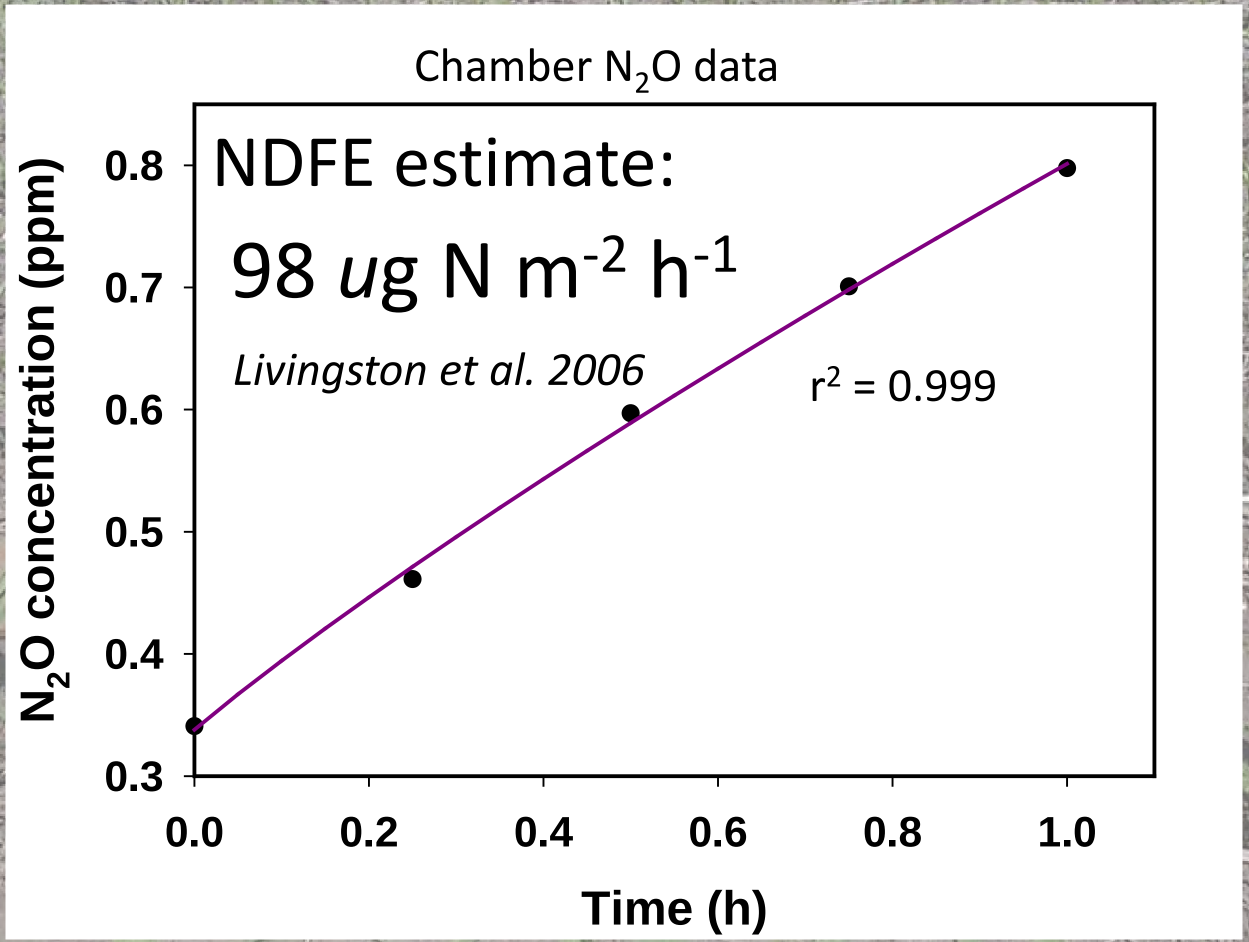
Sensitivity of flux estimate to FC method selection: Example



Sensitivity of flux estimate to FC method selection: Example



Sensitivity of flux estimate to FC method selection: Example



Sensitivity of flux estimate to FC method selection: Example

Individual chamber data set

Method	Flux (ug N m^{-2} h^{-1})	Model fit (r^2)	Deviation from LR estimate (%)
LR	72	0.996	---
QR	86	0.999	19%
HM	90	0.999	25%
HMR	87	0.999	21%
NDFE	98	0.999	36%

Measures of "best-fit" are often not useful in selecting the most accurate method

What is the best flux-calculation (FC) method?

1. **The “true” pre-deployment flux not known - no way to ground truth flux estimates**

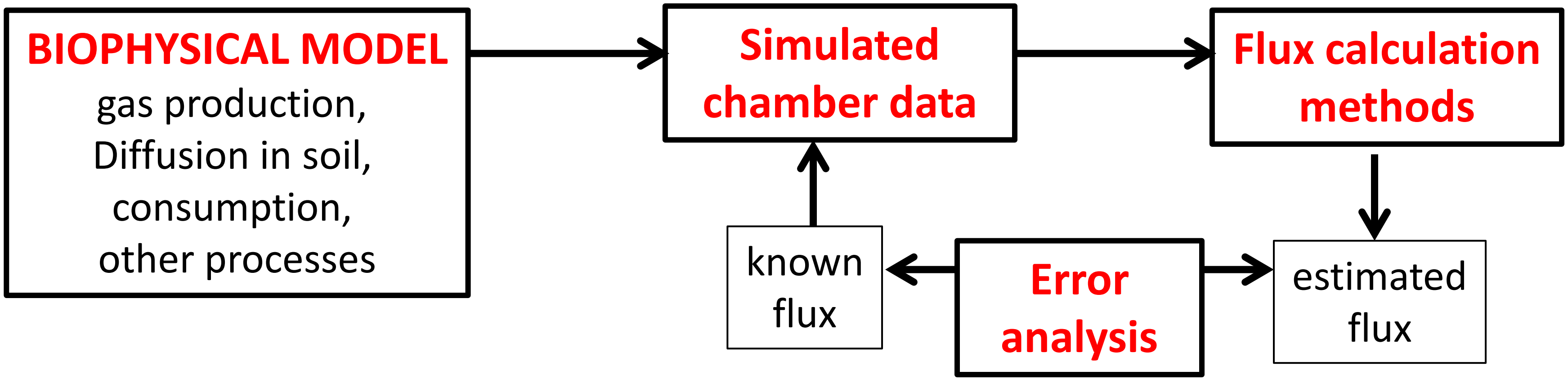
2. **Lab studies using flux-generating systems problematic**

   e.g. Martin et al 2004; Widen & Lindroth 2003

3. Theoretical approaches used in many studies:

Matthias et al 1978
Healy et al 1996
Conen & Smith 2000
Hutchinson et al 2000
Livingston et al 2006
Venterea & Baker 2008
Venterea et al. 2009
Venterea 2010, 2013

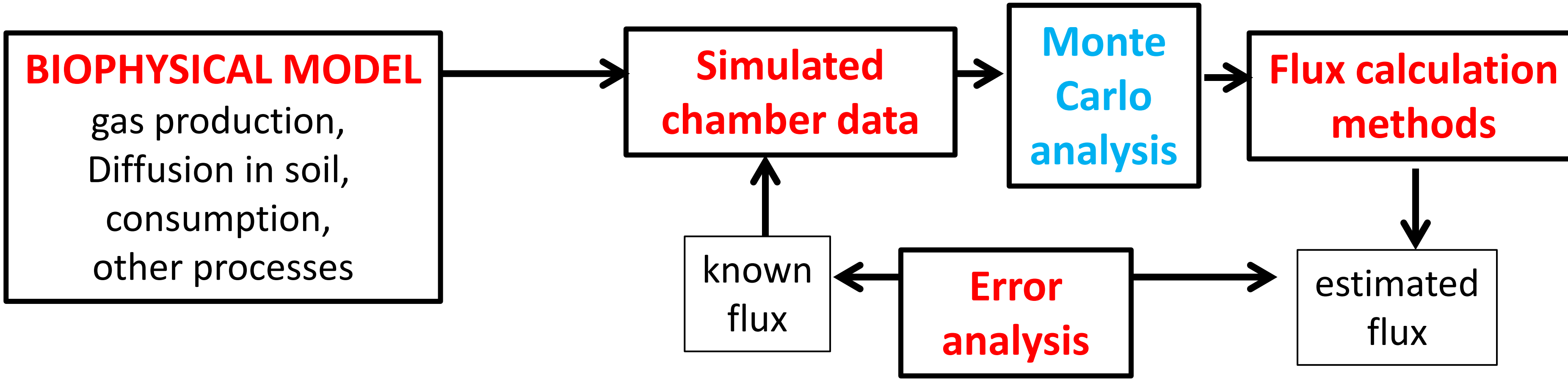
Theoretical Accuracy Analysis



Objective:

To evaluate and compare the performance of FC methods when the 'true' flux is known under specific sets of simulated biophysical conditions

Theoretical Accuracy and Precision Analysis



Objective:

To evaluate and compare the performance of FC methods when the ‘true’ flux is known under specific sets of simulated biophysical conditions

To quantify the sensitivity of FC schemes to measurement error

Some degree of simplification is required to apply diffusion theory to soil processes

Biophysical assumptions of most diffusion theory studies:

1. Flux is at steady-state prior to placement of chamber
2. Biochemical processes of N_2O production do not change after chamber placement.
3. Gas transport is dominated by 1-dimensional (1D) vertical diffusion.
4. Once the chamber is placed, diffusion responds according to Fick's Second Law (non-steady state diffusion).
5. N_2O is partitioned between gas- and liquid-phases according to Henry's Law.

Any conclusions are limited to the conditions assumed by the analysis

$$S\frac{\partial C_g}{\partial t} = D\frac{d^2 C_g}{dz^2} + P$$

The Diffusion Equation

Solution of diffusion equation by Livingston et al. (2006)

$$S\frac{\partial C_g}{\partial t} = D\frac{d^2C_g}{dz^2} + P$$

The Diffusion Equation

C_g is N_2O concentration in soil gas

Imposed boundary conditions for a well-mixed chamber

Solved analytically to yield useful algebraic expression

$$C(t) = C(0) + F_0\frac{H}{\lambda}\left[\frac{2}{\sqrt{\pi}}\sqrt{t/\tau} + \exp(t/\tau)erfc(\sqrt{t/\tau}) - 1\right]$$

C is N_2O concentration in chamber

1. FC scheme (NDFE)
-practical limitations

2. Error analysis
-useful analysis

Solution of diffusion equation by Livingston et al. (2006)

$$C(t) = C(0) + F_0 \frac{H}{\lambda}\left[\frac{2}{\sqrt{\pi}}\sqrt{t/\tau} + \exp(t/\tau)erfc(\sqrt{t/\tau}) - 1\right]$$

Non-steady Diffusive Flux Estimator (NDFE) method:

Solves for "true" pre-deployment flux (F_0)

<u>Uses iterative non-linear regression solver:</u>

-frequently converges to more than one solution for a given data set

-can generate extraordinarily high estimates

-not easy or efficient to use for large data sets

-not used much, will not consider here

Solution of diffusion equation by Livingston et al. (2006)

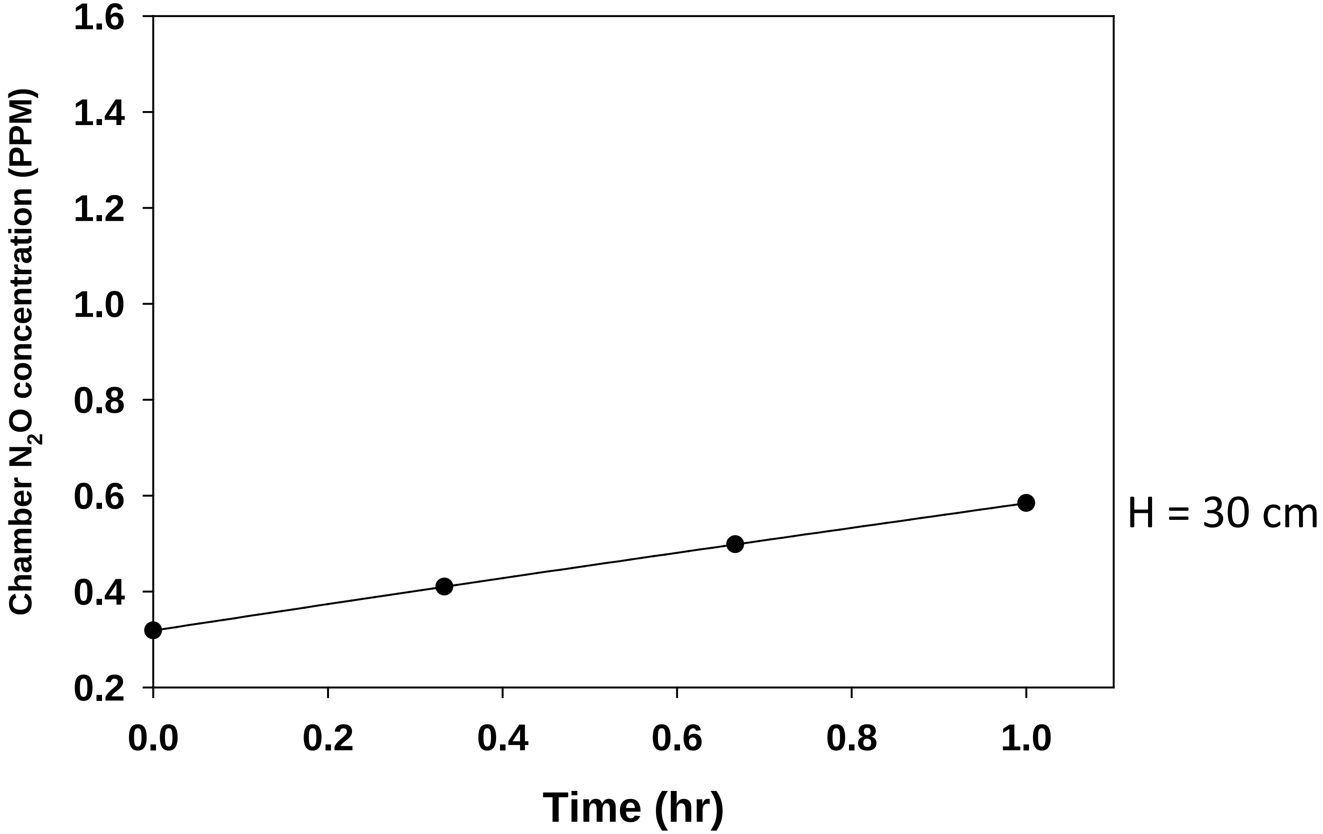
$$C(t) = C(0) + F_0 \frac{H}{\lambda}\left[\frac{2}{\sqrt{\pi}}\sqrt{t/\tau} + \exp(t/\tau)erfc(\sqrt{t/\tau}) - 1\right]$$

Allows calculation of theoretical chamber data for a given values of

1. **“true” flux (F_0)**
2. **chamber volume to area ratio (H)**
3. **soil physical properties (embedded in the λ term – BD , water content, temp)**
4. **chamber deployment period, no. of sampling points, and sampling interval (t)**

Theoretical chamber data

F_0 = 100 ug N m^{-2} h^{-1}
bulk density = 1.3 g cm^{-3}
water content = 0.20 g g^{-1}
DP = 1 hr sampled every 20 min



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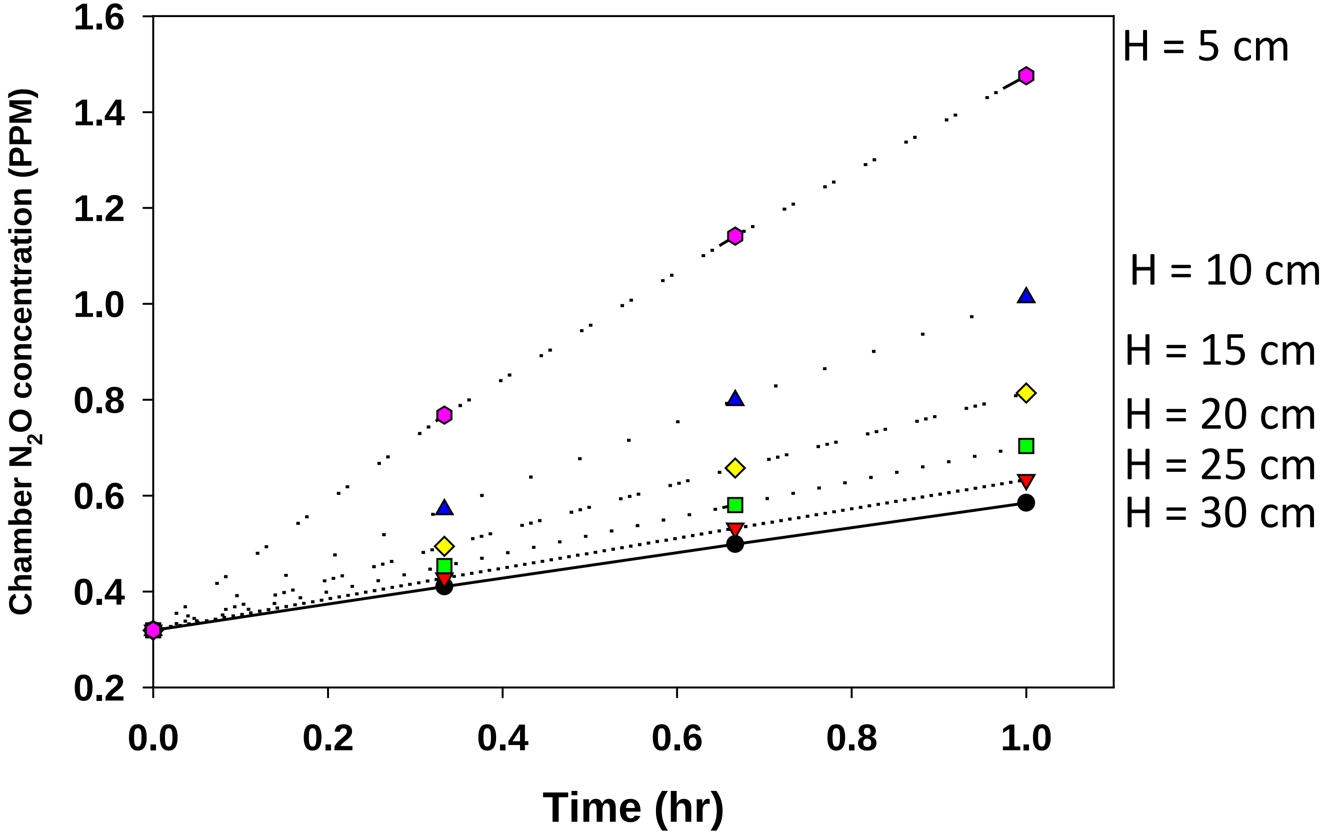
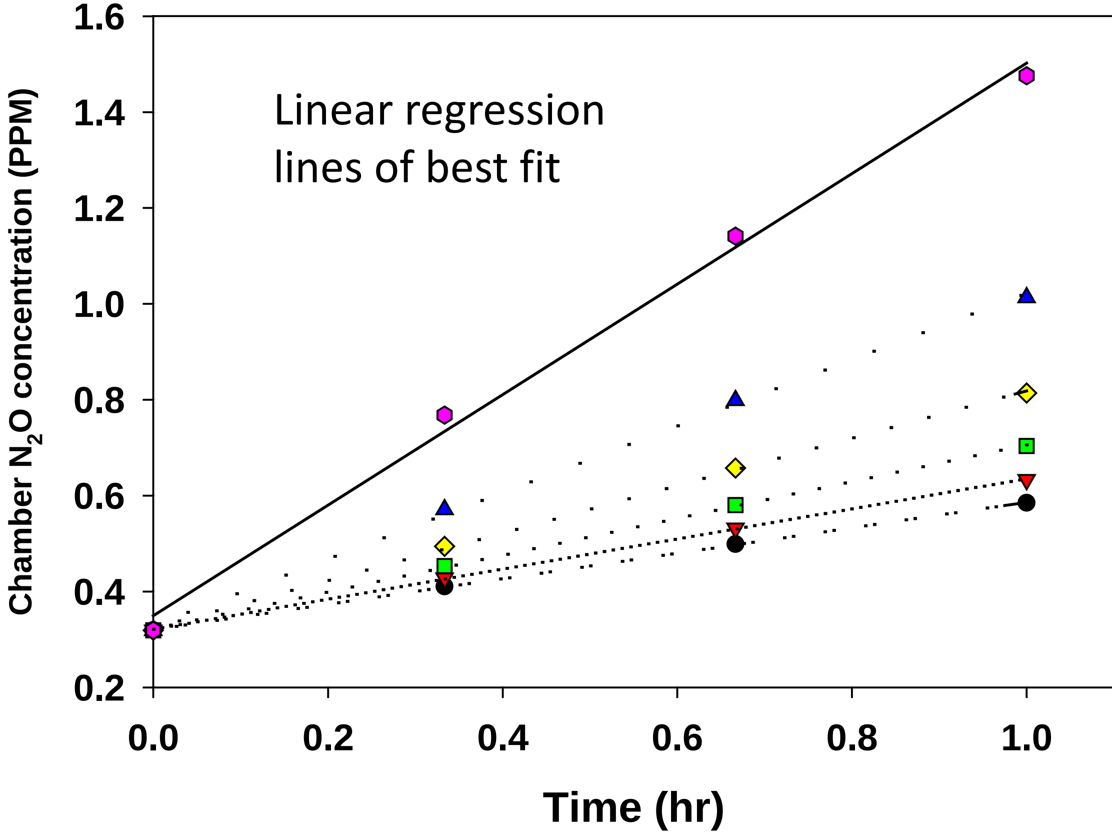


Error analysis using theoretical chamber data

F_0 = 100 ug N m^{-2} h^{-1}
bulk density = 1.3 g cm^{-3}
water content = 0.20 g g^{-1}
DP = 1 hr sampled every 20 min



Linear regression flux estimates

H = 5 cm	F_{est}= 67
H = 10 cm	F_{est}= 81
H = 15 cm	F_{est}= 86
H = 20 cm	F_{est}= 89
H = 25 cm	F_{est}= 91
H = 30 cm	F_{est}= 93

Relative Error in Flux Estimate

F_{est} = Flux estimated by FC scheme

$$\text{Relative error (\%)} = -100 \times (F_{est} - F_0)/F_0$$

(positive value => underestimation of F_0)

F_0 = "True" flux

Key Findings of Error Analysis using Theoretical Chamber Data

1. Relative error for any set of conditions is independent of F_0: The same relative error will be given regardless of the F_o value that is used.

2. Relative error for any set of conditions is also independent of the vertical distribution of the N_2O source in the soil (i.e., whether it is closer to surface or deeper in profile).

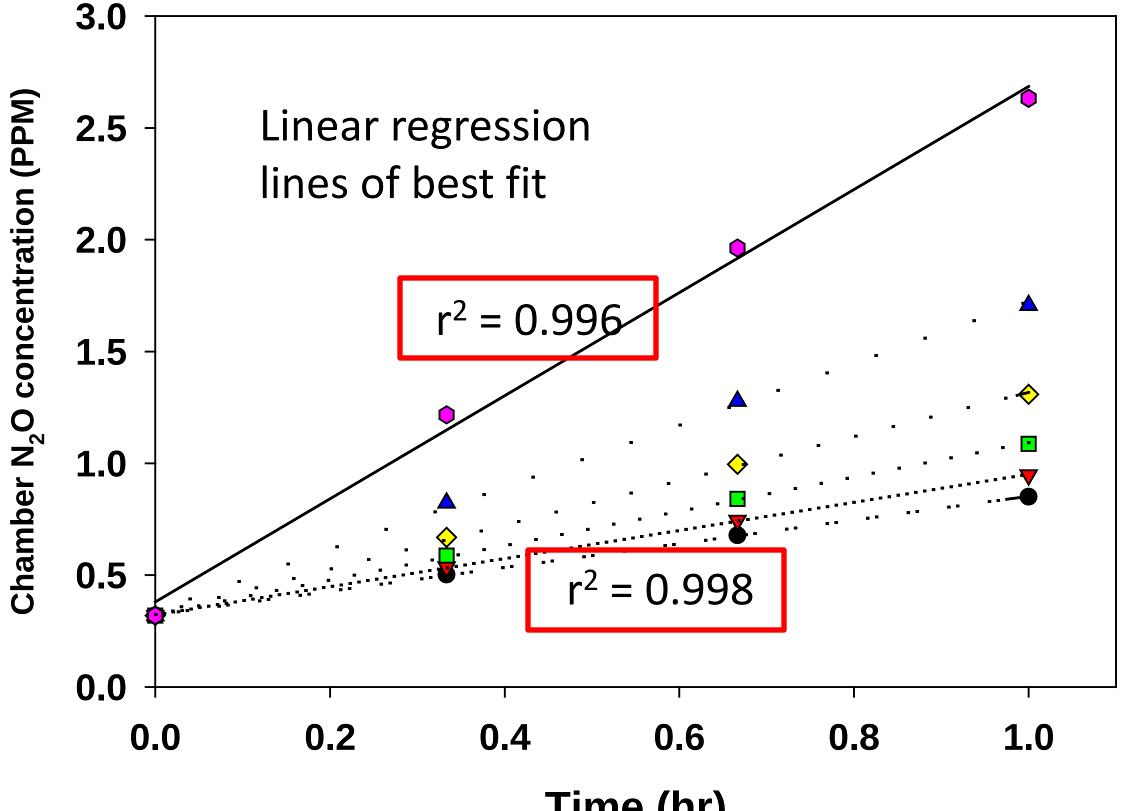
Error analysis using theoretical chamber data

F_0 = 200 ug N m^{-2} h^{-1} (Any value)

bulk density = 1.3 g cm^{-3}

water content = 0.20 g g^{-1}

DP = 1 hr sampled every 20 min



	RE (%)
H = 5 cm:	33%
H = 10 cm:	19%
H = 15 cm:	14%
H = 20 cm:	11%
H = 25 cm:	9%
H = 30 cm:	7%

Key Findings of Error Analysis using Theoretical Chamber Data

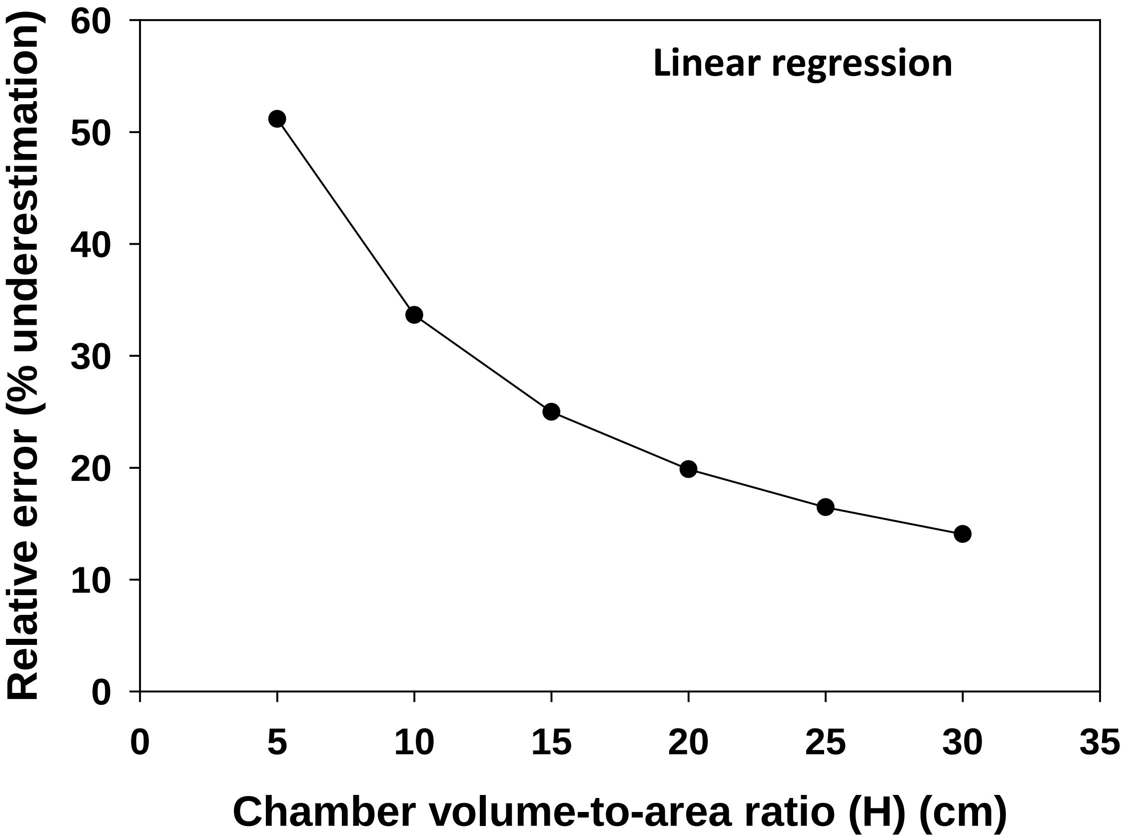
1. Relative error for any set of conditions is independent of F_0: The same relative error will be given regardless of the F_o value that is used.

2. Relative error for any set of conditions is also independent of the vertical distribution of the N_2O source in the soil (i.e., whether it is closer to surface or deeper in profile).

3. A high linear r^2 does NOT necessarily indicate that LR will yield an accurate flux estimate.

Error analysis using theoretical chamber data

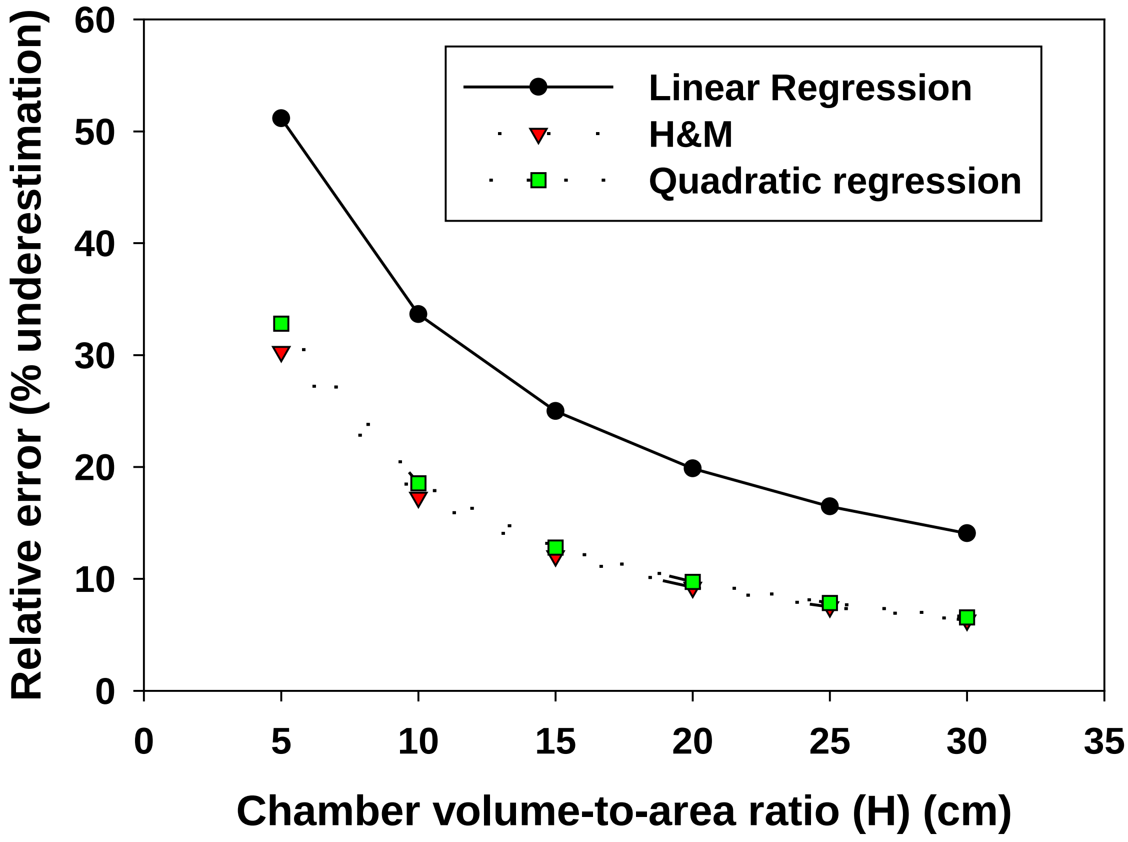
bulk density = 1.1 g cm^{-3}
water content = 0.15 g g^{-1}
DP = 1 hr



Error analysis using theoretical chamber data

bulk density = 1.1 g cm^{-3}
water content = 0.15 g g^{-1}
DP = 1 hr

H&M and QR decrease RE by about ½ compared with LR



Key Findings of Error Analysis using Theoretical Chamber Data

1. Relative error for any set of conditions is independent of F_0: The same relative error will be given regardless of the F_o value that is used.

2. Relative error for any set of conditions is also independent of the vertical distribution of the N_2O source in the soil (i.e., whether it is closer to surface or deeper in profile).

3. A high linear r^2 does NOT necessarily indicate that LR will yield an accurate flux estimate.

4. Commonly used non-linear FC schemes do NOT necessarily yield highly accurate estimates and they do NOT completely eliminate the disturbance caused by chamber placement.

Non-linear FC schemes do NOT necessarily yield highly accurate estimates

1. Quadratic regression (QR) (Wagner et al. 1997):
Has no theoretical basis, empirically based

2. Hutchinson & Mosier 1981 (H&M):
Theoretically based, but uses highly simplified set of assumptions

(a) Narrowly-defined assumptions originally meant to apply to specific set of conditions:
“The zone of N_2O *production lies somewhat below the surface and is overlain by a layer of relatively dry, loosely packed soil”*

(b) Uses Fick’s First Law to describe non-steady conditions for vertical diffusion

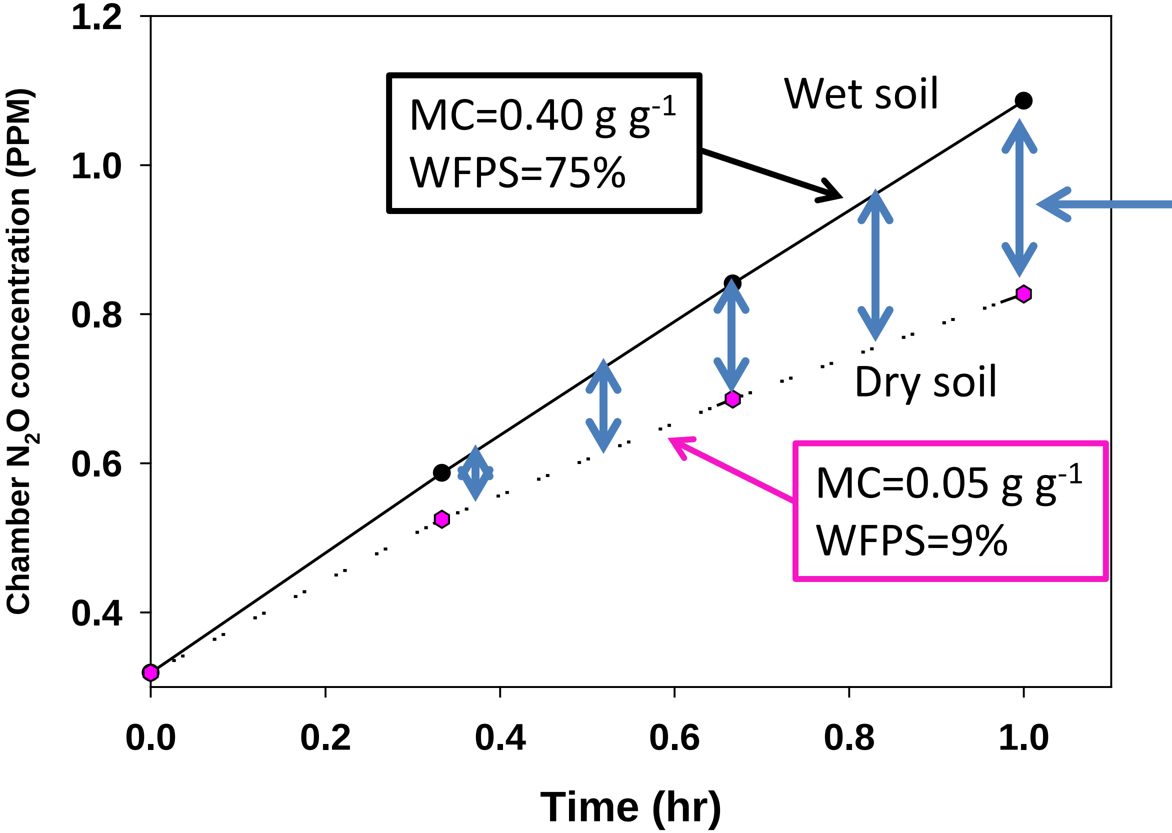
These two assumptions allow for easier mathematical treatment

3. HMR model (expanded H&M) Pedersen et al. (2010):
(a) Uses same simplifying assumption as H&M for vertical diffusion
(b) Uses Fick’s First Law for non-steady horizontal diffusion

Venterea (2013): Used biophysical model;
(a) Simulated the “layered production zone” described by H&M
(b) Accounted for 2D diffusion using Fick’s Second Law
Showed that both H&M and HMR do not describe non-steady diffusion very accurately

Soil property effects on chamber dynamics

F_0 = 100 ug N m^{-2} h^{-1}
bulk density = 1.1 g cm^{-3}
H = 10 cm
DP = 1 hr



Physical explanation:

-After chamber placement, N_2O accumulates in both the chamber and the soil pores.

-Drier soil has more capacity for N_2O accumulation

-More N_2O accumulates in soil and less accumulates in chamber compared to wet soil

Soil property effects on chamber dynamics

F_0 = 100 ug N m^{-2} h^{-1}

bulk density = 1.1 g cm^{-3}

H = 10 cm

DP = 1 hr

	ug N m^{-2} h^{-1}		
Method	Wet soil	Dry Soil	Difference
LR	**89.2**	**58.8**	**30.4**

Soil property effects on chamber dynamics

F_0 = 100 ug N m^{-2} h^{-1}

bulk density = 1.1 g cm^{-3}

H = 10 cm

DP = 1 hr

	ug N m^{-2} h^{-1}		
Method	Wet soil	Dry Soil	Difference
LR	**89.2**	**58.8**	**30.4**
QR	**95.1**	**75.8**	**19.3**

Chamber Bias Correction (CBC) Method

-Based on same rigorous diffusion theory as NDFE method but uses different approach:

Instead of treating the λ term as a regression parameter, measurements of soil bulk density, water content, and temperature are used to calculate λ .

This allows F_0 to be calculated directly without need for any iterative non-linear regression schemes:

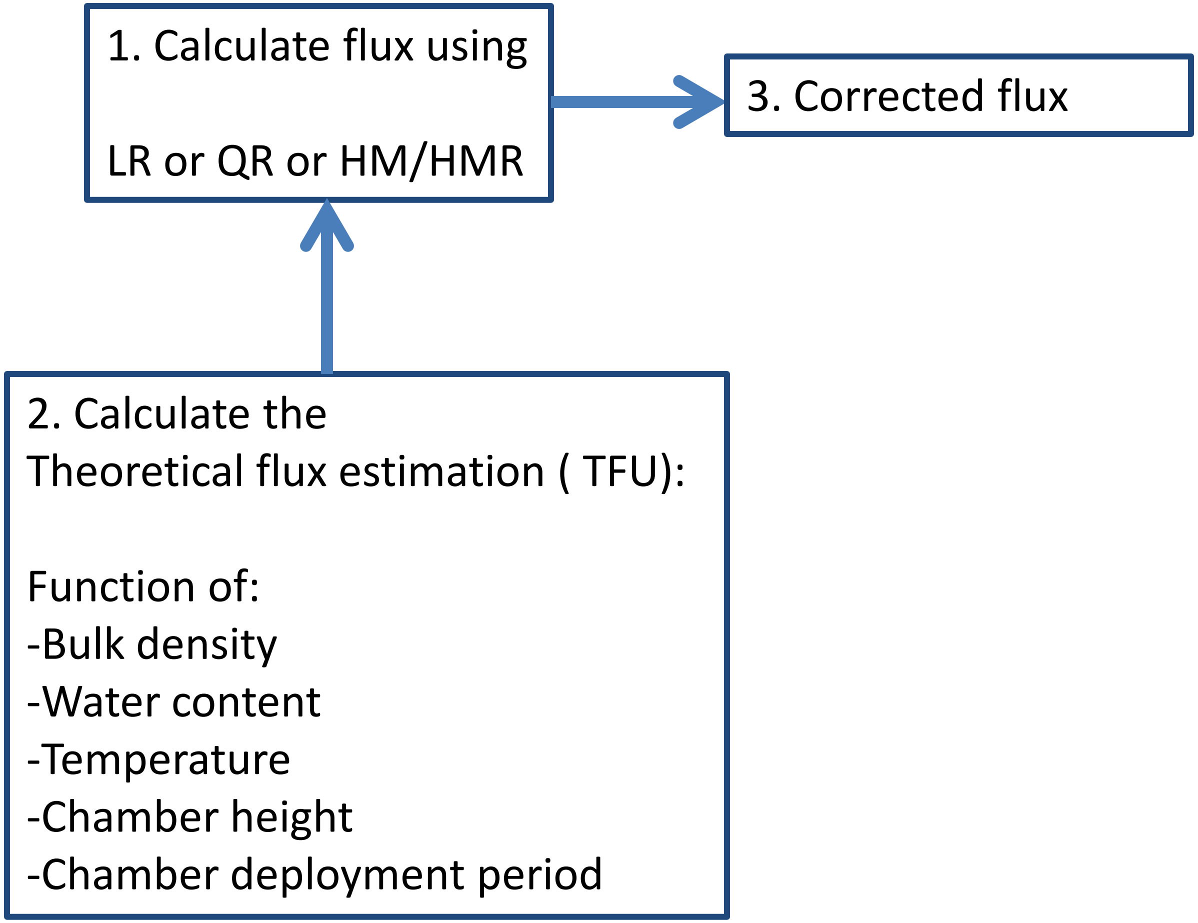
→ can be used in a simple spreadsheet calculations (website example)
→ delivers a single flux estimate
→ avoids extraordinary high estimates

-Requires measurements of soil bulk density, water content, and temperature.

-Final flux estimate will be affected by any errors in these measurements.

Venterea (2010). Simplified method for quantifying theoretical underestimation of chamber-based trace gas fluxes. J. Environ. Qual. 39:126-135

Chamber Bias Correction (CBC) Method



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Soil property effects on chamber dynamics

F_0 = 100 ug N m^{-2} h^{-1}
bulk density = 1.1 g cm^{-3}
H = 10 cm
DP = 1 hr

	ug N m^{-2} h^{-1}		
Method	Wet soil	Dry Soil	Difference
LR	**89.2**	**58.8**	**30.4**
QR	**95.1**	**75.8**	**19.3**
CBC	99.6	99.4	0.2

Key Findings of Error Analysis using Theoretical Chamber Data

1. Relative error for any set of conditions is independent of F_0: The same relative error will be given regardless of the F_o value that is used.

2. Relative error for any set of conditions is also independent of the vertical distribution of the N_2O source in the soil (i.e., whether it is closer to surface or deeper in profile).

3. A high linear r^2 does NOT necessarily indicate that LR will yield an accurate flux estimate

4. Commonly used non-linear FC schemes do NOT necessarily yield highly accurate estimates and they do NOT completely eliminate the disturbance caused by chamber placement.

5. Compared to LR, non-linear FC methods reduce errors due to differences in soil physical properties.

6. The CBC can reduce these errors further, but requires direct measurement of soil physical properties.

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Rodney T. Venterea (Rod)
Rod.Venterea@ars.usda.gov
Soil Scientist

Lead Scientist Soil & Water Mgmt Research Unit

Adjunct Professor, Dept. of Soil, Water & Climate, University of Minnesota
Graduate Faculty, Land and Atmospheric Science Program
Technical Editor, Journal of Environmental Quality

PhD Soil Science, University of California Davis 2000
MS Civil Engineering, University of Massachusetts Lowell 1991
BS Dartmouth College 1983

Publication List

Resources for chamber-based gas-flux measurement:

*Chamber Error Assessment Tool (CEAT):

-> Excel file
-> Related article: Venterea et al (2009)

*Chamber Bias Correction (CBC) Method:

->Article:Venterea (2010)
->Simplified calculations (Excel file)
->Related articles: Venterea (2013), Venterea & Parkin (2012) Venterea et al (2009), Venterea & Baker (2008)

*Detection Limit Estimation:

->Article:Parkin et al (2012)
->Supplement (step-by-step instructions)
->Simplified calculations (Excel file)

*Protocols:

->GRACEnet Chamber Measurement Protocol (Parkin & Venterea, 2010)
->GRA Nitrous Oxide Methodology Guidelines (Link to complete collection, Eds. de Klein & Harvey)
->Chapter 6. Data Analysis Considerations (PDF)

*Chamber design:

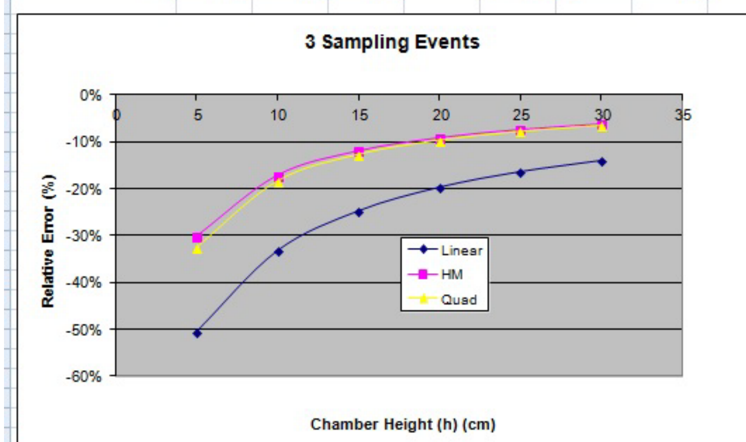
->Stainless steel chambers fabricated from steam pans

http://ars.usda.gov/mwa/stpaul/swmr/venterea

Chamber Error Assessment Tool (CEAT)

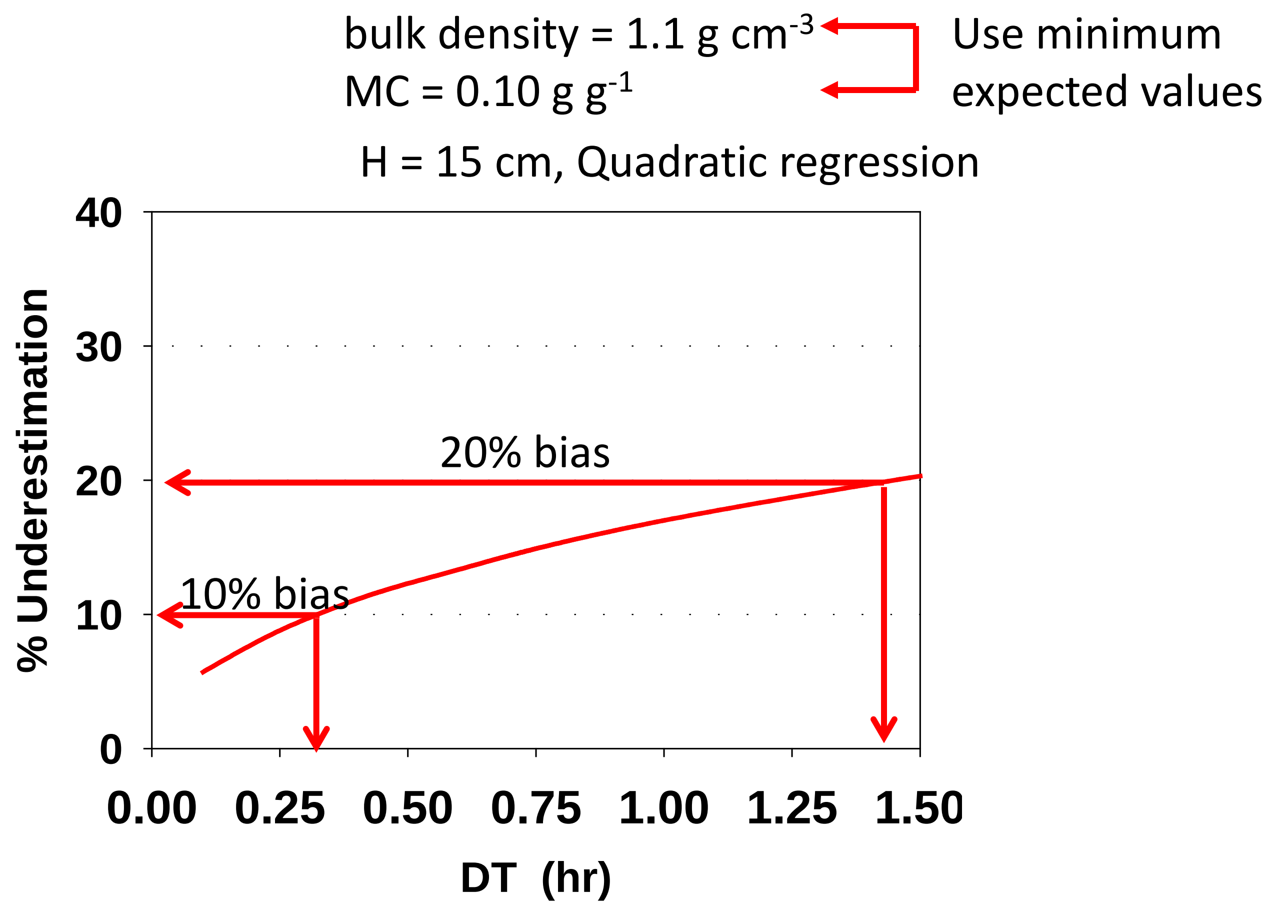
	A	B	C
1		DATA INPUT	
2		UNITS	ENTER VALUES
3	1. Soil Properties		
4	Bulk density	g dry soil/cm3 bulk soil	1.10
5	Gravimetric soil water content	g H2O/g dry soil	0.150
6	Volumetric water content	m3 H2O/m3 soil	
7	Soil temperature	degrees celsius	20.0
8	Air temperature	degrees celsius	20.0
9	Particle density	g dry soil/cm3 soil particle	2.65
10	Clay percentage	% clay by weight (range = 0 to 100)	22
11	Campbell b parameter	none	
12	2. Chamber method details		
13	Total Chamber Deployment Time	hours	1.00
14	Chamber volume to area ratio	cm	5
15	(enter 6 values to examine in rows	14 through 19)	10
16			15
17			20
18			25
19			30
20	3. Flux magnitude		
21		ug N/m2/h	100.00

Chamber Volume	3 sampling events			4 sampling events		
	Flux calculation Model			Flux calculation Model		
hours	Linear	HM	Quad	Linear	HM	Quadratic
5	-51%	-30%	-33%	-51%	n/a	-33%
10	-33%	-17%	-18%	-33%	n/a	-18%
15	-25%	-12%	-13%	-25%	n/a	-13%
20	-20%	-9%	-10%	-20%	n/a	-10%
25	-16%	-7%	-8%	-16%	n/a	-8%
30	-14%	-6%	-7%	-14%	n/a	-7%



Chamber Error Assessment Tool (CEAT): Determines the theoretical error for a given method

Example: Determine the theoretical 'worst-case' error for a given Deployment Time



Accuracy versus Precision

Why not use very low DP and very large H?   This should reduce RE.

1. Reduces the sensitivity (i.e., increases detection limit) of the measurement

2. Reduces the Precision of the measurement:

Inherent trade-off between Accuracy and Precision

Accuracy = the degree to which the result conforms to the correct or 'true' value

Precision = the degree to which repeated measurements under unchanged conditions show the same result (can also be described as sensitivity to measurement error)

Practices that Increase Accuracy tend to reduce Precision:
-decreasing DP
-increasing H
-using non-linear FC scheme instead of LR

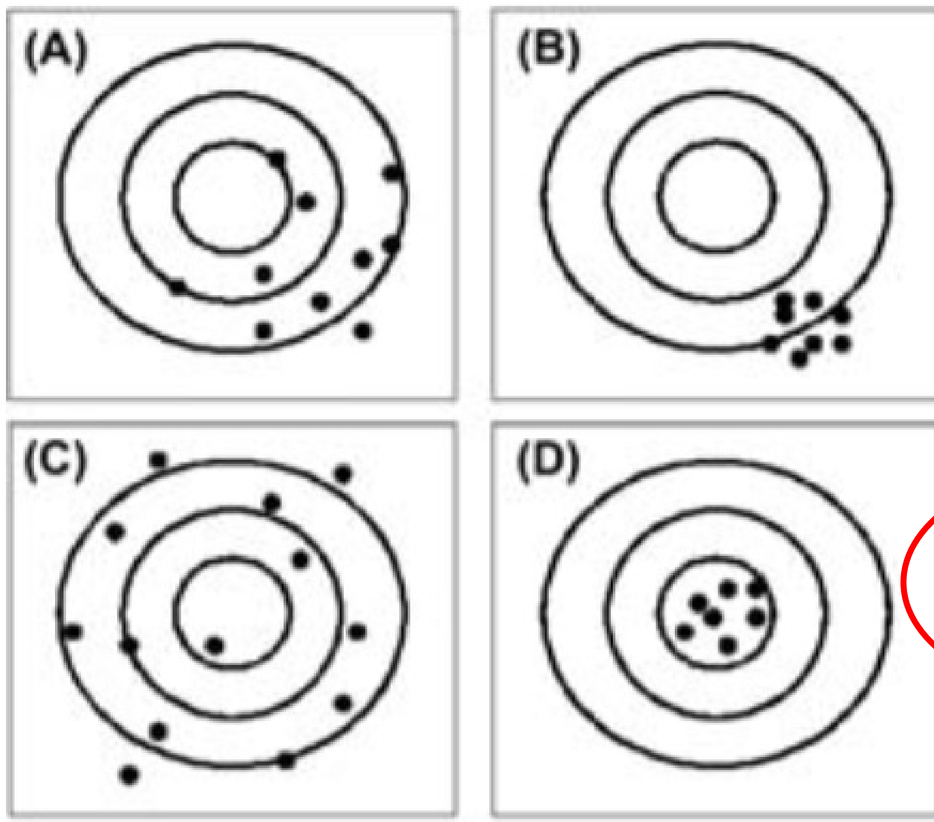
Accuracy versus Precision

Different non-linear FC schemes have differing degrees of both precision and accuracy:

What is the “best” method that balances higher accuracy with higher precision?

Low Accuracy
Low Precision

Low Accuracy
High Precision

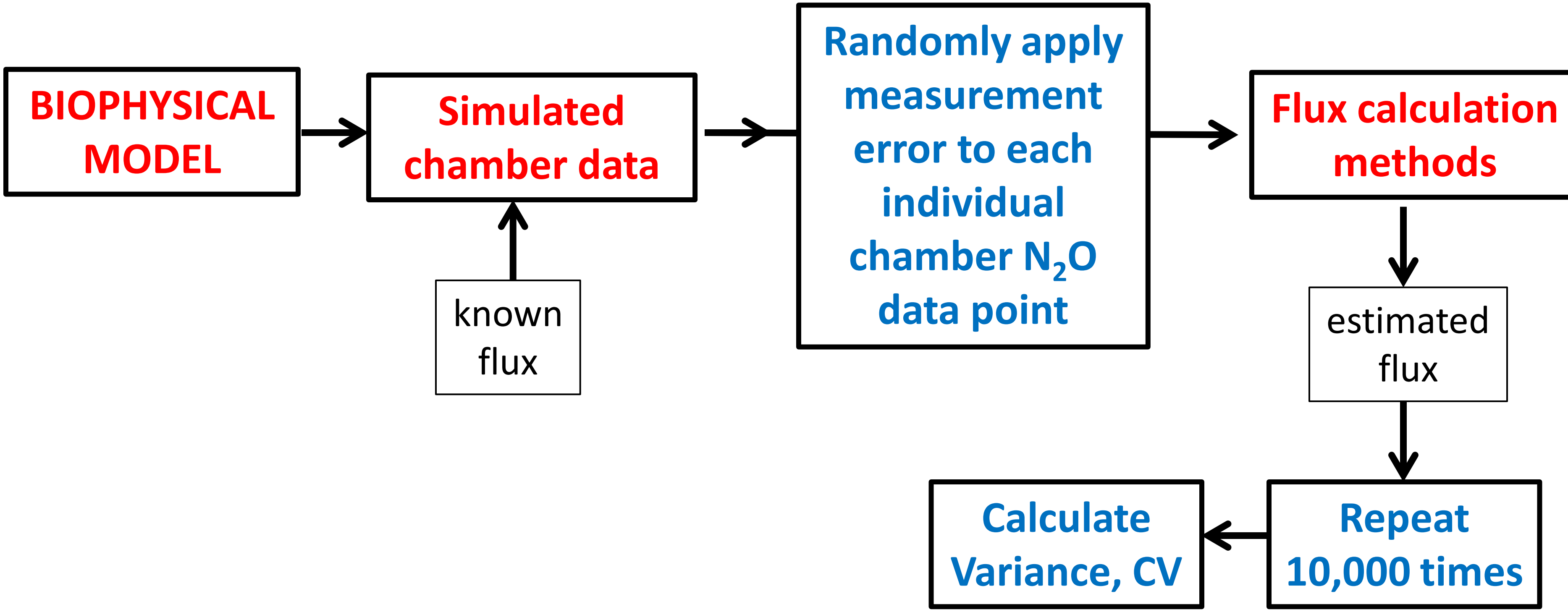


High Accuracy
Low Precision

High Accuracy
High Precision

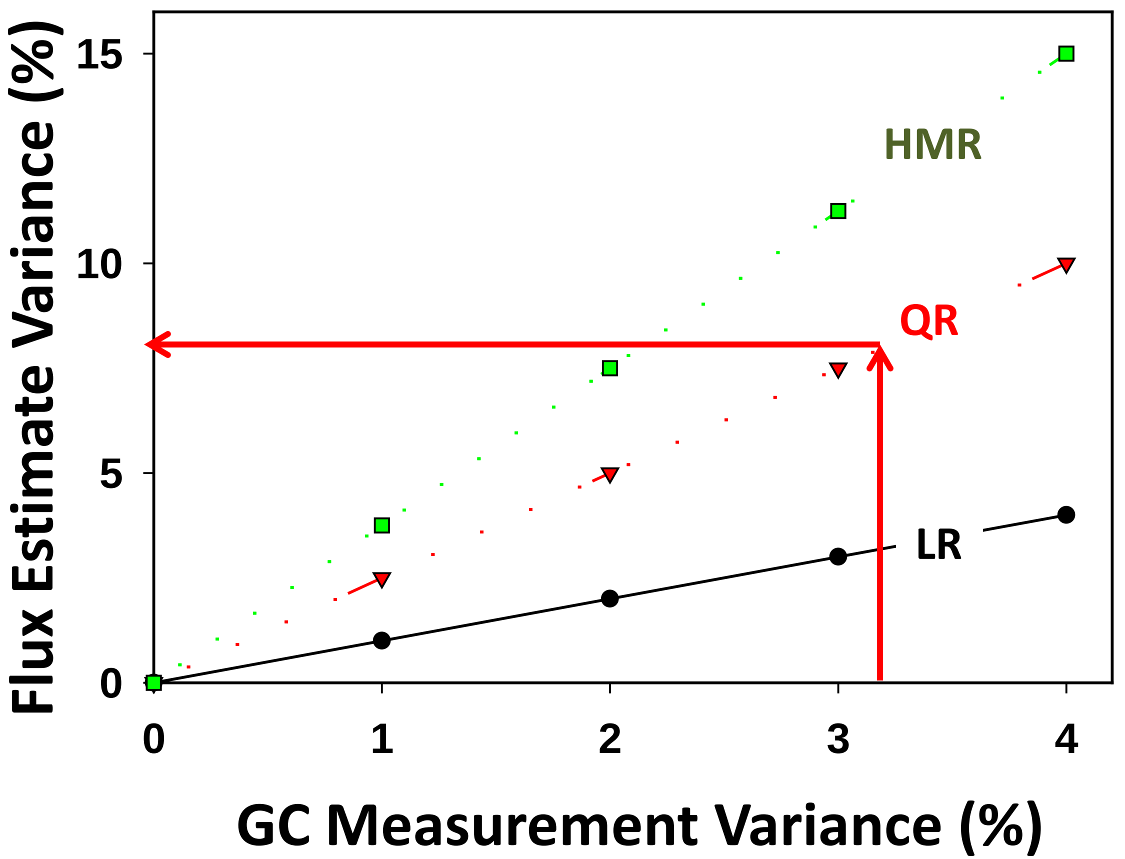
Venterea, R.T. and T.B. Parkin. 2012. Quantifying biases in non-steady state chamber measurements of soil-atmosphere gas exchange. In, Managing Agricultural Greenhouse Gases M. Liebig, et al. (Eds.). Elsevier.

Monte Carlo Analysis to Evaluate Precision



Venterea et al. 2009

Monte Carlo Analysis to Evaluate Precision



Translates GC imprecision into Flux imprecision

Determined by analyzing replicates of known standards

Each data point represents 10,000 Monte Carlo simulations

Accuracy versus Precision

What is the "best" method that balances higher accuracy with higher precision?

Not a clear winner

Accuracy (best to worst)

1. CBC
2. HMR
3. HM
4. QR
5. LR

Precision (best to worst)

1. LR
2. QR
3. CBC
4. HMR
5. HM

?????????????

Quantifying the optimum balance of Accuracy versus Precision

Mean Square Error (MSE) often used to determine the "best" model

MSE incorporates both the Bias (inverse of Accuracy) and Precision (Variance):

MSE = Variance + Bias^2

$$MSE = \frac{1}{n}\sum_{1}^{n}(F_{est} - F_0)^2$$

$$RMSE = \sqrt{MSE}$$

Criteria: Choose the method with the minimum MSE across a large number of measurements

Parkin, T.B., and R.T. Venterea. 2010. USDA-ARS GRACEnet Project Protocols, Chapter 3. Chamber-based trace gas flux measurements. In: Follett, R.F. (ed). Sampling Protocols. Beltsville, MD. p. 1-39.

Accuracy versus Precision

What is the “best” method that balances higher accuracy with higher precision?

Results of Monte Carlo-based MSE analysis (Parkin & Venterea, unpublished)

MSE (Best to Worst)

1. CBC
2. HMR
3. HM
4. QR
5. LR

Caveats:

1. If soil physical properties can be measured within +/- 25% of true value.
2. If horizontal diffusion is minimized by using adequate chamber insertion depth.
3. Otherwise, HMR is the best choice above CBC.

General Recommendations

Do some initial analysis to help in selecting a chamber design (DP, H) and FC method

1. Determine Method Detection Limit

-Parkin et al. 2012. J. Environ. Qual. 41(3):705-715.

-Requires quantification of precision of analytical instrument

-Enter different H and DP values into the spreadsheet and see how this affects MDL

-Determine what is acceptable MDL for your study

2. Use the Chamber Error Assessment Tool (CEAT):

-Assess the theoretical accuracy of your method for different H, DP and soil conditions

Our Approach (Venterea lab)

1. **Assume that non-linearity consistent with the chamber effect is the expected temporal pattern.**
- **Shown by diffusion modeling of many researchers assuming a variety of conditions**
- **Shown by majority of our data, esp. when fluxes are elevated above background**

2. **Use 4 sampling points**
- **Precision of a non-linear model is greatly reduced if only 3 points are used**
- **If there is one ‘bad’ data pt, throwing it out leaves 3 - more robust for LR than 2 pts**

3. Use the QR model as a first choice
- **QR is less sensitive than HM or HMR to measurement error-based imprecision**
- **QR is not restricted to 3 equally-spaced time points**
- **QR is spreadsheet friendly - can use LINEST in Excel with statistical output**

4. If horizontal diffusion is suspected (highly porous or rocky soils, shallow chamber insertion depth) – use HMR.
- **HMR accounts for horizontal diffusion better than any other method.**

Our Approach (Venterea lab)

5. Use LR if the data curvature is reversed ("upward" curvature)

- QR gives nonsensical result of having lower flux than LR under these conditions
- If flux is in fact increasing over time, LR gives more accurate flux –value averaged over the DP

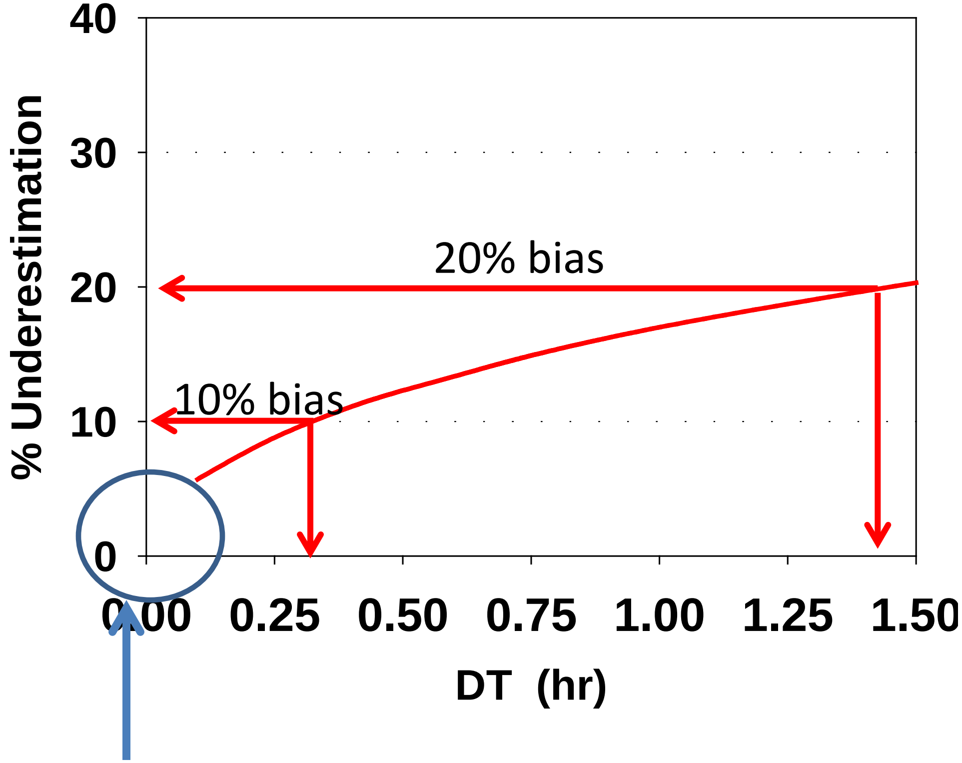
6. If accurate BD and SWC data content are available, apply the CBC method

- Yields flux value more consistent with diffusion theory than QR alone
- Reduces artifacts due to differences in physical properties between treatments or over time

7. If constraints do not allow for 4 sampling points, use LR and apply the CBC.

- LR reduces measurement-error based imprecision compared to non-linear models
- CBC reduces absolute errors, i.e. improve accuracy consistent with diffusion theory

Chamber Error Assessment Tool (CEAT): Determines the theoretical error for a given method



One potential solution: High-precision/high-frequency analyzers
Theoretical errors become marginal at short deployment periods