Energy research Centre of the Netherlands

Delft University of Technology

Calculation method of flux measurements by static chambers

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A NUMERICAL EVALUATION OF CHAMBER METHODS FOR DETERMINING GAS FLUXES

Allan D. Matthias, Douglas N. Yarger, and Robert S. Weinbeck

Departments of Agronomy and Earth Sciences, Iowa State University, Ames, Iowa, 50011

Abstract. Mathematical simulations of ni
oxide (N_2O) flux from homogeneous soil into a
surface chambers have been done for both a c
type of chamber in which soil air is statica
collected and an open type of chamber in whi
ambient air is dynamically drawn across the
surface. Results indicate that chamber-meas
fluxes over land surfaces may be subject to
siderable uncertainty, due in part to concen
tion gradient changes within the soil profil
that are a function of the type and the size
the chamber. Assessment of the uncertaintie
chamber flux determinations are reported. F
reasonable parameters closed-chamber flux va
may be underestimated by as much as 55%. Da
analysis procedures are described that can i
prove the flux estimates. Use of open chamb
may yield better flux estimates than closed
bers because of less disturbance to the natu
gas concentration profile within the soil.
application to N_2O flux measurements over wa
also is included.

Trace Gas Emission in Chambers: A Non-Steady-State Diffusion Model

Gerald P. Livingston,* Gordon L. Hutchinson, and Kevork Spartalian

ABSTRACT

Non-steady-state (NSS) chambers are widely u
gas emissions from the Earth's surface to the a
nately, traditional interpretations of time-depend
trations often systematically underestimate pred
rates because they do not accurately represent th
ics of diffusive soil gas transport that follows c
To address this issue, we formally derived a time
model applicable to NSS chamber observations
formance using simulated chamber headspace C
generated by an independent, three-dimensional
model. Using nonlinear regression to estimate th
we compared the performance of the non-stead
estimator (NDFE) to that of the linear, quadr
diffusion models that are widely cited in the liter
sensitivity to violation of the primary assumption
and addressed some of the practicalities of its
contrast to the other models, NDFE proved an
estimator of trace gas emissions across a wide r
design, and deployment scenarios.

CHAMBER MEASUREMENT OF SOIL-ATMOSPHERE GAS EXCHANGE: LINEAR VS. DIFFUSION-BASED FLUX MODELS

W. H. Anthony, G. L. Hutchinson,* and G. P. Livingston

We compared li
N_2O flux estimation
from a long-term s
sandy soil in southe
criteria established f
flux estimates that a
Although they repre
this group included
magnitude and dyna
263 fluxes >10 g N h
application of a line
represents a potenti
influence not only
larger scale budgets

Nutr Cycl Agroecosyst (2008) 82:175–186
DOI 10.1007/s10705-008-9179-x

RESEARCH ARTICLE

The importance of reducing the systematic error due to non-linearity in N_2O flux measurements by static chambers

P. S. Kroon · A. Hensen
P. A. C. Jongejan · A. T

Biogeosciences, 4, 1005–1025, 2007
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Biogeosciences

CO_2 flux determination by closed-chamber methods can be seriously biased by inappropriate application of linear regression

L. Kutzbach[1], J. Schneider[1], T. Sachs[2], M. Giebels[3], H. Nykänen[4], N. J. Shurpali[4], P. J. Martikainen[4], J. Alm[5], and M. Wilmking[1]

VOL. 5, NO. 9 GEOPHYSICAL RESEARCH LETTERS SEPTEMBER 1978

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Allan D. Matthias, Douglas N. Yarger, and Robert S. Weinbeck

Departments of Agronomy and Earth Sciences, Iowa State University, Ames, Iowa, 50011

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FLUX MODELS

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Biogeosciences

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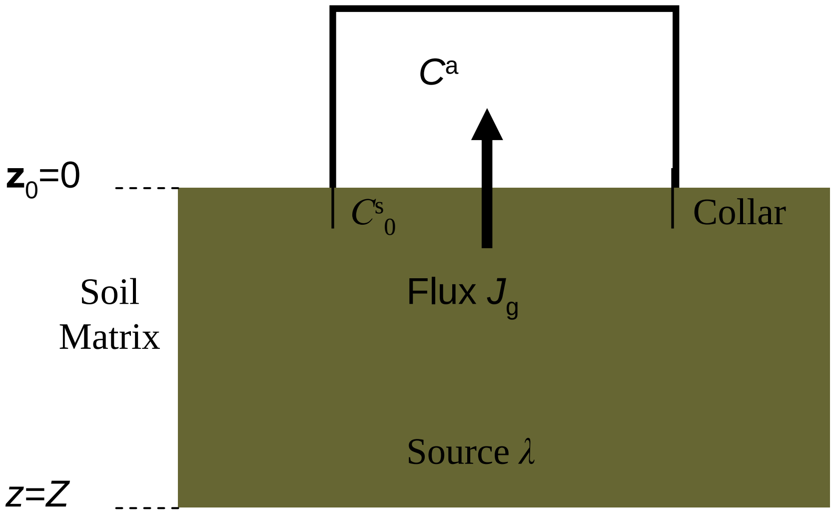
Outline

- Theoretical models
- Simplified models
- Comparison of the models
- Arguments for linear model
- Quality of chamber calculation methods
- Summary and recommendations

Theoretical models



1D diffusion equation

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2} + \lambda(z)$$

Mass balance

$$F_c = \frac{V}{A}\frac{dC^a}{dt}\bigg|_{t=0}$$

Researcher	C^a	C^s_0	J_g	λ
De Mello and Hines (1994)	$C^a(0)=C_{air}$	Constant	J_g(t)	Constant
Gao et al. (1998)	$C^a(0)=0$	Constant	J_g(t)	Constant
Conen and Smith (2000)	$C^a(0)=C_{air}$	C^s_0(t)	J_g(t)	Constant
Livingston et al. (2006)	$C^a(t)=C^s_0(t)$ $C^a(0)=C^s_0(0)$	C^s_0(t)	J_g(t)	λ(z)

Theoretical models

De Mello and Hines (1994), JGR

$$C^a(t) = C_0^s - (C_0^s - C_{t=0}^a)\exp\left(-\frac{h_{tc}}{V/A}t\right)$$

$$J_g(t) = h_{tc}\left(C_0^s - C_{t=0}^a\right)\exp\left(-\frac{h_{tc}}{V/A}t\right)$$

$$F_c = J_g(0) = h\frac{dC^a}{dt}\bigg|_{t=0}$$

$$F_c = h_{tc}\left(C_0^s - C_{t=0}^a\right)$$

Gao and Yates (1998), JGR

$$C^a(t) = C_0^s\left[1 - \exp\left(-\frac{h_{tc}}{V/A}t\right)\right]$$

$$J_g(t) = h_{tc}C_0^s\exp\left(-\frac{h_{tc}}{V/A}t\right)$$

$$F_c = J_g(0) = h\frac{dC^a}{dt}\bigg|_{t=0}$$

$$F_c = h_{tc}C_0^s$$

With $h_{tc} = \frac{\theta D}{h}$

$\theta \Rightarrow \frac{\text{m}^3\text{ air}}{\text{m}^3\text{ soil}}$

Theoretical models

General behaviour of models based on Gao and Yates (1998) and De Mello and Hines (1994)

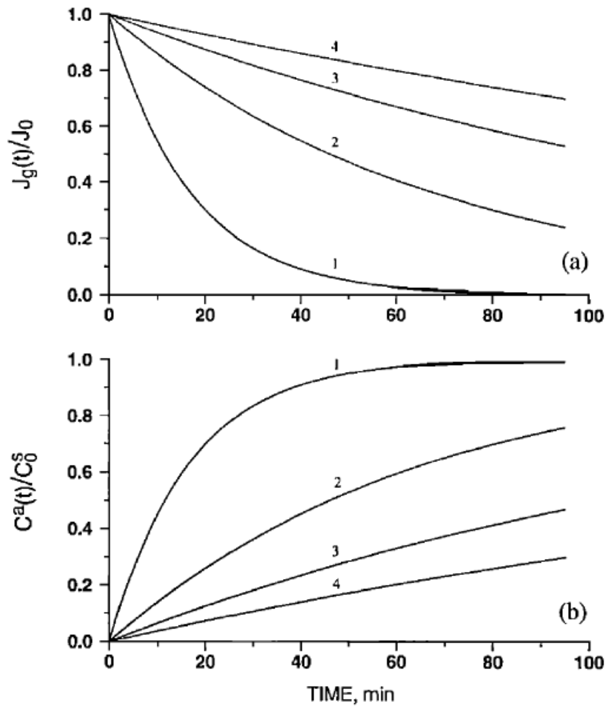


Figure 3. Behavior of shallow closed chamber with different *V*/*A* ratio (*H*). For curves 1, 2, 3, and 4 in the figure the *V*/*A* ratios are 10, 20, 30, and 40 cm, respectively.

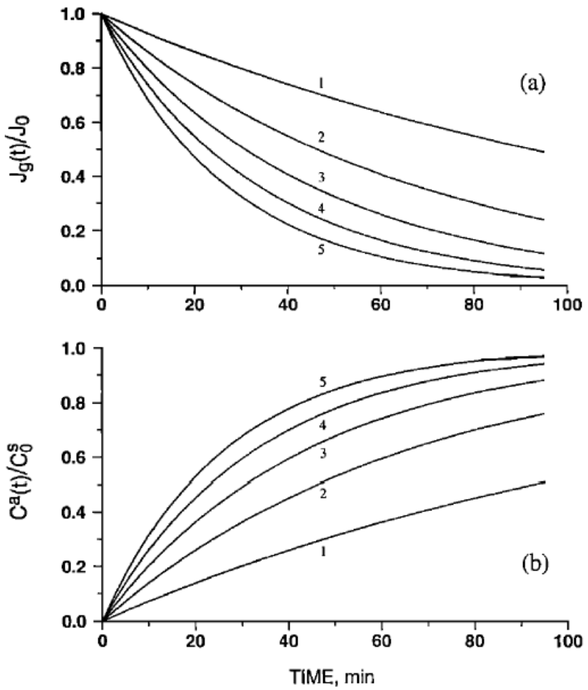


Figure 4. Behavior of a closed chamber with a *V*/*A* ratio of 20 cm when measuring gases with different D^a. For curves 1, 2, 3, 4, and 5 the D^a values are 0.05, 0.10, 0.15, 0.20, and 0.25 cm^2 s^{-1}, respectively.

Gao and Yates (1998)

Theoretical models

General behaviour of models based on Gao and Yates (1998) and De Mello and Hines (1994)

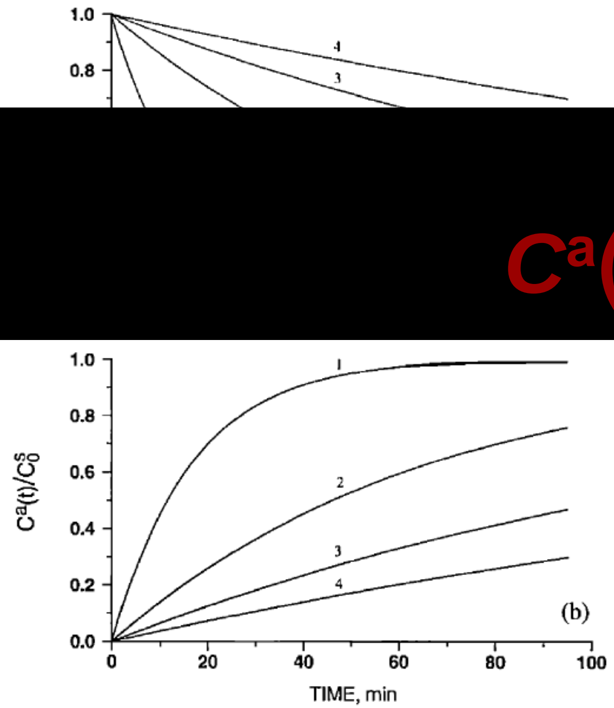
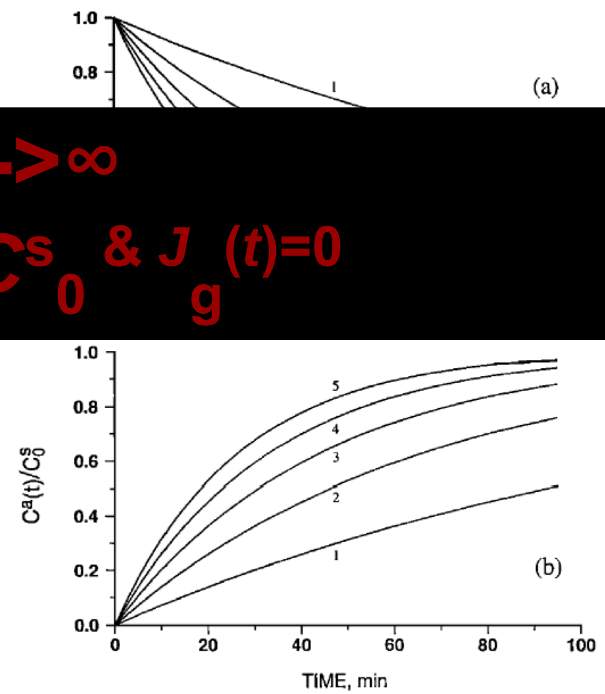


Figure 3. Behavior of shallow closed chamber with different V/A ratio (H). For curves 1, 2, 3, and 4 in the figure the V/A ratios are 10, 20, 30, and 40 cm, respectively.



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$$t \to \infty$$

$$C^a(t) = C^s_0 \;\&\; J_g(t) = 0$$

Gao and Yates (1998)

Theoretical models

Conen and Smith (2000),
European Journal of Soil Science

Researcher	C^a	C^s_0	J_g	λ
De Mello (1994)	$C^a(0)=C_{air}$	Constant	$J_g(t)$	Constant
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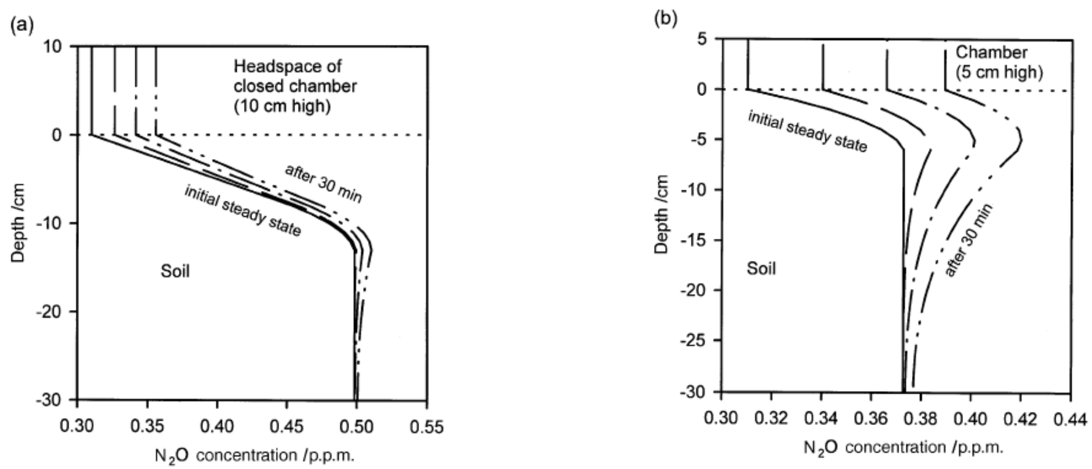

Figure 2 Development of N_2O concentration profiles in a soil with 20% air porosity, diffusivity of 1.673×10^{-6} $m^2 s^{-1}$, and initially steady-state concentrations at time 0 (continuous line). (a) The N_2O source (12 μg N_2O-N $m^{-2} h^{-1}$) is evenly distributed between 8 and 13 cm depth and the soil is covered with a 10-cm-high chamber. (b) The N_2O source (12 μg N_2O-N $m^{-2} h^{-1}$) is evenly distributed between 0 and 5 cm depth and the soil is covered with a 5-cm-high chamber. As concentrations increase within the headspace of the chamber, they also increase within the entire soil profile. Profiles are shown for 10 min (line with no short dashes), 20 min (line with one short dash), and 30 min (line with two short dashes) after chamber closure.

Theoretical models

Conen and Smith (2000),
European Journal of Soil Science

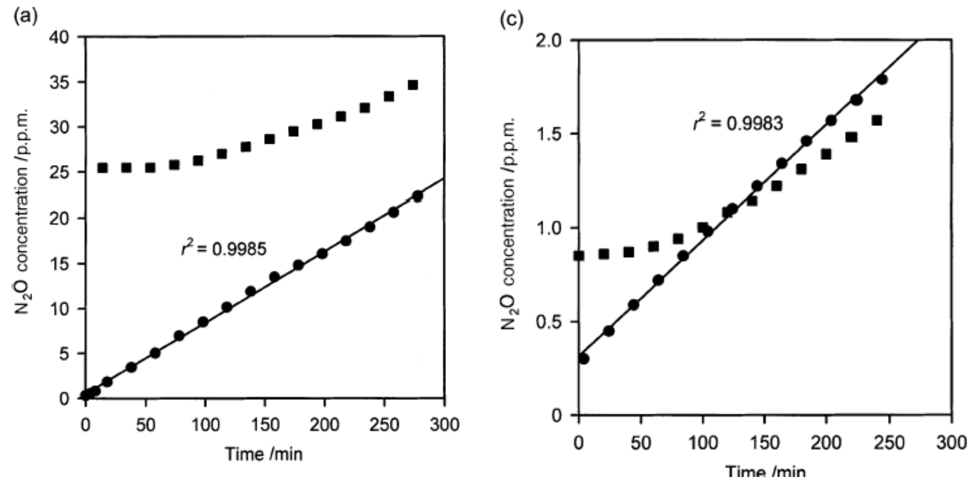

Figure 3 Measured changes in N_2O concentrations below the source of N_2O production (■) and in the headspace (●) of soil core for (a) wet core with low air-filled porosity; (b) core at intermediate air-filled porosity; (c) relatively dry soil core. A linear regression (continuous line) has been fitted to the headspace concentration over time.

Theoretical models

Conen and Smith (2000),
European Journal of Soil Science

$$J_g(t) = h_{tc}\left(C_0^s(t) - C^a(t)\right)$$

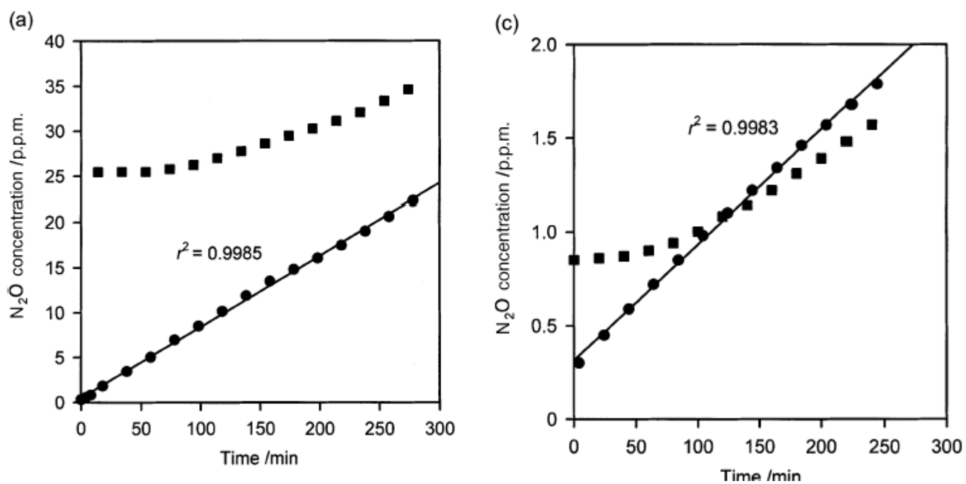

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Table 1 Linearity and proportion of total net N_2O production (J_m) measured with chambers of different height and on soils with different air porosity and a total depth of 30 cm

θ /%	D /$m^2 s^{-1} \times 10^{-6}$	Chamber height /cm	r^{2} [a]	J_m /%
20	1.673	5	0.9978	72
20	1.673	10	0.9994	84
20	1.673	20	0.9998	92
20	1.673	30	0.9999	94
10	0.664	5	0.9995	86
10	0.664	10	0.9999	93
10	0.664	20	1	96
10	0.664	30	1	97
5	0.264	5	0.9999	93
5	0.264	10	1	97
5	0.264	20	1	98
5	0.264	30	1	99

[a] Of linear regression; concentration over time.

Theoretical models

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European Journal of Soil Science

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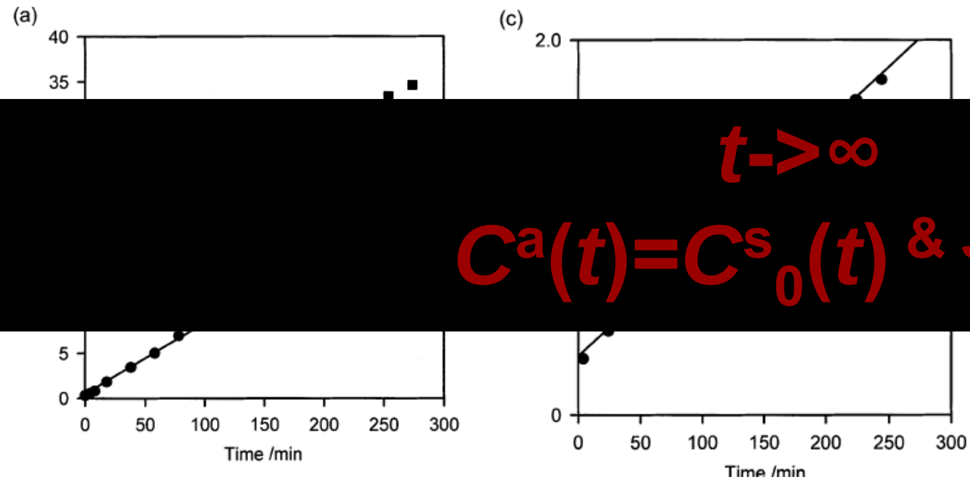

$t \to \infty$

$C^a(t) = C^s_0(t)$ & $J_g(t) = 0$

Figure 3 Measured changes in N_2O concentrations below the source of N_2O production (■) and in the headspace (●) of soil core for (a) wet core with low air-filled porosity; (b) core at intermediate air-filled porosity; (c) relatively dry soil core. A linear regression (continuous line) has been fitted to the headspace concentration over time.

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Theoretical models

Livingston et al. (2006), Soil science society of America journal

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$$C^a(t) = C^a_{t=0} + J_o \tau \left(\frac{A}{V}\right)\left[\frac{2}{\sqrt{\pi}}\sqrt{t/\tau} + e^{t/\tau}\,\mathrm{erfc}\left(\sqrt{t/\tau}\right) - 1\right]$$

$$\tau = \frac{(V/A)}{h_{tc}}$$

Theoretical models

Differences in theoretical models:

- Assumptions -> different equations for $C^a(t)$ and $J_g(t)$

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Livingston et al. (2006)	$C^a(t)=C^s_0(t)$ $C^a(0)=C^s_0(0)$	$C^s_0(t)$	$J_g(t)$	$\lambda(z)$

Similarity in theoretical models:

- $J_g(t)$ is not constant
- No leakage taken into account
- No vegetation taken into account

Theoretical models

Kutzbach et al. (2007), Biogeosciences:

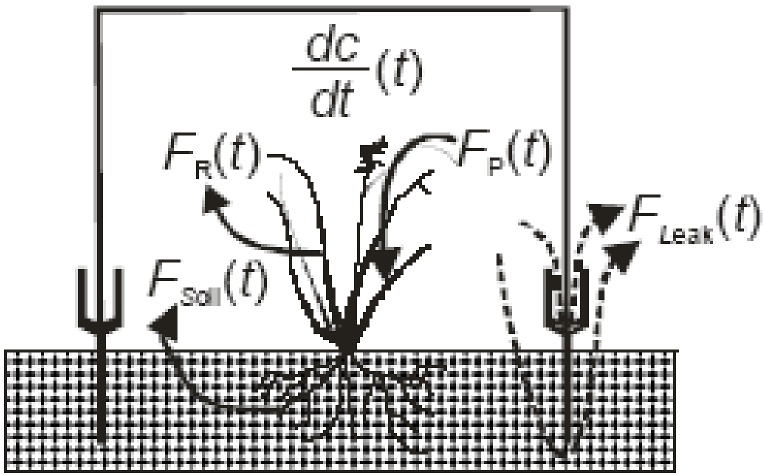

Fig. 1. Schematic of the CO_2 fluxes in the chamber headspace which make up to the net CO_2 flux F_{net} (details in the text, Eq. (1)). $F_{Soil}(t)$ is the diffusive efflux from the soil, $F_P(t)$ is photosynthesis, $F_R(t)$ is aboveground plant respiration, $F_{Leak}(t)$ is leak flux. $dc/dt(t)$ is the CO_2 concentration change over time t in the chamber headspace.

$$F_c(t) = F_{soil}(t) + F_p(t) + F_R(t) + F_{\mathrm{Leak}}(t)$$

$$c(t) = f_{\exp}(t) + \varepsilon(t) = p_1 + p_2 \exp(p_3 t) + \varepsilon(t)$$

$$F_c(0) = \frac{V}{A}\frac{dC}{dt}\bigg|_{t=0} = \frac{V}{A} p_2 p_3$$

$$p_2 = B$$

$$p_3 = \left(-\frac{D}{d} + k_p - K_{\mathrm{Leak}}\right)$$

Simplified models

Linear model:

(e.g. Ruser et al. 1998; Hendriks et al. 2007)

$$c(t) = f_{lin}(t) + \varepsilon(t) = a + bt + \varepsilon(t)$$

Quadratic model:

(e.g. Wagner et al. 1997)

$$c(t) = f_{\text{qua}}(t) + \varepsilon(t) = a + bt + ct^2 + \varepsilon(t)$$

$$F_c = \frac{V}{A}\frac{dC^a}{dt}\bigg|_{t=0}$$

H-M model:

(e.g. Hutchinson and Mosier, 1984)

$$F_c = \frac{V(C_1 - C_0)^2}{A(t_1 - t_0)(2C_1 - C_2 - C_0)} \ln\left[\frac{C_1 - C_0}{C_2 - C_1}\right]$$

for $t_2 = t_1$ and $\frac{C_1 - C_0}{C_2 - C_1} > 1$

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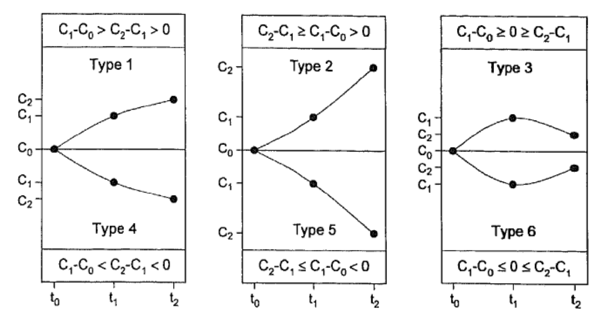


Fig. 1. The defining inequality and an example of each of the six possible curve shapes for N_2O accumulation in a non-steady-state chamber during two successive equal periods beginning with chamber deployment.

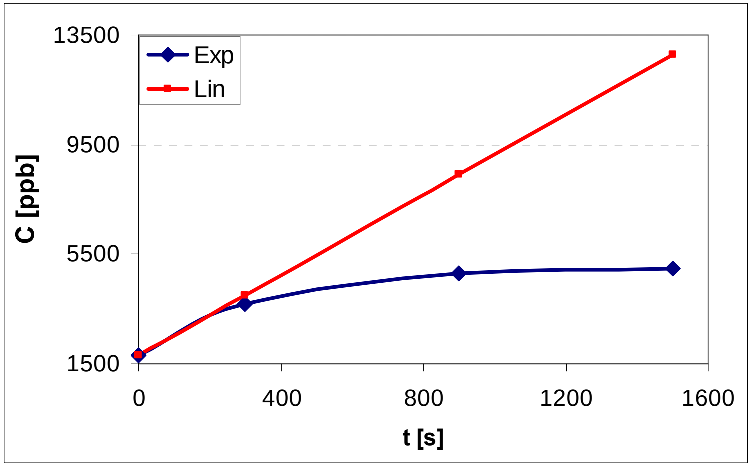
Anthony et al. (1995)

Simplified models

Slope-intercept model:

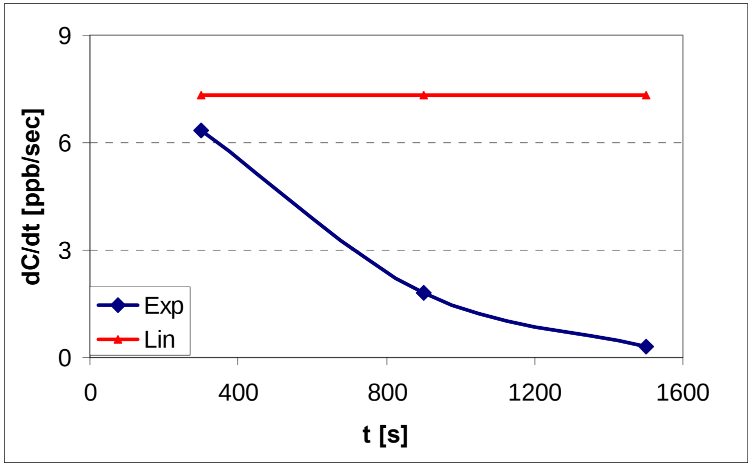
(Kroon et al. 2008)

$$\left.\frac{dC}{dt}\right|_{\mathrm{i}} = \frac{C_{\mathrm{i}} - C_{\mathrm{i-1}}}{t_{\mathrm{i}} - t_{\mathrm{i-1}}} \quad \mathrm{i} = 1,2,..,\mathrm{N}-1$$



$$J_g(t) = h.\left(f_{lin}(t) + \varepsilon(t)\right) = h.\left(a + bt + \varepsilon(t)\right)$$

$$F_c = J_g(0) = h.a$$



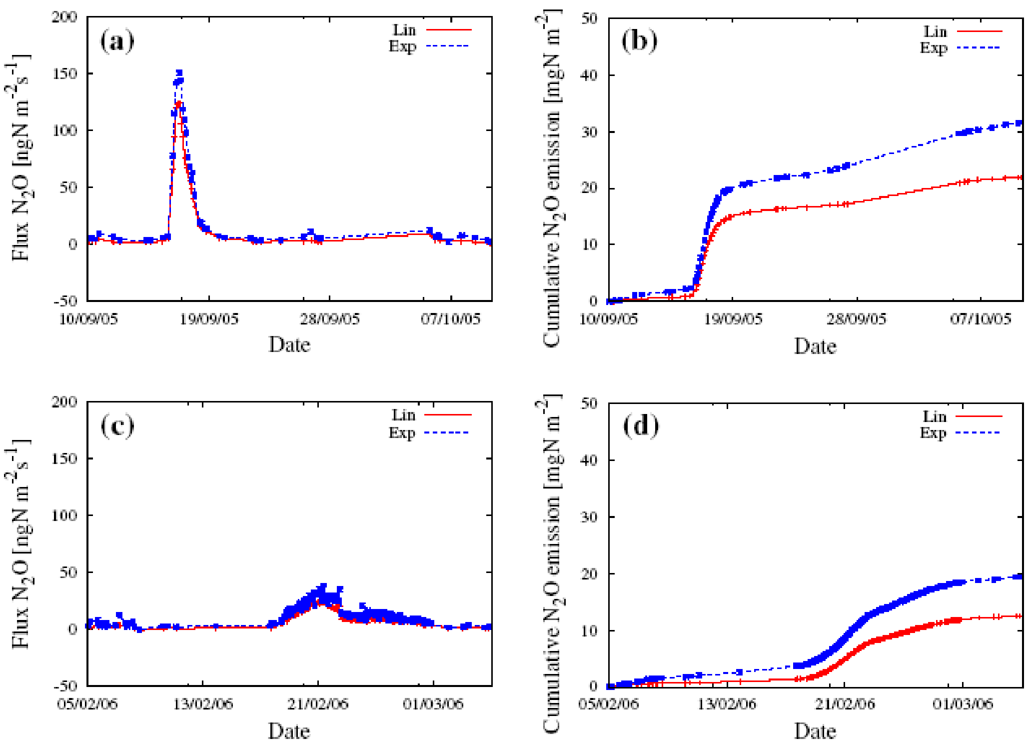
Comparison of the models

Linear **versus** De Mello and Hines (1994)

$$c^a(t) = a + bt$$

$$C^a(t) = C_0^s - (C_0^s - C_{t=0}^a)\exp\left(-\frac{h_{tc}}{V/A}t\right)$$

Based on measurements at Cabauw in the Netherlands



Cum(Lin)/Cum(Exp):

69% and 63%

Kroon et al. (2008)

Comparison of the models

Linear versus Conen and Smith (2000)

$$c^a(t) = a + bt$$

$$C_i = C_{i-1} + \frac{J_{i-1}A}{V} + C_p$$

Based on model

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[a] Of linear regression; concentration over time.

(Lin flux)/(Real flux) range: 72% and 99%

Conen and Smith (2000)

Comparison of the models

Intercept versus De Mello and Hines (1994)

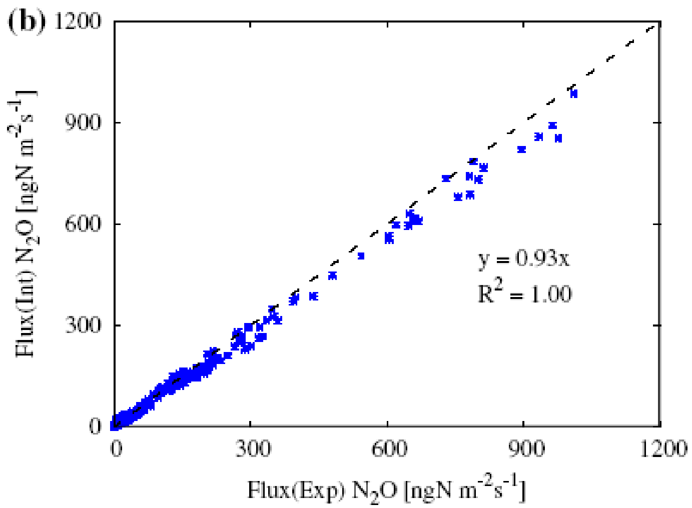
$$\left.\frac{dC}{dt}\right|_{\mathrm{i}} = \frac{C_{\mathrm{i}} - C_{\mathrm{i-1}}}{t_{\mathrm{i}} - t_{\mathrm{i-1}}} \quad \mathrm{i} = 1,2,..,\mathrm{N}-1$$

$$F_c = J_g(0) = h.(a + b.0)$$

$$C^a(t) = C_0^s - (C_0^s - C_{t=0}^a)\exp\left(-\frac{h_{tc}}{V/A}t\right)$$

$$F_c = J_g(0) = h\left.\frac{dC^a}{dt}\right|_{t=0}$$

Based on measurements at Cabauw in the Netherlands



Kroon et al. (2008)

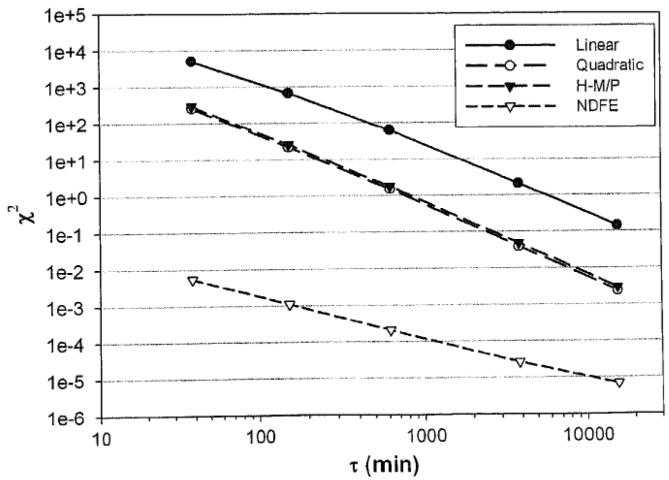
Comparison of the models

What's the most accurate model?

- Determination by goodness-of-fit analyses

$$\chi^2 = \sum_{i=1}^{N} (y_i - \hat{y}_i)^2$$

Livingston et al. (2006)



Flux difference dependent on: $\tau = \dfrac{(V/A)}{h_{tc}}$

Kroon et al. (2008)

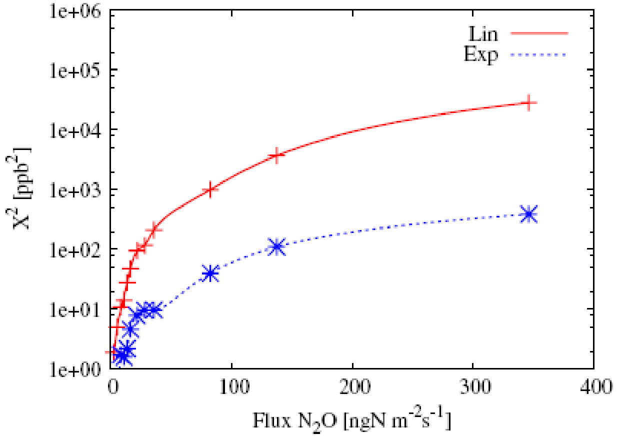


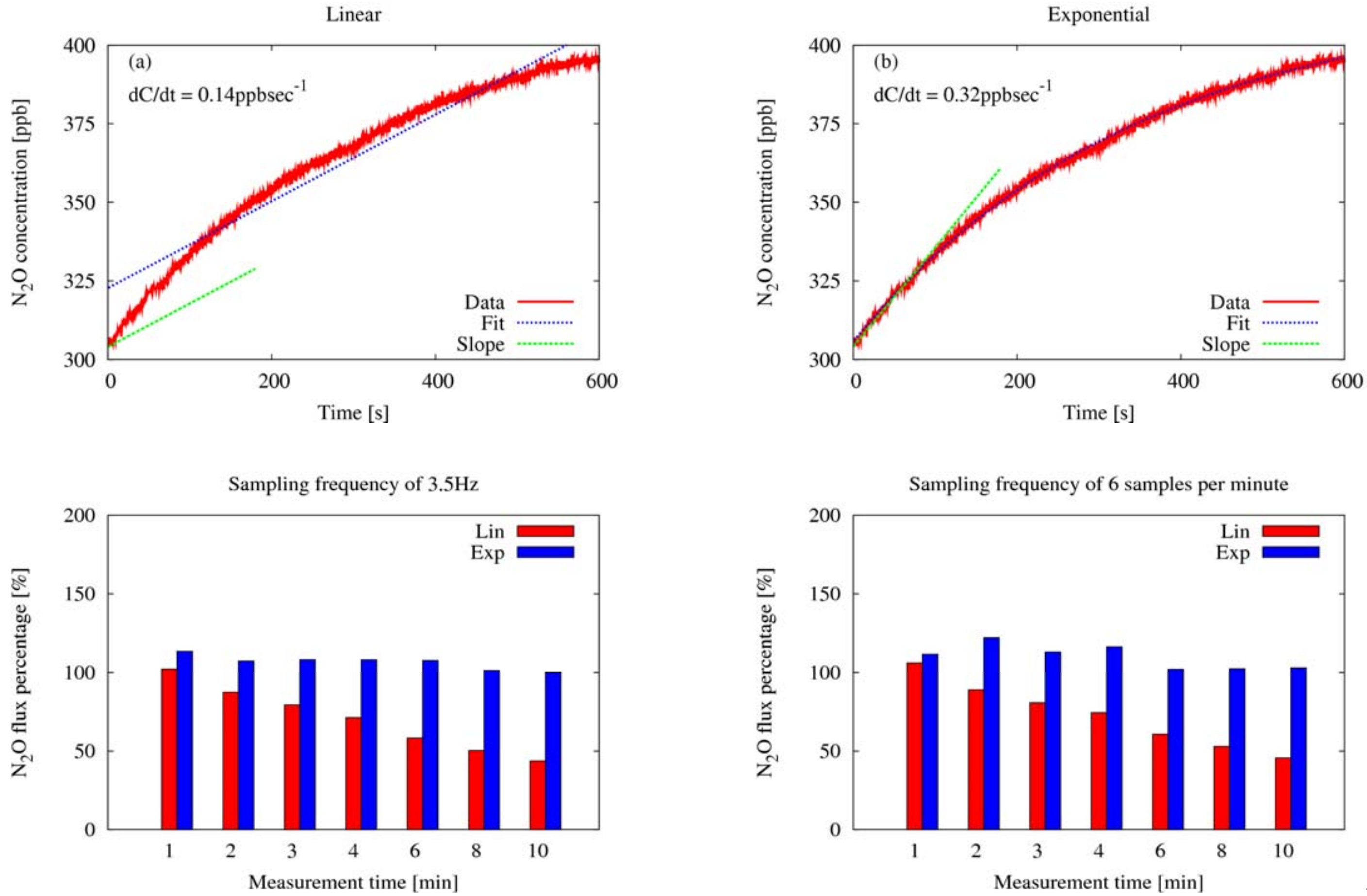
Fig. 7 Goodness-of-fit (χ^2) of linear and exponential regression method to N_2O automatic chamber measurements as a function of the N_2O flux. Data points represent the average goodness-of-fit and average N_2O flux over a bin including hundred N_2O fluxes

Why do most of the people still use a linear regression?

Possible reasons:

- Assumption that conentration behaviour is linear over short measurement times.
- Assumption that non-linear concentration behaviour can only be caused by leakage.
- Assumption that uncertainty due to spatial and temporal variation is much larger than the biases due to linear regression.

Assumption I:
Short measurement times



Kroon et al. (2008)

Assumption II:
Non-linearity can only occur due to leakage

Based on theoretical Gao model without leakage

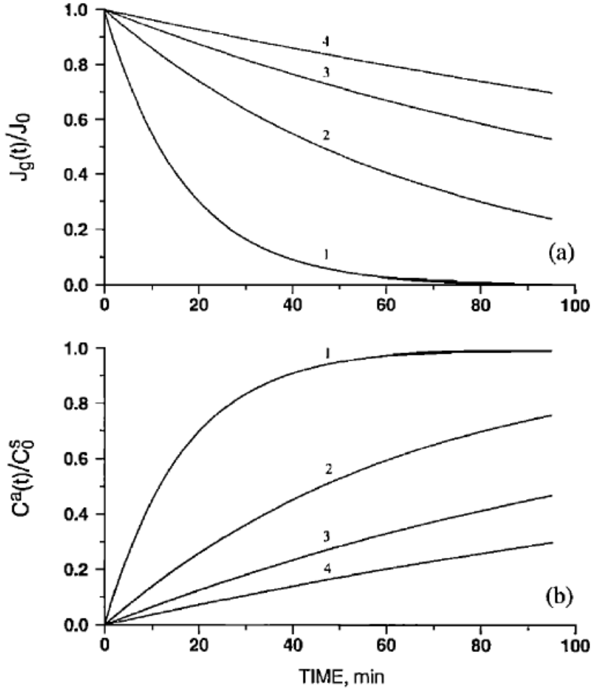


Figure 3. Behavior of shallow closed chamber with different V/A ratio (H). For curves 1, 2, 3, and 4 in the figure the V/A ratios are 10, 20, 30, and 40 cm, respectively.

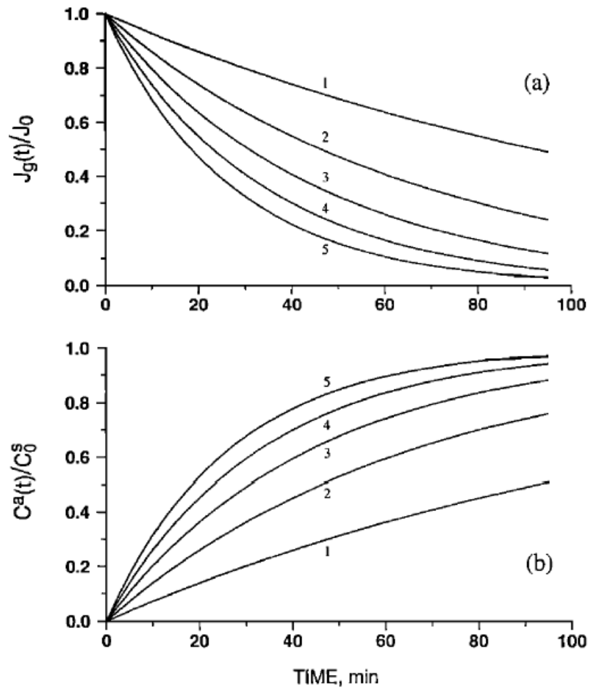
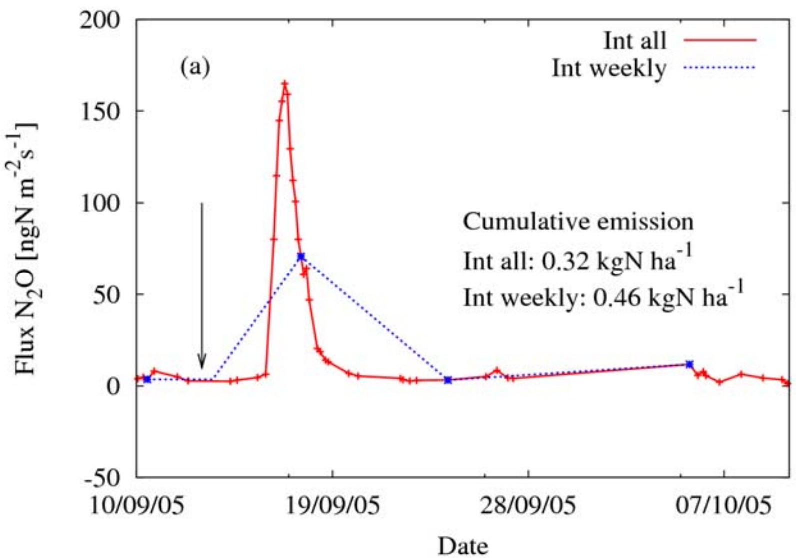


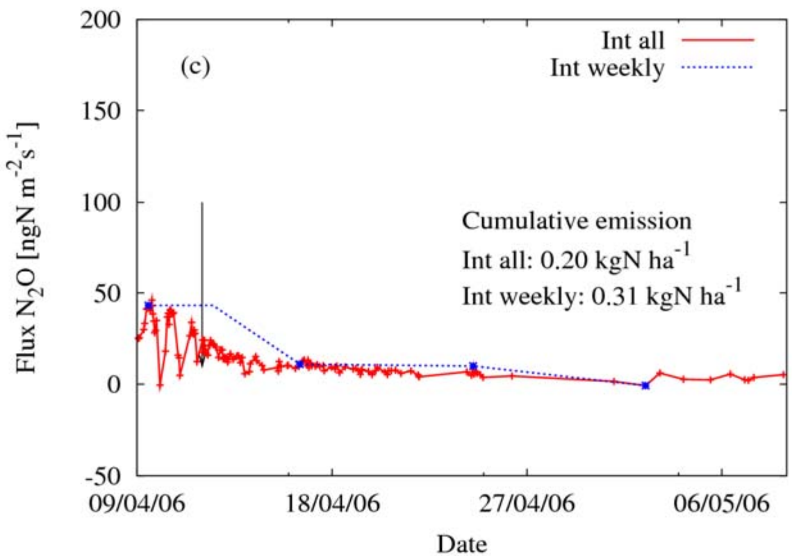
Figure 4. Behavior of a closed chamber with a V/A ratio of 20 cm when measuring gases with different D^a. For curves 1, 2, 3, 4, and 5 the D^a values are 0.05, 0.10, 0.15, 0.20, and 0.25 cm^2 s^{-1}, respectively.

Gao and Yates (1998)

Assumption III:

Uncertainty due to spatial and temporal variation is much larger than biases due to linear regression





Why do most of the people still use a linear regression?

Possible reasons:

- Assumption that conentration behaviour is linear over short measurement times

Assumptions are not definitely truth!

caused by leakage.

- Assumption that uncertainty due to spatial and temporal variation is much larger than the biases due to linear regression.

Quality of chamber calculation methods

Rochette and Eriksen-Hamel (2008)

Table 1. Score assigned to each characteristic of non-flow-through, non-steady-state chamber design and deployment. The importance (score) of each characteristic to the quality of N_2O emission data is based on estimated impact of each characteristic on the measurement error.

Chamber characteristics	Symbol	Unit	Very poor (0)	Poor (1)	Good (2)	Very good (3)
			Binary and Non-numerical Characteristics			
Type of chamber	*c*			push-in		base and chamber
Insulation	*i*			no		yes
Vent	*v*			no		yes
Pressurized sample (fixed-volume container only)	*p*			no		yes
Quality control sample	qc		no			yes
Time zero sample taken	t_0			no		yes
Nonlinear model considered	nl		no			yes
Zero slope tested	*z*			no	yes	
Temperature corrections	tc			no		yes
Type of sample vial	*s*		plastic syringe	glass syringe	all other vials	exetainers, vacutainers, Al tubes, gas chromatography in the field, photoacoustic
			Numerical Characteristics			
Height of chamber	*h*	cm h^{-1}	<10	10 to <20	20 to <40	≥40
Chamber base insertion†	d	cm h^{-1}	<5	5 to <8	8 to <12	≥12
Area/perimeter ratio	ap	cm	<2.5	2.6 to <6.25	6.26 to <10	≥10
Duration of deployment	t	min	>60	>40–60	>20–40	≤20
Number of samples	n	no.	1	2	3	>3
Duration of sample storage: plastic syringe	y	d	>2	1–2	<1	
Duration of sample storage: glass syringe	y	d	>4	>2–4	1–2	<1
Duration of sample storage: other	y	d	>90	>45–90	>15–45	≤15

† Chamber base insertion in ecosystems with saturated soil conditions such as paddy rice and natural wet ecosystems is assumed as "very good".

Quality chamber calculation methods

Rochette and Eriksen-Hamel (2008)

Time interval	Studies (*n*)	Base & chamber	Insulation	Vent	Pressurized sample†	Quality control sample tested	Sample taken at time zero	Nonlinear model tested	Zero slope tested	Temperature corrections	Quality of sample vial‡				
											No info	0	1	2	3
		%§													
1978–1989	34	85	56	56	13 (*n* = 8)	21	74	15	0	35	15	38	15	21	12
1990–1994	28	71	36	43	25 (*n* = 12)	14	61	7	4	21	14	39	0	18	29
1995–1999	102	94	57	52	29 (*n* = 51)	13	56	12	4	25	15	25	4	29	26
2000–2004	127	91	46	44	27 (*n* = 51)	20	72	17	7	36	8	34	2	24	32
2005–2007	65	95	46	48	62 (*n* = 37)	20	71	25	12	46	6	22	0	37	35
All studies	356	90	49	48	35 (*n* = 159)	17	66	16	6	33	11	30	3	27	29

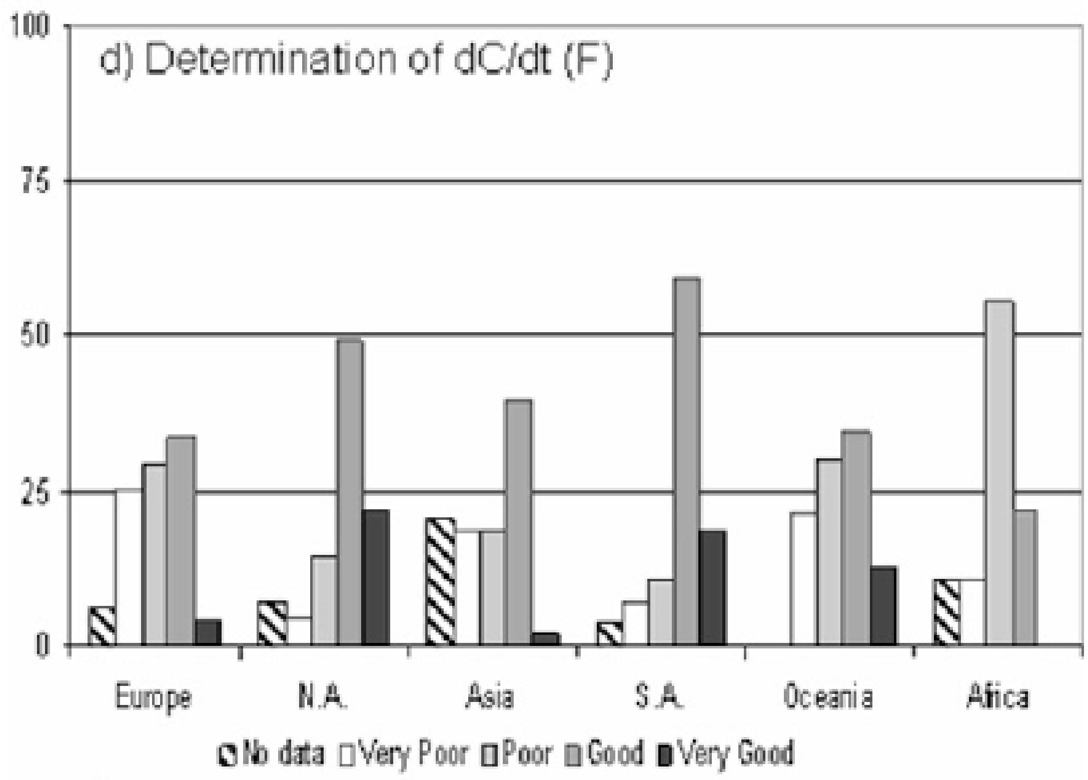
† Fixed-volume containers only.

‡ The quality of each type of sample vial is reported as very poor (0), poor (1), good (2), or very good (3).

§ Percentages are reported on the number of studies (*n*) in each time interval except where indicated.

Quality chamber calculation methods

Rochette and Eriksen-Hamel (2008)



Summary

- There are several studies given in the literature for calculating fluxes by static chambers. They are based on the mass equation and diffusion equation. The models are based on different assumptions. However, they all indicate that the fluxes are not constant.

- The concentration behaviour is dependent on the height of the chamber and the air filled porosity. Underestimation increases with decreasing height and increasing air filled porosity.

- There are several simplified models for calculating fluxes by static chambers, like quadratic, linear and H-M model. These simplified models underestimate the flux. The amount of underestimation can be more than 40%.

Summary

- The linear method underestimate the flux even for short measurement times and without leakage of the chamber.

- Using an incorrect method lead to a systematic underestimation which is very significant even in comparison with the spatial and temporal variation.

- The quality of the flux estimation is dependent on the used model, the amount of measurement points and measurement time.

Recommendations

- A non-linear method should be used.

  Compare different non-linear methods using a goodness-of-fit analyses to choose the most appropriate method.

Method	**References**	**Model available online**
Exp1	De Mello and Hines (1994)	
Exp2	Gao et al. (1998)	
Exp3	Kutzbach et al. (2007)	X*
NDFE	Livingston et al. (2006)	X**
Slope intercept	Kroon et al. (2008)	

- Amount of measurement points should be at least 3.

- The height of the chamber should be at least 40 $cmhr^{-1}$.

*http://biogeo.botanik.uni-greifswald.de/index.php?id=264 (Lin&Non-linear)

**http://arsagsoftware.ars.usda.gov (Excell comparison Lin,Qua&NDFE)

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Calculation method of flux measurements by static chambers

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