Gas flux calculations from chamber data

Annika Nordbo, Janne F.J. Korhonen, Antti-Jussi Kieloaho

August 31, 2010

This document includes the equations used in a Matlab script ChamFlux.m, which is used for calculating fluxes from chamber gas concentration measurements. Five different methods (linear, quadratic, Livingston, intercept, exponential) are used for making a fit to the measured concentrations as a function of time. All of the fits except the Livingston give the time derivative of the concentration from which the flux is eventually calculated. The time derivative at closure (t=0) is used so that the flux represents an undisturbed environment. Livingston fit gives the flux directly.

About the methods: The chamber measurement inherently disturbs the flux. The purpose of the flux calculation is usually not to calculate how much there was gas exchange during the measurement. Instead, the purpose is to calculate UNDISTURBED flux: the flux that would have been there without the chamber, or even further to quantify the processes behind the fluxes. The undisturbed flux is often estimated by calculating the flux at the moment of the closure, when the effect due to gas saturation is the lowest. We call linear, exponential and NDFE (Livingston) functions models, because they are based on physics and in the latter two the flux at the closure is actually modelled.

In mechanistic point of view, by using the linear model one assumes that 1-dimensional concentration gradient between the source/sink and atmosphere does not change during the measurement (Fick's first law). This applies when the measurement period is very short.

The exponential model takes into account that the 1-dimensional concentration gradient changes during the measurement between the source/sink and the atmosphere. The NDFE (Livingston et al.) model also takes into account that the concentration at the source/sink changes in time.

All the three models assume that the gas transport is driven by diffusion. Any of the three models do not take into account the horizontal gas gradient in the soil. This is not important if the characteristic diameter of the chamber is much larger than the effective depth of gas source/sink.

None of the models take into account the gas diffusion from/to source/sink to another direction than to the atmosphere.

Quadratic function and NDFE method are not based on physics. They are have been established for practical reasons.

Exponential, linear and quadratic fits

As an example of a plant leaf closure, in wide form the exponential equation is derived in the following.

$$V\frac{dC(t)}{dt} = \underbrace{q(C_a - C(t))}_{\text{air flow through the couvette}} + \underbrace{A_l g(C_i - C(t))}_{\text{gas to the stomata}} - \underbrace{A_c k C(t)}_{\text{reactions with the couvette walls}}$$

V = chamber volume [m^3]
C(t) = concentration in the chamber
q = volume flow rate [m^3/s]
C_a = concentration in the air
A_l = leaf or soil surface area [m^2]
g = stomatal conductance/transport coefficient [m/s]
C_i = concentration inside the stomata/in soil
A_c = chamber wall area [m^2]
k = reaction unit [m/s]

$$\frac{dC(t)}{dt} = \underbrace{-\left(\frac{q}{V} + \frac{A_l g}{V} + \frac{A_c k}{V}\right)}_{=\alpha\ =\text{constant}} C(t) + \underbrace{\frac{qC_a}{V} + \frac{A_l g C_i}{V}}_{=\beta\ =\text{constant}}$$

Solution

$$\begin{aligned} C(t) &= \frac{\beta}{\alpha} + \left(C_o - \frac{\beta}{\alpha}\right) e^{-\alpha t} \\ &= C_\infty + (C_0 - C_\infty) e^{-kt} \end{aligned}$$

Fit type	equation	$dC(t)/dt$	$dC(t)/dt, t = 0$
Linear	$C(t) = a + bt$	b	b
Quadratic	$C(t) = a + bt + ct^2$	$b + 2c \cdot t$	b
Exponential	$C(t) = a + be^{ct}$	$b \cdot c \cdot e^{ct}$	$b \cdot c$

In the fitting the first parameter is C_∞, the second parameter is C_0 and the third parameter is k. In static (non-flow-trough) chambers and for non-reactive gases $-c$ represents the transport coefficient of the compound.

check the static/dynamic definitions from Jukka's paper

Livingston fit

Livingston et al. 2006

$$C(t) = C_0 + f_0\tau\left(\frac{A}{V}\right)\left[\frac{2}{\sqrt{\pi}}\sqrt{\frac{t}{\tau}} + e^{t/\tau}\cdot \mathrm{erfc}\sqrt{\frac{t}{\tau}} - 1\right] + \epsilon(t)$$

The Livingston fit (NDFE) only works for emission fluxes (fluxes to the atmosphere). In the model three parameters are estimated. The parameters are gas concentration at the closure (C_0), $flux at the closure (f_0) and time constant of flux saturation \tau$. The model can be run with only one parameter (F_0)$estimated, as C_0 can be measured and \tau$ can be derived from the measurements of soil properties. For soil parameters, see Matsunaga et al. (1998) and perhaps Pumpanen et al. (2003)

This needs further explanations!

Intercept fit

Kroon et al. 2008
Slopes are calculated between two adjacent measured concentrations:

$$\hat{\gamma}_i = \frac{C_i - C_{i-1}}{t_i - t_{i-1}}$$

A linear fit is done to the slopes and the slope at time of closure (t=0) is the intercept point of the fit. This assumes implicitly that the time development of the concentration is quadratic.

This needs to be explained in more detail

Explain also the quadratic fit!

Goodness of fit parameters

Goodness of fit (GoF) can not be used for the intercept fit.

Neter et al XXXX

Find more references

Sum of squared errors

$$SSE = \sum_{i=1}^{n} (C_{fit,i} - C_i)^2$$

Root mean square error

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (C_{fit,i} - C_i)^2}$$

Coefficient of determination

$$r^2 = 1 - \frac{SSE}{\sum_{i=1}^{n} (C_{mean_i} - C_i)^2}$$

Adjusted coefficient of determination

$$r_a^2 = 1 - \left(\frac{n-1}{n-p} \right) \frac{SSE}{\sum_{i=1}^{n} (C_{mean,i} - C_i)^2}$$

n = number of datapoints and p = order of the fit. Nonlinearity occurs if $r_a^2(lin) << r_a^2(non-lin)$

Calculating the flux from the slope

$$Flux = \frac{dC(t)}{dt} \cdot M \cdot \frac{273}{V_m} \cdot \frac{1}{273+T} \cdot \frac{V}{A} \cdot \frac{1}{3600}$$

Molecular weights [g/mol] normalized by carbon or nitrogen (currently not?):
$M_{N_2O} = 44.013 * 28/44$
$M_{CH_4} = 16.042 * 12/16$
$M_{CO_2} = 44.01 * 12/44$

$V_m = 0.0224 m^3/mol$ ideal gas mole volume
T = temperature in Celcius
V = volume of the chamber
A = base area of the chamber (m^2)
Flux is in $\mu gC/m^2h$ or $\mu gN/m^2h$ (check this)

Quality criteria of the fit

It is recommended that bad measurements are filtered out using the flux and quality files created by the script. However, the script can also be used to filter out bad data. The filtered data is written in dummies flux file. Filtering includes automatic and manual filtering.

Manual filtering: When manual filtering is enabled, you can visually look at the measurement and determine if the measurement is valid or not. The results are written in a file () and used next time when analyzing the data. The fits of the different functions can also be filtered out separately.

Automatic filtering: Automatic filtering rejects the measurement based if RMSE and NRMSE of the fit and data is larger than a specific treshold. The use of these parameters is briefly explained in Korhonen et al. (2010). NRMSE is a relative measure, and suitable in conditions where a clear flux should be determined. In cases of very small fluxes NRMSE is not suitable GOF parameter, because using it leads to rejection of good measurements as well. In these cases RMSE works better as it describes the absolute noise in the data. From the fitting parameters one can define the initial concentration (expect for the intercept fit). The range of accepted initial concentrations per fit can also be used for filtering out bad fits.

Measurement points per closure

The required amount of measurement points per closure comes from the equation

$$n - k \geq 4,$$

Fit type	parameters	measurement points
Linear	2	6
Quadratic	3	7
Exponential	3	7
Livingston	3	7

where n = number of data points and k = number of parameters. The number of parameters and required measurement points per fit type are below. Masa does 8 measurements per closure and the data is thus sufficient for all fits, Smear and Kulotus have 5 points and Kaulaus 4 points. Consequently the fits must be done with caution for the last three data sets.

The script has no limit for the data points in a fit. However, problems may arise is the number of data points is very high. We have tested the script with 1900 data points with no problems.

Input file

The script will use Excel 97-2003 workbooks (.xls) as input. The first sheet of the file will be used. All the cells must be formatted as "general" or "number", except columns 8, 9 and 10, which may also contain "NaN", indicating missing data. Also the cells may not contain formulas or references to other cells. Note that though data in a cell may be shown as a number, it may be formatted into for example"date"

The columns of the input file are explained in the table. The code will calculate time moment after the closure in seconds by multiplying column 6 by 60 and adding column 7 to it. Therefore, column 7 is not actually needed, but can be used. Note that column 7 can only contain numeric values and not NaNs (use 0).

Setup parameters

Output files

The script will produce four output files. The files are named after the input file, adding "_flx", "_flx_dummies" or "_quality" to the end of the filename and ".dat" as a suffix. The files are normal ASCII-files, and can be opened to any data-analysis program. The columns are separated either by space or tab (we would prefer tabs and should fix this).

	The columns of the input file
1	year [YYYY]
2	month [M/MM]
3	day [d/dd]
4	hour [h/hh]
5	minute [m/mm]
6	minutes after the start of enclosure [m/mm]
7	seconds after the start of enclosure [s/ss]
8	N_2O concentration [ppm], GC data [value or NaN]
9	CH_4 concentration [ppm], GC data [value or NaN]
10	CO_2 concentration [ppm], GC data [value or NaN]
11	Chamber temperature [$^\circ C$]
12	Chamber / closure ID
13	Chamber height (not used by the script) [m]
14	Area of object studied (collar area, leaf area) [m^2]
15	Chamber volume [m^3]
16	Soil air-filled porosity (optional, fraction (0-1))

The flux-file (_flx.dat) contains calculated fluxes for defined gases with all the different calculation methods. Nothing has been filtered out, and you need to use the Quality-file for determining what are the good fluxes and what not. Additionally, it contains the fitting parameters for the exponential function (C_∞, (C_0) and k.

The dummies-file (_flx_dummies.dat) is a file, where part of the data is roughly been filtered out (see Quality criteria of the fit). Originally this was a file for dummies, who do not have any idea how to filter out data. However, in the recent versions of the script, the filtering capabilities of the script has been improved markedly and one should not be offended even if using the dummies-file.

The quality-file (_quality.dat) contains the quality parameters for the fits. The beginning of the file contains the results of the internal Quality check of the script (see Quality criteria of the fit). 1 indicates accepted and 0 rejected measurements. The latter part of the file contains values for SSE, RMSE, R^2 and R^2_{adj} for the defined gases.

The fit coefficients file (_fit_coefficients.dat) contains the fitting parameters for all the gases.

References

Livingston et al. 2006
Korhonen et al. 2010 (FCoE). Kroon et al. 2008
Neter et al. XXXX
Vesala et al. 2009 (FCoE)

	The columns of the flux and dummy output-file
1	year
2	month
3	day
4	hour (currently NaN)
5	Chamber/closure ID
6	N_2O flux - linear fit
7	N_2O flux - quadratic fit
8	N_2O flux - Livingston fit
9	N_2O flux - intercept fit
10	N_2O flux - exponential fit
11	CH_4 flux - linear fit
12	CH_4 flux - quadratic fit
13	CH_4 flux - Livingston fit
14	CH_4 flux - intercept fit
15	CH_4 flux - exponential fit
16	CO_2 flux - linear fit
17	CO_2 flux - quadratic fit
18	CO_2 flux - Livingston fit
19	CO_2 flux - intercept fit
20	CO_2 flux - exponential fit
21	N_2O - parameter a of exponential fit
22	N_2O - parameter b of exponential fit
23	N_2O - parameter c of exponential fit
24	CH_4 - parameter a of exponential fit
25	CH_4 - parameter b of exponential fit
26	CH_4 - parameter c of exponential fit
27	CO_2 - parameter a of exponential fit
28	CO_2 - parameter b of exponential fit
29	CO_2 - parameter c of exponential fit

	The columns of the quality output-file
1	year
2	month
3	day
4	hour (currently NaN)
5	Chamber/closure ID
6	N_2O - initial concentration of exponential fit test (0/1)
7	N_2O - RMSE - linear fit test (0/1)
8	N_2O - RMSE - quadratic fit test (0/1)
9	N_2O - RMSE - Livingston fit test (0/1)
10	N_2O - RMSE - power fit test (0/1)
11	N_2O - RMSE - exponential fit test (0/1)
12	N_2O - NRMSE - linear fit test (0/1)
13	N_2O - NRMSE - quadratic fit test (0/1)
14	N_2O - NRMSE - Livingston fit test (0/1)
15	N_2O - NRMSE - power fit test (0/1)t
16	N_2O - NRMSE - exponential fit test (0/1)
17	CH_4 - initial concentration of exponential fit test (0/1)
18	CH_4 - RMSE - linear fit test (0/1)
19	CH_4 - RMSE - quadratic fi test (0/1)
20	CH_4 - RMSE - Livingston fit test (0/1)
21	CH_4 - RMSE - power fit test (0/1)
22	CH_4 - RMSE - exponential fit test (0/1)
23	CH_4 - NRMSE - linear fit test (0/1)
24	CH_4 - NRMSE - quadratic fi test (0/1)
25	CH_4 - NRMSE - Livingston fit test (0/1)
26	CH_4 - NRMSE - power fit test (0/1)
27	CH_4 - NRMSE - exponential fit test (0/1)
28	CO_2 - initial concentration of exponential fit test (0/1)
29	CO_2 - RMSE - linear fit test (0/1)
30	CO_2 - RMSE - quadratic fit test (0/1)
31	CO_2 - RMSE - Livingston fit test (0/1)
32	CO_2 - RMSE - power fit test (0/1)
33	CO_2 - RMSE - exponential fit test (0/1)
34	CO_2 - NRMSE - linear fit test (0/1)
35	CO_2 - NRMSE - quadratic fit test (0/1)
36	CO_2 - NRMSE - Livingston fit test (0/1)
37	CO_2 - NRMSE - power fit test (0/1)
38	CO_2 - NRMSE - exponential fit test (0/1)
39	N_2O - SSE - linear
40	N_2O - RMSE - linear
41	N_2O - NRMSE - linear
42	N_2O - R^2 - linear
43	N_2O - R^2_{adj} - linear
44	N_2O - Chi^2 - linear

	The columns of the quality output-file (continued)
45	N_2O - SSE - quadratic
46	N_2O - RMSE - quadratic
47	N_2O - NRMSE - quadratic
48	N_2O - R^2 - quadratic
49	N_2O - R^2_{adj} - quadratic
50	N_2O - Chi^2 - quadratic
51	N_2O - SSE - Livingston
52	N_2O - RMSE - Livingston
53	N_2O - NRMSE - Livingston
54	N_2O - R^2 - Livingston
55	N_2O - R^2_{adj} - Livingston
56	N_2O - Chi^2 - Livingston
57	N_2O - SSE - power
58	N_2O - RMSE - power
59	N_2O - NRMSE - power
60	N_2O - R^2 - power
61	N_2O - R^2_{adj} - power
62	N_2O - Chi^2 - power
63	N_2O - SSE - exponential
64	N_2O - RMSE - exponential
65	N_2O - NRMSE - exponential
66	N_2O - R^2 - exponential
67	N_2O - R^2_{adj} - exponential
68	N_2O - Chi^2 - exponential
69	CH_4 - SSE - linear
70	CH_4 - RMSE - linear
71	CH_4 - NRMSE - linear
72	CH_4 - R^2 - linear
73	CH_4 - R^2_{adj} - linear
74	CH_4 - Chi^2 - linear
75	CH_4 - SSE - quadratic
76	CH_4 - RMSE - quadratic
77	CH_4 - NRMSE - quadratic
78	CH_4 - R^2 - quadratic
79	CH_4 - R^2_{adj} - quadratic
80	CH_4 - Chi^2 - quadratic
81	CH_4 - SSE - Livingston
82	CH_4 - RMSE - Livingston
83	CH_4 - NRMSE - Livingston
84	CH_4 - R^2 - Livingston
85	CH_4 - R^2_{adj} - Livingston
86	CH_4 - Chi^2 - Livingston

	The columns of the quality output-file (continued)
87	CH_4 - SSE - power
88	CH_4 - RMSE - power
89	CH_4 - NRMSE - power
90	CH_4 - R^2 - power
91	CH_4 - R^2_{adj} - power
92	CH_4 - Chi^2 - power
93	CH_4 - SSE - exponential
94	CH_4 - RMSE - exponential
95	CH_4 - NRMSE - exponential
96	CH_4 - R^2 - exponential
97	CH_4 - R^2_{adj} - exponential
98	CH_4 - Chi^2 - exponential
99	CO_2 - SSE - linear
100	CO_2 - RMSE - linear
101	CO_2 - NRMSE - linear
102	CO_2 - R^2 - linear
103	CO_2 - R^2_{adj} - linear
104	CO_2 - Chi^2 - exponential
105	CO_2 - SSE - quadratic
106	CO_2 - RMSE - quadratic
107	CO_2 - NRMSE - quadratic
108	CO_2 - R^2 - quadratic
109	CO_2 - R^2_{adj} - quadratic
110	CO_2 - Chi^2 - quadratic
111	CO_2 - SSE - Livingston
112	CO_2 - RMSE - Livingston
113	CO_2 - NRMSE - Livingston
114	CO_2 - R^2 - Livingston
115	CO_2 - R^2_{adj} - Livingston
116	CO_2 - Chi^2 - Livingston
117	CO_2 - SSE - power
118	CO_2 - RMSE - power
119	CO_2 - NRMSE - power
120	CO_2 - R^2 - power
121	CO_2 - R^2_{adj} - power
122	CO_2 - Chi^2 - power
123	CO_2 - SSE - exponential
124	CO_2 - RMSE - exponential
125	CO_2 - NRMSE - exponential
126	CO_2 - R^2 - exponential
127	CO_2 - R^2_{adj} - exponential
128	CO_2 - Chi^2 - exponential