

## Supplementary Material

### Calculating the Detection Limits of Chamber-Based Soil Greenhouse Gas Flux Measurements

T. B. Parkin, R. T. Venterea, and S. K. Hargreaves

#### Step by Step Detection Limit Calculations

Table 8 outlines the procedure for calculating detection limits for N<sub>2</sub>O, CO<sub>2</sub> and CH<sub>4</sub> fluxes when the rQuad model is used when 3 time points are collected at equal time spacing's over the total chamber deployment time of 0.667 h. In this example the chamber used is circular (0.3 m diameter) with a headspace height is 0.15 m, the air temperature is 20°C, and the atmospheric pressure is 0.965. Application of this procedure for other chamber configurations requires use of appropriate chamber volume and surface area values. Detection limits for the other flux calculation models can be computed using the procedure described here if the appropriate 'a' and 'b' coefficients (Table 7) are applied as described in Step 2.

*Step 1. Determine the mean ambient concentration and sampling/analytical variability for each gas component.* Collect and analyze 20 to 30 ambient gas samples in the same manner as the chamber headspace samples are collected. Calculate the mean and standard deviation for each gas component. The precision is calculated as the Coefficient of Variation (Mean / Standard Deviation). For this illustration the experimentally determined mean ambient concentrations and sampling/analytical precisions of N<sub>2</sub>O, CH<sub>4</sub> and CO<sub>2</sub> are used (Fig. 2)

*Step 2. Compute the scaled slope factor ( $\theta$ ) for the rQuad model.* Theta ( $\theta$ ) is

calculated using the regression coefficients shown for the rQuad model (3 sampling points) selected from Table 7 (a=7.095, b=.9944) along with the chamber deployment time (0.667 h) as illustrated in the equation below:

$$\theta = 7.095 * 0.667^{-0.9944} = 10.61$$

This scaled slope factor (10.61) is the same for all the gases. **Note 1:** Since the 'a' coefficient (7.095) has units of  $\text{h}^{-2} \text{CV}^{-1}$ , the resulting units of  $\theta$  are  $\text{h}^{-1} \text{CV}^{-1}$ . **Note 2:** The scaled slope factors for other models can be calculated in the same manner using the appropriate 'a' and 'b' regression coefficients from Table 7. For example to calculate the scaled slope factor for the linear model (with three sampling points) values of 'a' and 'b' would be 2.314 and 1.005, respectively.

Step 3. *Compute the slope factor for the individual gases.* Multiply the scaled slope factor calculated in step 2 by the mean ambient concentration of each gas. For  $\text{N}_2\text{O}$  this value is  $10.61 * 323 = 3428$ . For  $\text{CH}_4$  this value is  $10.61 * 1.79 = 19.0$ . For  $\text{CO}_2$  this value is  $10.61 * 385.5 = 4091$ . **Note:** Units of the slope factors for each gas is the volumetric concentration \*  $\text{CV}^{-1}$ . Thus, the  $\text{N}_2\text{O}$  slope factor has units of  $\text{nL L}^{-1} \text{h}^{-1} \text{CV}^{-1}$ . For  $\text{CH}_4$  and  $\text{CO}_2$ , the slope factors have units of  $\mu\text{L L}^{-1} \text{h}^{-1} \text{CV}^{-1}$ .

Step 4. *Compute the positive flux detection limit.* The slope factors computed in Step 3 for each gas are multiplied by the analytical precision (C.V.) associated with each gas. For  $\text{N}_2\text{O}$  this value is  $3428 * 0.044 = 150.8 \text{ nL L}^{-1} \text{h}^{-1}$ . For  $\text{CH}_4$  this value is  $19.0 * 0.071 = 1.349 \mu\text{L L}^{-1} \text{h}^{-1}$ . For  $\text{CO}_2$  this value is  $4091 * 0.0014 = 5.727 \mu\text{L L}^{-1} \text{h}^{-1}$ .

Step 5. *Compute the negative flux detection limit.* Negative flux detection limits for each

gas are computed by multiplying the positive flux detection limits by -1. The values are  $-150.8 \text{ nL L}^{-1} \text{ h}^{-1}$ ,  $-1.349 \text{ }\mu\text{L L}^{-1} \text{ h}^{-1}$ , and  $-5.727 \text{ }\mu\text{L L}^{-1} \text{ h}^{-1}$ , for  $\text{N}_2\text{O}$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ , respectively.

Step 6. *Convert the flux detection limits to a vol/vol basis to a vol/area basis.* The flux detection limits have units of volume gas (nL or  $\mu\text{L}$ ) per L of chamber headspace air per hour. So, the first step is to multiply the volumetric flux detection limit by the chamber headspace volume (L). For a 0.3 m diameter circular chamber with a chamber headspace height of 0.15 m, the chamber volume is 10.6 L. Multiplying the  $\text{N}_2\text{O}$  flux detection limit of  $150.8 \text{ nL L}^{-1} \text{ h}^{-1}$  by 10.6 L results in a value of  $1599 \text{ nL N}_2\text{O h}^{-1}$ . For  $\text{CH}_4$ , multiplying  $1.349 \text{ }\mu\text{L CH}_4 \text{ L}^{-1} \text{ h}^{-1}$  by 10.6 L results in a value of  $14.3 \text{ }\mu\text{L CH}_4 \text{ h}^{-1}$ , and for  $\text{CO}_2$ , multiplying  $5.727 \text{ }\mu\text{L CO}_2 \text{ L}^{-1} \text{ h}^{-1}$  results in a value of  $60.73 \text{ }\mu\text{L CO}_2 \text{ h}^{-1}$ .

Conversion of these values to soil area units is done by dividing by the surface area covered by the chamber. For a 0.3 m diameter circular chamber, the soil area covered is  $0.0707 \text{ m}^2$ . For  $\text{N}_2\text{O}$ :  $1599 \text{ nL N}_2\text{O h}^{-1} / 0.0707 \text{ m}^2 = 22600 \text{ nL N}_2\text{O m}^{-2} \text{ h}^{-1}$ . For  $\text{CH}_4$ :  $14.3 \text{ }\mu\text{L CH}_4 \text{ h}^{-1} / 0.0707 \text{ m}^2 = 202 \text{ }\mu\text{L CH}_4 \text{ m}^{-2} \text{ h}^{-1}$ . For  $\text{CO}_2$ :  $60.73 \text{ }\mu\text{L CO}_2 \text{ h}^{-1} / 0.0707 \text{ m}^2 = 859 \text{ }\mu\text{L CO}_2 \text{ m}^{-2} \text{ h}^{-1}$ .

Step 7. *Convert the flux detection limits to a volume/area basis to a mass/area basis.* A flux calculated from either from linear regression or a non-linear model will have units of nL (or  $\mu\text{L}$ ) trace gas  $\text{m}^{-2} \text{ h}^{-1}$ . As described by Parkin and Venterea (2010), an additional calculation must be performed in order to convert flux values from a volumetric basis to a mass basis. To perform this conversion the ideal gas law is used:

$$PV = nRT$$

where P = pressure, V = volume, n = the number of moles of gas, R = the gas law constant, and T = temperature. The ideal gas law quantifies the relationship between pressure, volume, mass and temperature of a gas. The ideal gas law constant (R) can be expressed in many different forms, but when R = 0.08206, the units are L Atm Mol<sup>-1</sup> °K<sup>-1</sup>, and the corresponding units of P, V, N and T are Atmospheres, Liters, Moles, and degrees Kelvin, respectively. The goal of applying the idea gas law is to convert μL (or nL) trace gas to μMol (or nMol) trace gas. To do this, one must have knowledge of both the air temperature and atmospheric pressure. An example of this calculation for an atmospheric pressure of 0.965 Atm and at 20°C is presented below.

$$1 \mu\text{L trace gas} * 0.965 \text{ Atm} / ((0.08206 \text{ L Atm Mol}^{-1} \text{ } ^\circ\text{K}^{-1}) * (273 + 20)^\circ\text{K}) * 1 \text{ L}/10^6 \\ \mu\text{L} * 10^6 \mu\text{Mol}/\text{Mol} = 0.0401 \mu\text{Mol trace gas}.$$

Similarly, at an atmospheric pressure of 0.965 Atm and 20°C, 1 nL trace gas = 0.0401 nMol trace gas. Thus multiplication of the trace gas detection limits calculated in Step 6 by 0.0401 will yield units of nMol (or μMol) trace gas m<sup>-2</sup> h<sup>-1</sup>. For N<sub>2</sub>O: 22600 nL N<sub>2</sub>O m<sup>-2</sup> h<sup>-1</sup> \* 0.041 = 907 nMol m<sup>-2</sup> h<sup>-1</sup>. For CH<sub>4</sub>: 202 μL CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup> \* 0.041 = 8.28 μMol CH<sub>4</sub> m<sup>-2</sup> h<sup>-1</sup>. For CO<sub>2</sub>: 859 μL CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup> \* 0.041 = 35.2 μMol CO<sub>2</sub> m<sup>-2</sup> h<sup>-1</sup>. Since each nMol of N<sub>2</sub>O contains 28 ng of N, multiplication of the N<sub>2</sub>O detection (907 nMol m<sup>-2</sup> h<sup>-1</sup>) by 28 results in a detection limit of 25400 ng N<sub>2</sub>O-N m<sup>-2</sup> h<sup>-1</sup>. Since each μMol of CH<sub>4</sub> or CO<sub>2</sub> contains 12 μg C, multiplication by 12 yields values of 97.4 μg CH<sub>4</sub>-C m<sup>-2</sup> h<sup>-1</sup> and 413 μg CO<sub>2</sub>-C m<sup>-2</sup> h<sup>-1</sup>. Conversion of the N<sub>2</sub>O flux detection limit to units of g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup> is done by: 1) dividing by 10<sup>9</sup> ng g<sup>-1</sup>, 2) multiplying by 10<sup>4</sup> m<sup>2</sup> ha<sup>-1</sup>, and 3) multiplying by 24 h d<sup>-1</sup>, yielding a N<sub>2</sub>O positive flux detection limit of 6.1 g N<sub>2</sub>O-N ha<sup>-1</sup> d<sup>-1</sup>. If the CH<sub>4</sub>

detection limit of  $97.4 \mu\text{g CH}_4\text{-C m}^{-2} \text{ h}^{-1}$  is divided by  $10^6 \mu\text{g g}^{-1}$ , multiplied by  $10^4 \text{ m}^2 \text{ ha}^{-1}$  and multiplied by  $24 \text{ h d}^{-1}$  a value of  $23.4 \text{ g CH}_4\text{-C ha}^{-1} \text{ d}^{-1}$  is obtained. Similarly, when the  $\text{CO}_2$  detection limit of  $413 \mu\text{g CO}_2\text{-C m}^{-2} \text{ h}^{-1}$  is divided by  $10^6 \mu\text{g g}^{-1}$ , multiplied by  $10^4 \text{ m}^2 \text{ ha}^{-1}$  and multiplied by  $24 \text{ h d}^{-1}$  a minimum detection limit of  $99.2 \text{ g CO}_2\text{-C ha}^{-1} \text{ d}^{-1}$  is obtained. The corresponding negative detection limits for each gas species are obtained by multiplication by -1.