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# Estimating greenhouse gas emissions from soil following liquid manure applications using a unit response curve method

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#### ABSTRACT

Quantitative information is critical in policy making related to the roles of agriculture in greenhouse gas (GHG) emissions. A Unit Response (UR) curve method was developed in this study for modeling GHG emissions from soil after liquid manure applications. The emission sources (soils and liquid manures) are conceptualized as a set of linear cascaded chambers with equal storage-release coefficients, or two sets of cascaded chambers in parallel, each set having equal storage-release coefficients. The model is based on a two-parameter gamma distribution. Three parameters in this model denote the number of cascaded chambers, the storage-release coefficient, and the multiplier (referring to the total net emissions) added to the gamma distribution function. These parameters can be expressed as functions of site-specific background fluxes without applications of manure/fertilizer. The method was assessed with emissions data from five fields in Washington State. The results showed that at the WSU and Lynden sites, the average excess  $CO_2$  emissions were 216.50 and 25.20 kg  $CO_2$ -C ha<sup>-1</sup>, respectively; and the average excess  $N_2O$  were 0.37 and 0.03 kg  $N_2O$ -N ha<sup>-1</sup>, respectively. The UR method may fill the gaps between field measurements, simple emission factor (EF) method, and complex process-oriented models. This method has the potential to be used for estimating additional GHG emissions due to manure/fertilizer applications.

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#### 1. Introduction

Field measurements of greenhouse gas (GHG) fluxes are usually required to estimate GHG emissions from soil after manure or fertilizer applications (Arah et al., 1997; Beheydt et al., 2007; Frolking et al., 1998; Haile-Mariam et al., 2008). Long-term field experiments are able to provide ample data for this purpose (Behevdt et al., 2007: Smith et al., 1997). However, in situ data collection is not only timeconsuming but also limited by the financial resources. Therefore, process-based mathematical models have been developed to validate and extend the results based on field observations, such as CENTURY/ DAYCENT (Del Grosso et al., 2005; Parton et al., 1987), DNDC (Li et al., 1992a, 1992b), NLEAP (Shaffer et al., 2001), DAISY (Hansen et al., 1990), ECOSSE (Smith et al., 2007), ECOSYS (Grant, 2001), CropSyst (Stöckle et al., 2003), and many other models (Smith et al., 1997; Wu and McGechan, 1998). While the process-based models can provide more detailed temporal and spatial outputs as well as predictions and scenario analysis, their use is hampered by difficulties with data availability and model verifications. Therefore, simple emission factor (EF) approach is used to estimate the total annual emissions in cases of data scarcity (Del Grosso et al., 2005; Kuikman et al., 2006). However, the EF method only yields an estimate of the total emission and is unable to provide information on temporal variation of fluxes and the peak flux.

For these reasons, new methodologies are needed to fill the gaps between field measurements, simple EF method, and complex process-oriented modeling. Such methodologies should have the capacity of (i) fully utilizing short-term field experimental data; (ii) simulating GHG fluxes over time; and (iii) accommodating explanatory parameters related to site-specific properties.

The methodology of the unit hydrograph (UH) in hydrology can be adapted to describe the emission processes of GHGs. Unit hydrograph is a direct runoff hydrograph produced by one unit of excess precipitation over a specified duration. It has been successfully used to convert excess rainfall to streamflow process in a watershed for event-based rainfall-runoff modeling (Singh, 2004). The unit excess rainfall is assumed to occur for an effective duration uniformly over the watershed. The unit hydrograph is expressed by an instantaneous UH (IUH) if this effective duration is infinitely close to zero (Bhunya et al., 2008). Typically, Nash IUH is represented by a two-parameter gamma distribution (Bhunya et al., 2003; Kumar et al., 2007; Singh, 2004). The two parameters denote the number of linear reservoirs and the storage coefficient of reservoirs. The rationale of UH is



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validated not only by its applicability (Bhunya et al., 2008; Rai et al., 2009), but also by its connection with the geomorphological characteristics as well as flow velocities, which is well known as geomorphological IUH (GIUH) (Bhunya et al., 2008; Kumar et al., 2007). The gamma distribution was determined to be the most suitable in a comparative study by Rai et al. (2009). Even better, Cudennec et al. (2004) provided theoretical explanations for some assumptions of UH and GIUH, especially the gamma law and the exponential distribution of residence time.

The purpose of this paper is to report a new method – unit response (UR) curve – to estimate the total excess emissions and the temporal emission pattern of three major GHGs ( $CO_2$ ,  $N_2O$ , and  $CH_4$ ). Similar to UH, UR can be used to quantify the additional GHG emission process produced by one unit of carbon/nitrogen input in manure or fertilizer over a specified duration. The assumptions of UR include: (i) the UR curve reflects the ensemble of characteristics of the soil; (ii) the shape characteristics of UR are time invariant; (iii) the emission sources (soils and liquid manures) are conceptualized as a set of linear cascaded chambers with equal storage-release coefficients, or two sets of cascaded chambers in parallel, each set having equal storage-release coefficients.

#### 2. Materials and methods

#### 2.1. Study sites and data analysis

Baseline monitoring of GHG emissions before and after field applications of dairy waste was conducted on three dairy farms in Washington State in 2005 and 2006 (Table 1). Two dairy farms, labeled Lynden1 and Lynden2, both of which utilized anaerobic digestion (AD) technology and therefore applied digested manure (DM), are located in Lynden, Washington (48° 54' N, 122° 30' W), and are characterized by medial-skeletal and medial soils formed in volcanic ash and loess over glacial outwash terraces (Boling et al., 1998). The surface layer and subsoil are sandy loam, and the substratum is sand (Goldin, 1992). Based on the long-term daily baseline climate data (period: 1915-2008; data source: http://www.ncdc.noaa.gov/oa/ ncdc.html at Bellingham, Washington (48° 47' N, 122° 29' W), 21 km south of Lynden), the mean annual precipitation is about 902 mm and the average air temperature is about 10.1 °C. Both dairies applied their DM in Spring of 2006 via injection on farm lands prepared for production and harvest of hay.

The other dairy, with three fields of manure application, WSU Dairy Field 8, WSU Dairy Field 22, and WSU Dairy North Pasture (hereinafter referred to as WSU8, WSU22, and WSUNorth), is located in Pullman, Washington (46° 45′ N, 117° 11′ W) and are dominated by loam soils. According to the historical climate data (1941–2008) for Pullman, the annual precipitation ranges from 308 to 758 mm, with average annual precipitation of about 535 mm. The mean annual air temperature is about 8.4 °C. Rotational grazing of perennial grasses and periodic undigested manure (UDM) application were conducted at all three Pullman sites. The field experiments were carried out during August 2006 on WSU8 and WSU22, and during August 2005 on WSUNorth.

Soil samples were collected before the manure applications to determine soil water content (SWC). Soil samples were dried in a ventilated drying oven (105 °C) for 24 h. Soil bulk density, SWC and soil waterfilled pore space (WFPS) were calculated thereafter (Haile-Mariam et al., 2008). Soil temperature at 4-cm depth was measured every 30 min using thermocouples and recorded on a CR10X data logger (Campbell Scientific Inc., Logan, UT). Manure gauges (open chambers) were deployed before manures were applied. The gauges were placed on level ground among sampling chambers to represent the amount of manure applied to the chambers. After application and after the first hour, samples were collected and the depth of manure in each gauge was measured with a ruler. After measurement, manure in the gauges was stirred to suspend all the solids, and 1-L sample was collected from the gauge into a labeled sample bottle. The manure samples were then frozen to be shipped to the lab for analysis. Total Kjeldahl Nitrogen (TKN) with units of mg  $L^{-1}$  was analyzed using a Tecator 2300 Kjeltec Analyzer (Eden Prairie, MN, USA; SM 4500-Norg B procedure). The total nitrogen per unit area (kg N ha<sup>-1</sup>) applied was calculated via TKN and liquid manure depth (see Table 1).

The static closed-chamber method (Haile-Mariam et al., 2008; Rochette and Eriksen-Hamel, 2008) was used to measure GHG fluxes. Generally, the gas sampling followed the USDA-ARS GRACEnet protocol (Parkin et al., 2003). Twelve PVC chambers (28.3 cm in diameter) were randomly placed in the undisturbed soils where manure was applied. The chambers were driven 6 cm into the soil and extended 16 cm above the soil surface. Before manure spraying, background trace gas samples were collected to be compared with the gas emission rates after manure applications. In general, except for one set of background samples, 12 or 13 sets of samples after manure application were collected during a 10 day period with each set including 12 replicates. During each 1-h period after placing the chamber cap, four gas samples were collected at an interval of 20 min (i.e., 0-min, 20-min, 40-min, and 60min). 35 mL of air was withdrawn from the headspace of the chamber using a 60-mL syringe. The gas temperature in the chamber was measured by a thermocouple while sampling. Gas samples were injected into evacuated 12-mL Labco Exetainer vials (Labco Limited, High Wycombe, Buckinghamshire, UK) for lab analysis.

Cumulative concentrations in ppm(v) or volumetric parts per million of N<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>4</sub> were determined using a Varian CP-3800 Gas Chromatograph (Varian, Palo Alto, CA). The GHG gas flux was calculated using the rate of change of the concentration (i.e., the slope of the cumulative gas concentration over time) (Parkin et al., 2003; Rochette and Eriksen-Hamel, 2008; Teepe et al., 2004).

In order to intuitively understand the gas flux, it is necessary to covert gas flux values from a volumetric basis (ppm min<sup>-1</sup>) to a mass basis (kg ha<sup>-1</sup> h<sup>-1</sup> or kg ha<sup>-1</sup> d<sup>-1</sup>) (Parkin et al., 2003). Generally, mass fluxes have units of kg CO<sub>2</sub>–C ha<sup>-1</sup> d<sup>-1</sup>, kg CH<sub>4</sub>–C ha<sup>-1</sup> d<sup>-1</sup>, and kg N<sub>2</sub>O–N ha<sup>-1</sup> d<sup>-1</sup>. The ideal gas law (Campbell and Norman, 1998) is used to calculate the number of moles of gas per unit volume:

$$PV = nRT \Rightarrow \rho_{mole} = \frac{n}{V} = \frac{P}{RT}$$
(1)

where  $\rho_{mole}$  denotes the number of moles per unit volume (mol m<sup>-3</sup>); *V* is the volume of the vessel (m<sup>3</sup>); *n* is the number of moles of gas (mol); *R* is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>); *T* is the absolute temperature (K); and *P* is the atmospheric pressure (Pa).

 Table 1

 Experimental sites for greenhouse gasses sampling.

Site	Geographical location (Latitude, Longitude, Elevation)	Sampling period	Treatment <sup>a</sup>	Nitrogen in manure application (kg N ha $^{-1}$ )
WSU8	46°41′9″N, 117°14′40″ W, 792 m	8/28/2006-9/1/2006	NM, UDM	282.5
WSU22	46°41′14″ N, 117°14′33″ W, 796 m	8/7/2006-8/11/2006	NM, UDM	241.1
WSUNorth	46°41′38″ N, 117°14′12″ W, 750 m	8/11/2005-8/20/2005	NM, UDM	309.2
Lynden1	48°59′58″ N, 122°28′57″ W, 30 m	3/28/2006-3/30/2006	NM, DM	222.0
Lynden2	48°57′39″ N, 122°29′26″ W, 30 m	2/28/2006-3/1/2006	NM, DM	235.0

<sup>a</sup> NM, UDM, and DM denote no manure application, undigested manure application, and digested manure application, respectively.

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