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A mass balance model to estimate the rate of composting, methane oxidation and anaerobic digestion in soil covers and shallow waste layers

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ABSTRACT

Although CH_4 oxidation in landfill soil covers is widely studied, the extent of composting and CH_4 oxidation in underlying waste layers has been speculated but not measured. The objective of this study was to develop and validate a mass balance model to estimate the simultaneous rates of anaerobic digestion (r_{AD}), CH_4 oxidation (r_{OX}) and composting (r_{COM}) in environments where O_2 penetration is variable and zones of aerobic and anaerobic activity are intermingled. The modelled domain could include, as an example, a soil cover and the underlying shallow waste to a nominated depth. The proposed model was demonstrated on a blend of biogas from three separate known sources of gas representing the three reaction processes: (i) a bottle of laboratory grade 50:50% CH_4:CO_2 gas representing anaerobic digestion biogas; (ii) an aerated 250 mL bottle containing food waste that represented composting activity; and (iii) an aerated 250 mL bottle containing non-degradable graphite granules inoculated with methanotrophs and incubated with CH_4 and O_2 to represent methanotrophic activity. CO_2, CH_4, O_2 and the stable isotope ^{13}C-CO_2 were chosen as the components for the mass balance model. The three reaction rates, $\mathbf{r}$ (=r_{AD}, r_{OX}, r_{COM}) were calculated as fitting parameters to the overdetermined set of 4 mass balance equations with the net flux of these components from the bottles $\mathbf{q}$ (=q_{CH_4}, q_{CO_2}, q_{O_2} and $q_{CO_2} \times \delta^{13}C$-$CO_2$) as inputs to the model. The coefficient of determination (r^2) for observed versus modelled values of $\mathbf{r}$ were 1.00, 0.97, 0.98 when the stoichiometry of each reaction was based on gas yields measured in the individual bottles and $\mathbf{q}$ was calculated by summing yields from the three bottles. r^2 deteriorated to 0.95, 0.96, 0.87 when using an average stoichiometry from 11 incubations of each of the composting and methane oxidation processes. The significant deterioration in the estimation of r_{COM} showed that this output is highly sensitive to the evaluated stoichiometry coefficients for the reactions. r^2 deteriorated further to 0.86, 0.77, 0.74 when using the average stoichiometry and experimental measurement of the composition and volume of the blended biogas to determine $\mathbf{q}$. This was primarily attributed to average errors of 8%, 7%, 11% and 14% in the measurement of q_{CH_4}, q_{CO_2}, q_{O_2} and $q_{CO_2} \times \delta^{13}C$-$CO_2$ relative to the measurement of the same quantities from the individual bottles.

1. Introduction

The oxidation of CH_4 in landfill cover systems is widely studied. However, few studies have explored aerobic processes in waste beneath soil covers, even though a number of authors have observed O_2 penetration into landfilled waste (Kallel et al., 2006; Lefebvre et al., 2000; Yoshida et al., 2012). Peneteration of oxygen into the waste layer can be variable and channelled, leading to intermingled zones of aerobic and anaerobic activity. It is proposed that high concentrations of CO_2 relative to CH_4 in gaseous emissions from the surface of soil covers in active landfill cells could be partially attributed to aerobic activity within shallow waste (Abushammala et al., 2013; Bogner et al., 2011).

Three main techniques are used to measure the fraction of CH_4 that is oxidized in a landfill cover: (1) a mass balance approach (Bogner and Spokas, 1993; Christophersen et al., 2001); (2) a stable carbon isotope method (Bergmaschi and Harris, 1995; Liptay et al., 1998b) and (3) an approach based on the ratio of CH_4:CO_2 (Gebert et al., 2011a). These approaches assume CO_2 production from composting activity in the soil layer is insignificant compared to CO_2 production from CH_4 oxidation. Scheutz et al. (2011) and Röwer et al. (2011) accounted for composting activity in their measure-

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ments of CH_4 oxidation activity in organic rich soil by performing parallel aerated incubations of the soil without CH_4.

The aim of this paper was to develop and validate a mass balance model to estimate the rate of anaerobic digestion, CH_4 oxidation and composting from gas blended from three sources, each source representing biogas generated by one reaction process. Validation of the model was performed by comparing reaction rates calculated from measurements of the blended gas, as would be made when measuring gas fluxes in any real system such as a landfill, with the rates based on gas production from the individual sources.

2. Materials and methods

A key assumption in the mass balance model is that the stoichiometry of each of the three reaction processes is stable. Although composition of biogas from a landfill cell will change with time, these changes are gradual and the assumption of stable yields for each degradation process over the duration of flux measurements (e.g., with a static chamber on the surface of a landfill) is adopted.

In order to validate the model, stable sources of gas representative of each reaction process was required. This is readily achieved with composting where the product gas will be CO_2 provided conditions are fully aerobic, regardless of the stage of decomposition of the waste. A stable CH_4 oxidation process can also be maintained by feeding CH_4 to a methanotrophic culture supported on an inert substratum (Xie et al., 2016). Maintaining stable biogas production from the anaerobic digestion of organic waste is more difficult and not achievable in batch mode because faster fermentation processes would dominate before establishment of methanogenic activity (Nopharatana et al., 2003). A stable biogas from anaerobic digestion could be achieved with continuous operation; however this would still require careful maintenance of reactor conditions and feedstocks. A further complication is that anaerobic conditions are difficult to maintain in the experimental procedure described below, where the headspaces of the anaerobic digestion, composting and CH_4 oxidation reactors are connected to produce a blended gas. This would expose the anaerobic reactor to O_2. Therefore, a bottle of laboratory grade 50:50% CH_4:CO_2 gas was used as a source of biogas from anaerobic digestion.

2.1. Experimental plan

In order to validate the model, the model was applied to 11 gas blends generated by 11 sets of composting and CH_4 oxidation incubations blended with the 50:50% CH_4:CO_2 gas. Apart from this, an additional 22 composting incubations and 29 CH_4 oxidation incubations were performed. The average yields from all 33 composting incubations and 40 CH_4 oxidation incubations were used to determine global molecular stoichiometric coefficients for the composting and CH_4 oxidation reactions.

2.2. Batch incubation experiments

The composting incubations were conducted in 250 mL serum bottles amended with 3.0 g of blended synthetic waste (Table 1), flushed with compressed air and sealed with butyl rubber septum (20 mm thick) and aluminium crimps. All incubations were performed in a clean bottle with fresh waste. The butyl septum allowed gas samples to be withdrawn or injected using 22G hypodermic needles and gas-tight syringes. An initial sample of 10 mL was collected to characterise O_2 and background CO_2 levels. These incubations were performed over 24 h at 25 °C.

Table 1
Composition of synthetic organic waste.

Composition	Type	Weight (w/w, wet basis %)
Vegetable	Lettuce Cauliflower Cabbage Potato and onion peel	20
Fruit	Banana Golden apple Red apple Orange	30
Food scraps	Lamb meat Rice Macaroni Bread	50

The CH_4 oxidation test was performed using 3.0 g of graphite granules colonised with methanotrophic bacteria (Xie et al., 2016). 5 mL of a nutrient solution with the following composition was added to the granules: KH_2PO_4 (0.26 g/l), $Na_2HPO_4{\cdot}7(H_2O)$ (0.62 g/l), $(NH_4)_2SO_4$ (0.25 g/l), $FeSO_4$ (5 mg/l) and $CuCl_2{\cdot}2H_2O$ (0.07 mg/l).

The headspace of the 250 mL bottle was flushed with compressed air and sealed. 100 mL of laboratory grade 50:50% CH_4:CO_2 gas (BOC) and 200 mL of additional air was then injected to the bottle. Temperature, pressure and concentration of CH_4, CO_2 and O_2 were recorded initially ($t = 0$ h) and after 24 h to calculate gas generation and consumption.

2.3. Blending of source gases

To blend the source gases (i.e., the 50:50% CH_4:CO_2 gas mixture and the product and residual reactant gases in the composting and CH_4 oxidation incubations), the headspace of the 250 mL bottles were connected by Tygon Master Flex tubing (ID 6 mm) with each bottle headspace readily isolated by a two-way valve. The volume and composition of each headspace was characterised before the headspaces were mixed.

To ensure that the gas from the three bottles was thoroughly mixed, all two-way valves were opened and a 200 mL syringe was used to drive gas movement into each bottle headspace by drawing and pushing the plunger several times. A one hour time period was used to allow the combined headspace to reach an equilibrated state. The pressure, temperature and composition of the mixed gas were measured. The entrained O_2 in the connection tubes was accounted for in the calculations.

2.4. Analytical methods

For molecular gas composition monitoring, samples were analysed using a Shimadzu GC-8A FID with 100/120 mesh ShinCarbon 73 ST micropacked column for CH_4 and CO_2 analysis and a Shimadzu GC-8A TCD with a 80/100 mesh Molecular Sieve 5A column for O_2 and N_2 analysis. Calibrations for both GCs were performed using external gas standards (BOC).

Headspace temperatures were measured by an infrared thermometer (Testo-model 830-T1) and the pressure was monitored using an Omega gauge (Omega, model DPG 1001B-15G). Pressure and temperature were measured at the start and the end of the 24 h incubation period.

2.4.1. Isotope analysis

Like the molecular components, the concentration of the isotope $\delta^{13}C$-CO_2 in the blended gas depends on the rate of each reac-

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