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Adsorption and transport of methane in landfill cover soil amended with waste-wood biochars

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ABSTRACT

The natural presence of methane oxidizing bacteria (MOB) in landfill soils can stimulate the bio-chemical oxidation of CH_4 to CO_2 and H_2O under suitable environmental conditions. This mechanism can be enhanced by amending the landfill cover soil with organic materials such as biochars that are recalcitrant to biological degradation and are capable of adsorbing CH_4 while facilitating the growth and activity of MOB within their porous structure. Several series of batch and small-scale column tests were conducted to quantify the CH_4 sorption and transport properties of landfill cover soil amended with four types of waste hardwood biochars under different levels of amendment percentages (2, 5 and 10% by weight), exposed CH_4 concentrations (0–1 kPa), moisture content (dry, 25% and 75% water holding capacity), and temperature (25, 35 and 45 °C). The linear forms of the pseudo second-order kinetic model and the Langmuir isotherm model were used to determine the kinetics and the maximum CH_4 adsorption capacity of cover materials. The maximum CH_4 sorption capacity of dry biochar-amended soils ranged from 1.03×10^{-2} to 7.97×10^{-2} mol kg^{-1} and exhibited a ten-fold increase compared to that of soil with 1.9×10^{-3} mol kg^{-1}. The isosteric heat of adsorption for soil was negative and ranged from −30 to −118 kJ/mol, while that of the biochar-amended soils was positive and ranged from 24 to 440 kJ/mol. The CH_4 dispersion coefficients for biochar-amended soils obtained through predictive transport modeling indicated that amending the soil with biochar enhanced the methane transport rates by two orders of magnitude, thereby increasing their potential for enhanced exchange of gases within the cover system. Overall, the use of hardwood biochars as a cover soil amendment to reduce methane emissions from landfills appears to be a promising alternative to conventional soil covers.

1. Introduction

Landfill gas (LFG) mainly comprises greenhouse gases (GHGs) such as CH_4 and CO_2 in equal volumetric ratio (50% v/v) and are produced by the decomposition of waste under limited oxygen environments. LFG emissions significantly contribute to global warming and its associated negative impacts. CH_4 is considered to be a much powerful GHG with a Global Warming Potential (GWP) of 28 over a 100 yr time scale when compared to CO_2 (IPCC, 2013). Landfills are ranked third highest among the potential anthropogenic sources for CH_4 emissions in the U.S. The use of engineering controls such as gas collection and flaring systems aim to achieve effective capture and re-use of methane as an energy source. The use of engineered, bio-based cover systems in combination with collection systems during its active phase, or just the use of bio-based cover systems in case of an old and/or abandoned landfill, can help minimize the overall CH_4 emissions. A holistic approach needs to be adopted for an effective design of bio-based cover system in which, considerable reduction in CH_4 emissions can be achieved by a combination of both, adsorption as well as biochemical oxidation processes (Sadasivam and Reddy, 2014).

The use of organic amendments to landfill cover soils enhances the CH_4 oxidation rates and reduces the CH_4 fluxes emitted from landfills (Park et al., 2004; Stern et al., 2007; Nikiema et al., 2007; Huber-Humer et al., 2008, 2009; Pedersen et al., 2011; Scheutz et al., 2011; Roncato and Cabral, 2011). Albeit the addition of organic rich compost amendments to landfill cover soils enhances the microbial methane oxidation capacity, exo-polymeric substances form over time within the cover system that clog the pores and hinder the diffusion of gases (Wilshusen et al., 2004; Hilger et al., 2000; Powelson et al., 2006). In order to design an efficient

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biocover system for methane emissions from landfills, a stable biocover material needs to be selected where the material has a high porosity with the capability to enhance the methane adsorption capacity as well as favor the growth of methanotrophs and promote the microbial methane oxidation process. Limited studies have been conducted that investigate such porous, organic amendments, which have a high potential for the adsorption of CH_4 and also facilitate enhanced gas transport properties that can together increase the CH_4 oxidation rates by minimizing the adverse impacts due to the clogging of pores (Sadasivam and Reddy, 2014).

Biochar is a porous, organic material produced by the pyrolysis or gasification of waste biomass (Lehmann and Joseph, 2009). The process of biomass conversion and the treatment conditions are based on the desired end product, which can be biofuel for energy (Lehmann, 2007) or biochar for the purpose of environmental management (Lal, 2004; Lehmann and Joseph, 2009). The physicochemical properties of biochars are controlled by the initial characteristics of the feedstock, reactor treatment conditions such as temperature and residence time and also the post-treatment processes (if any) such as activation (Lua et al., 2004; Boateng, 2007). The porosity and specific surface area of biochars are dictated by the highest treatment temperature (Brown et al., 2006) and post-processing such as activation (Zhang et al., 2004). The increased presence of micropores in biochars makes it highly preferable for gas adsorption purposes (Rouquerol et al., 1999). Biochars, when used as a soil amendment, have a high potential to increase the sorption ability of soils mainly due to their pyrogenic production process. Several studies that compared the sorption properties of pyrogenic and non-pyrogenic or fresh biomass have found that the sorption ability of pyrogenic substances such as biochars is a couple of orders of magnitude higher than that of fresh biomass (Baring et al., 2002; Huang et al., 2003; Nguyen et al., 2004). The highly porous structure of biochars was previously shown to favor the growth and activity of methanotrophs when amended to a cover soil and enhance the potential for increased methane oxidation (Reddy et al., 2014).

The purpose of this study is to investigate and compare the CH_4 sorption and transport properties of four waste-wood derived biochars amended to landfill cover soil at varying percentages (2, 5 and 10% by weight) as opposed to that of soil when used solely as a cover material. The specific objectives of this study are to: (1) quantify the kinetic rate of CH_4 adsorption and the maximum methane adsorption capacity of landfill cover soil and biochar-amended landfill cover soils under three levels of moisture (dry, 25% WHC and 75% WHC) and temperature (25 °C, 35 °C and 45 °C); (2) determine the effects of moisture, temperature and biochar-amendment percentages on CH_4 adsorption and transport; and (3) determine the effect of landfill gas (LFG) inflow rate and presence of moisture on the CH_4 transport and diffusion through soil and biochar-amended soils. The results from this study can help identify the potential use of biochars as amendments to landfill soil with the aim of achieving effective methane mitigation.

2. Materials and methods

2.1. Biochars and soil

Four types of biochars produced from waste-wood were chosen for this study based on preliminary screening and tests conducted on seven waste-wood biochar types (Yargicoglu et al., 2015). The waste-wood biochars were obtained from Chip Energy Inc. (Goodfield, IL) in 5-gallon buckets, and were stored in labeled, airtight containers. The biochars were produced by gasification using an updraft gasifier at a temperature of about 500 °C. The feedstock for all the biochars was hardwood either in the chipped or pelleted forms. The fine ash fraction of the pelleted hardwood was retained in the case of CE-WP1, whereas, the ash fraction was sieved in the case of CE-WP2. CE-AWP was made out pelleted hardwood and the biochar was allowed to age under room temperature in a sealed drum for 3 years prior to its use in this study. CE-WC was made of hardwood chips. The cover soil for the biochar amendment studies was obtained from the top 12 inches of an intermediate cover area in a DeKalb County, IL landfill. The cover soil was sieved using a 2 mm mesh and the fraction of soil passing the sieve was homogenized and stored in plastic bags at 4 °C prior to usage. All the test materials were autoclaved using a Napco® model 8000-DSE autoclave at 121 °C for 30 min for two consecutive days (Bennett et al., 2003) and were sealed at 22 °C for 24 h between autoclave treatments (Carter et al., 2007) prior to conducting adsorption experiments.

2.2. Physicochemical characterization testing

In this study, the physicochemical properties of soil and biochar-amended soils were characterized in accordance with specific ASTM methods. The test materials were characterized for pH (ASTM D 4972), moisture content (MC) (ASTM D2216), organic content (OC) (ASTM D2974 by Loss-on-Ignition), average particle size (ASTM D422), specific gravity (SG) (ASTM D854), water holding capacity (WHC) (ASTM D2980), and dry density (ASTM D2937). All the physical-chemical characterization tests were conducted in duplicate on the sterilized materials. SEM images of soil and biochars were used to quantify the porosities using Particles (Pores) and Cracks Analysis System (PCAS) software (Liu et al., 2011). Elemental C was determined using Perkin Elmer Elemental Analyzer. Further details on the characterization test procedures can be found in Yargicoglu et al. (2015).

2.3. Batch adsorption testing

Batch adsorption tests were conducted to determine the methane adsorption capacity of soil and biochar-amended soils under different levels of MC, temperature and exposed methane concentrations. Sterilization was performed on the materials prior to the adsorption tests to eliminate microbial interference on methane adsorption during the tests. A total of 5 g of the test material was placed inside 250 ml amber glass bottles and sealed tight using long sleeved rubber stoppers. Then, 10, 25, 40, 50, 75, and 100 ml of air from the headspace of the test units was replaced with respective volumes of synthetic landfill gas comprising 50% CH_4 and 50% CO_2 in order to achieve headspace CH_4 concentrations of 2, 5, 8, 10, 15, and 20% (v/v), respectively. Control test units were set up similar to the sample test units that did not include the adsorbents, to determine the initial CH_4 headspace concentration (v/v) achieved for each experimental set. In order to determine the effects of biochar-amendment percentages on CH_4 adsorption, three amendment levels (2, 5 and 10% w/w) were selected by mixing the appropriate mass of biochars to the soil, keeping the total mass of the amended cover material constant at 5 g for all the tests. To determine the effects of moisture content on the methane adsorption, test units were set up that followed the procedure above, but with the addition of measured volumes of de-ionized water using a calibrated pipette to achieve moisture levels of 25 and 75% with respect to the biochar's WHC based on dry weight. The temperature in the test units was maintained at 25 °C and the CH_4 gas pressure ranged from 0.15 to 1 KPa for all the tests conducted to study the effects of MC on the adsorption of CH_4 onto cover materials. A hydrometer water bath (Model H − 4239A) manufactured by Humboldt Co. was used to maintain the specified