



Effect of Methanotrophic-Activated Biochar-Amended Soil in Mitigating CH₄ Emissions from Landfills

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Abstract

Laboratory based long-term batch incubation study was carried out to assess the methane (CH₄) uptake or removal capacity in the landfill cover soil, biochar-amended cover soil, and methanotrophic-activated biochar-amended cover soil. The soil was amended with biochar or activated biochar in two proportions: 2% and 10% by weight. The results indicate that the methanotrophic-activated biochar-amended soil exhibited higher CH₄ uptake and oxidation rates when compared to soil and biochar-amended soil. The 10% methanotrophic-activated biochar-amended soil showed the highest CH₄ uptake with the CH₄ oxidation rate of 518.6 µg CH₄/g/day and the landfill cover soil showed the least uptake with the CH₄ oxidation rate of 88 µg CH₄/g/day. Overall, this study demonstrates that the biochar activated with methanotrophs expedited the CH₄ uptake process when compared to non-activated biochar-amended soil that takes longer time for microbial colonization and acclimatization. Furthermore, column studies and field scale studies under dynamic environmental conditions are being undertaken to evaluate the maximum removal of CH₄ under typical landfill conditions.

Keywords: Activated biochar; biochar; biocover; landfill cover soil; methane emissions; methanotrophs; methane oxidation

Introduction

Municipal solid waste (MSW) landfills are regarded as the third largest anthropogenic source of methane (CH₄) emissions in the United States. The landfill gas (LFG), generated due to the anaerobic decomposition of the organic fraction in the waste, typically comprises of 50% CH₄ and 50% CO₂ (carbon dioxide) by volume, both of which are major greenhouse gases causing global climate change. The CH₄ emissions from the landfills are known to be partially converted to CO₂ by the naturally existing CH₄ oxidizing bacteria (methanotrophs) in the cover soil. For nearly two decades, many researchers investigated the CH₄ oxidation capacity of the landfill cover soils based on batch tests, small-scale to near full-scale column tests, and field-scale tests (Sadasivam and Reddy, 2014).

In recent years, a number of studies have investigated a variety of amendments to landfill cover soil to enhance CH₄ oxidation and promote microbial activity (Mor et al., 2006; Stern et al., 2007; Scheutz et al., 2011; Pedersen et al., 2011; Sadasivam and Reddy, 2014).



Previous research indicates organic amendments such as compost or biosolids can increase CH₄ oxidation rates by enhancing the growth of methanotrophs (Wilshusen et al., 2004; Stern et al., 2007; Scheutz et al., 2009). However, the use of compost over long term is susceptible to degradation and has been identified with performance issues such as pore clogging due to exopolymeric substance (EPS) formation and reduced activity due to heterotrophic bacteria (Sadasivam and Reddy, 2014). Hence, a more stable material “biochar”, which is less prone to degradation and has good physico-chemical properties supporting microbial growth, was investigated in our laboratory as a soil amendment in biocovers (Reddy et al., 2014). Biochar is a carbon-rich solid product obtained from pyrolysis or gasification in the absence of oxygen. Studies from our laboratory have demonstrated biochar amendment to be effective in increasing methanotrophic population and promoting CH₄ oxidation in the long term due to its high porosity and surface area, which makes it a suitable habitat for methanotrophic bacterial growth and multiplication (Yaghoubi, 2012; Reddy et al., 2014; Yargicoglu et al., 2015; Yargicoglu and Reddy, 2017). However, microbial colonization and acclimatization in the biochar-amended soil was found to take relatively longer time in oxidizing CH₄. The present study investigates the use of methanotrophic-activated biochar-amended soil in comparison to non-activated biochar-amended soil in order to expedite the CH₄ oxidation process in the landfill biocovers and mitigate CH₄ emissions in MSW landfills.

Materials and Methodology

Materials

Soil

Soil was collected from Zion landfill site, located in Zion, Illinois, USA. Soil samples were collected from an interim cover at a depth of ~1 to 2 feet and were shipped to the Geotechnical and Geoenvironmental Engineering Laboratory at the University of Illinois at Chicago (UIC) where it was stored at room temperature (23 ± 2°C). Soil samples were air dried (moisture content <0.5%), pulverized and screened through a 2 mm sieve prior to conducting the experiments.

Biochar

Biochar was obtained from a commercial vendor in Illinois, USA. The biochar used in this study was produced from waste pinewood subjected to gasification at a high temperature of ~520°C. In this study, biochar in pellet form was used with fines sieved and discarded. The biochar was oven-dried at 105°C to remove any moisture content before conducting the experiments.

Methodology

Methanotrophic Culture Consortium

The methanotrophic mixed culture consortium was prepared by enriching landfill cover soil in modified Nitrate Mineral Salts (NMS) (Whittenbury et al., 1997) and a mixture of 7% CH₄, 7%



CO₂ balanced in air at a room temperature of 23°C. The culture consortium was then used for microbial colonization in the biochar.

Activating Biochar with Culture Consortium

The biochar was activated with methanotrophs by inoculating 10 g of biochar pellets in 10 mL of culture consortium, in the presence of 5% (v/v) CH₄ and 5% (v/v) CO₂ in 90% of air and was incubated at a room temperature of 23°C under static condition. The headspace gas concentrations were monitored regularly by collecting and analyzing the gas samples using gas chromatography (GC) until the headspace concentration dropped to less than 1%. The CH₄ oxidation rates were calculated from the linear regression analysis of CH₄ concentration versus elapsed time, based on the zero-order kinetics.

Long Term Batch Incubation Tests

For these tests, 10 g of the total material was placed in 125 mL-serum vials and the moisture content was adjusted to 40% (w/w) using deionized water (field capacity of the soil), except activated biochar that was soaked in the culture. The soil was amended with 2% and 10% (w/w) of non-activated biochar or methanotrophic-activated biochar. The vials were sealed airtight using butyl rubber septa and secured using crimp caps. Next, 20 mL of air from the headspace was replaced with equal volume of synthetic landfill gas comprising of 50% (v/v) CH₄ and 50% (v/v) CO₂ to achieve a headspace concentration of ~5-6% CH₄ (v/v), ~5-6% CO₂ (v/v) and a balance (~88-90%) of air. The change in the headspace gas concentrations were determined by collecting and analyzing the gas samples on a regular basis using gas chromatography (GC) until the headspace concentration dropped to less than 1%. Each time the vials were flushed with air to remove the CO₂ produced and replenished with ~5-6% (v/v) CH₄ and ~5-6% (v/v) CO₂ in ~88-90% of air to analyze the long-term microbial activity and evaluate the oxidation rates. All the experiments were conducted in triplicate along with the controls (with synthetic LFG without any material).

Gas Analysis

The gas samples were analyzed at regular time intervals using an SRI 9300 GC equipped with a thermal conductivity detector (TCD) and CTR-1 column capable of separating CH₄ and CO₂. Gas samples were withdrawn using 1 mL syringe where 0.5 mL of the sample was discarded and remaining 0.5 mL was injected into the GC to reduce any pressure effects due to sampling. A calibration curve for a minimum of three points was established using high purity standard gas mixtures ranging from 1% to 50% (v/v) CH₄ and CO₂.

Results and Discussion

Figure 1 shows typical CH₄ removal response by the methanotrophic-activated biochar. As seen, a gradual decrease in the headspace CH₄ concentration with time was observed in the first stage (before second replenishment). A second replenishment with the mix gas (CH₄/CO₂/Air) was performed on 7th day of the experiment to keep the microbes active and to analyze the CH₄ uptake trend in long term. The methanotrophic-activated biochar showed similar CH₄ uptake

rate as in the first phase (before replenishment), indicating that the biochar was successfully colonized with methanotrophs and were not affected by substrate diffusion, thereby persisting CH_4 oxidation.

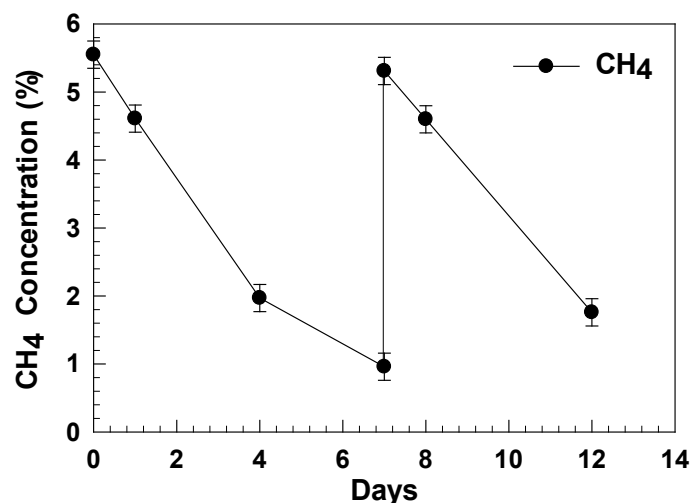


Figure 1. Typical methane removal response by methanotrophic-activated biochar

The long-term experiments were conducted in three phases: Phase I, Phase II, and Phase III. These phases and the corresponding results are described below:

Phase I Testing

In Phase I, the experiments were carried out for ~90-95 days. The CH_4 uptake/consumption and rates were calculated for each replenishment. The following experimental sets were investigated: soil, biochar-amended soil (2% w/w), biochar-amended soil (10% w/w), methanotrophic-activated biochar-amended soil (2% w/w), and methanotrophic-activated biochar-amended soil (10% w/w).

Figure 2(a) compares the cumulative uptake of CH_4 in the first 30 days for each experimental set. The methanotrophic-activated biochar-amended soil showed highest CH_4 uptake among all the experimental sets; the test with 10% methanotrophic-activated biochar-amended soil exhibiting highest CH_4 uptake (3371 $\mu\text{g CH}_4/\text{g}$) followed by the 2% methanotrophic-activated biochar-amended soil (2341 $\mu\text{g CH}_4/\text{g}$). The soil alone and 2% biochar-amended soil showed similar uptakes (1323 and 1311 $\mu\text{g CH}_4/\text{g}$, respectively), and the 10% biochar-amended soil showed an uptake of 1278 $\mu\text{g CH}_4/\text{g}$. The results from the methanotrophic-activated biochar suggests that the methanotrophs colonized in the biochar were in their growth phase and were able to oxidize CH_4 when amended with soil without substrate limitation to the microbes. On the other hand, in the biochar-amended soil, the CH_4 oxidizing bacteria present in the soil were not acclimated to the biochar, which could be the reason for the lower CH_4 uptake.

The CH_4 oxidation rates for all the experimental sets were calculated based on the zero-order kinetics. The average CH_4 oxidation rates for the initial 30 days in soil, 2% biochar-amended soil, 10% biochar-amended soil, 2% methanotrophic-activated biochar-amended soil,



and 10% methanotrophic-activated biochar-amended soil were 46.4 $\mu\text{g/g/day}$, 45.6 $\mu\text{g/g/day}$, 36 $\mu\text{g/g/day}$, 81.8 $\mu\text{g/g/day}$ and 111.8 $\mu\text{g/g/day}$, respectively. The CH_4 oxidation rates in soil and biochar-amended soil were similar which implies that the biochar was not initially colonized with the methane oxidizing bacteria (MOB), thereby showing similar trend as the soil. Whereas, in the methanotrophic-activated biochar-amended soil, the CH_4 oxidation rates were $\sim 1.7 - 3.1$ times of soil/biochar-amended soil due to the combined effect of colonization of the microbes in the biochar and the pre-existing MOB in the soil resulting in enhanced CH_4 uptake in the system.

Figure 2(b) shows the cumulative uptake of CH_4 in the experimental sets extended to time interval of 60 days. The 10% methanotrophic-activated biochar-amended soil showed continued increase in the CH_4 uptake (7287 $\mu\text{g CH}_4/\text{g}$) followed by the 2% methanotrophic-activated biochar-amended soil (4466 $\mu\text{g CH}_4/\text{g}$). Both of the biochar-amended soil sets (2% and 10%) showed similar cumulative CH_4 uptake (3243 $\mu\text{g CH}_4/\text{g}$) and the soil alone system showed the lowest CH_4 uptake (2727 $\mu\text{g CH}_4/\text{g}$) among all. The CH_4 oxidation rates also increased significantly at an interval of 60 days and resulted to be 139.2 $\mu\text{g/g/day}$ in 10% methanotrophic-activated biochar-amended soil and 92 $\mu\text{g/g/day}$ in 2% methanotrophic-activated biochar-amended soil. The 10% and 2% biochar-amended soil showed significant increase in the CH_4 oxidation rates from 36.01 $\mu\text{g/g/day}$ to 68.1 $\mu\text{g/g/day}$ and 45.6 $\mu\text{g/g/day}$ to 67.4 $\mu\text{g/g/day}$, respectively. It suggests colonization of the MOB in the biochar in the long run thereby amplifying CH_4 oxidation rates. On the other hand, the soil alone system did not show significant increase in CH_4 oxidation rates (from 46.44 $\mu\text{g/g/day}$ to 49.8 $\mu\text{g/g/day}$) which further confirms the role of biochar in the colonization of MOB in the long run.

Figure 2(c) shows the cumulative uptake of CH_4 in the experimental sets for further extended time interval of 90 days for soil and biochar-amended soils. The 10% biochar-amended soil showed significant increase in the CH_4 uptake (7221 $\mu\text{g CH}_4/\text{g}$) when compared to 2% biochar-amended soil (6279 $\mu\text{g CH}_4/\text{g}$) and soil alone system (5599 $\mu\text{g CH}_4/\text{g}$). The corresponding CH_4 oxidation rates at this time interval were 140.7 $\mu\text{g/g/day}$, 104.8 $\mu\text{g/g/day}$ and 98.5 $\mu\text{g/g/day}$. The biochar-amended soil showed significant increase in the CH_4 uptake and oxidation rates in the long run which is in agreement with the previous study from our lab by Yargicoglu and Reddy (2017). It is to be noted that no data was available for methanotrophic-activated biochar-amended soil at this time interval, as these experimental sets were started 30 days later than the tests with soil and biochar-amended soil systems.

Phase II Testing

In Phase II, all the experimental sets were incubated by flushing the gas mixture of $\text{CH}_4/\text{CO}_2/\text{air}$ on a weekly basis at a room temperature of 23°C without analyzing the samples for a period of 2 months. This phase allowed a long-term incubation of methanotrophs in the experimental sets.

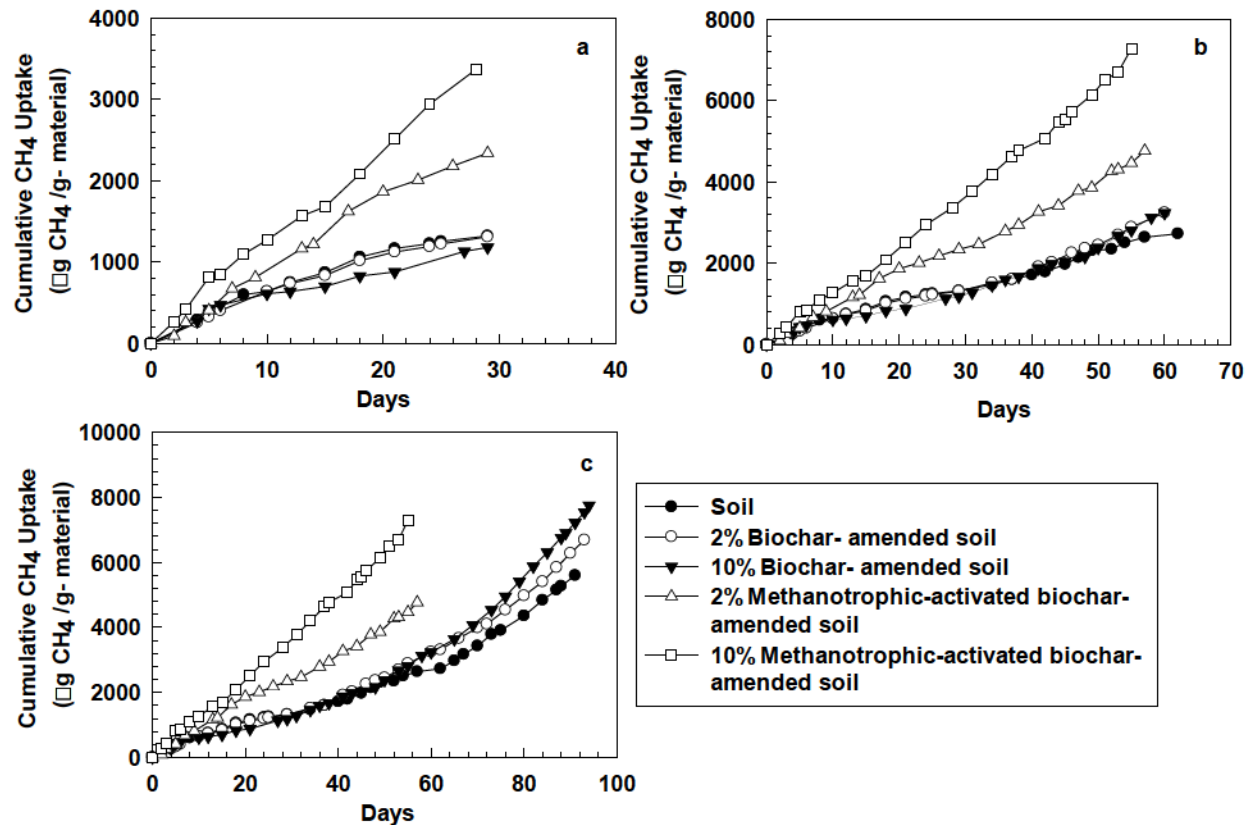


Figure 2. Phase I testing showing cumulative uptake of methane in soil, 2% biochar-amended soil, 10% biochar-amended soil, 2% methanotrophic-activated biochar-amended soil, and 10% methanotrophic-activated biochar-amended soil during test duration of: (a) 30 days, (b) 60 days, and (c) 90 days

Phase III Testing

In Phase III, the gas samples from all the experimental sets were analyzed on a regular basis to evaluate the performance of these systems after long-incubation period during Phase II. **Figure 3** shows the cumulative CH_4 uptake in the experimental sets after Phase II incubation period for an interval of 30 days. These results show that the 10% and 2% methanotrophic-activated biochar-amended soil systems continued to consume CH_4 at a faster rate when compared to the results from Phase I with a cumulative CH_4 uptake of $16039 \mu\text{g CH}_4/\text{g}$ and $5969 \mu\text{g CH}_4/\text{g}$, respectively. However, soil and biochar-amended soil showed reduced and steady uptake of CH_4 throughout phase III, with a total CH_4 uptake of $3924 \mu\text{g CH}_4/\text{g}$, $2960 \mu\text{g CH}_4/\text{g}$ and $2756 \mu\text{g CH}_4/\text{g}$ in 10% biochar-amended soil, 2% biochar-amended soil and soil system, respectively. The plausible explanation for reduced CH_4 uptake during post-incubation could be that the microbes may have reached their capacity to further consume the substrates and reached stationary or death phase following a typical bacterial growth curve. The CH_4 oxidation rates in 2% ($169.2 \mu\text{g/g/day}$) and 10% ($518.6 \mu\text{g/g/day}$) methanotrophic-activated biochar-amended soil were ~ 1.8 – 3.7 times the rates before incubation period (Phase I). Whereas, in soil and biochar-amended soil, the CH_4 oxidation rates declined after 2 months of incubation to a steady state condition with CH_4 oxidation rate of $88.3 \mu\text{g/g/day}$, $97.4 \mu\text{g/g/day}$ and $116.1 \mu\text{g/g/day}$ in

soil alone, 2% biochar-amended soil and 10% biochar-amended soil, respectively. Similar trends of peak oxidation rates followed by a decline in the oxidation rates leading to a lower steady state values were reported in many column studies (Kightley et al., 1995; Hilger et al., 1999; Scheutz and Kjeldsen, 2003; Streese and Stegmann, 2003; Wilshusen et al., 2004; Yargicoglu and Reddy, 2017) and was attributed to the production of EPS, impeding substrate/nutrients transfer to the microbes (Hilger et al., 2000) or loss of moisture content. Our studies cannot confirm if production of EPS had limited CH_4 oxidation capacity in the soil or biochar-amended soil. Therefore, further tests determining the production of EPS are needed. However, loss of moisture due to air flushing from our samples that extended for > 150 days could be one of the factors causing decline in the CH_4 oxidation rates. As the final moisture content of all the samples at the end of the experiment showed significant loss of moisture by ~13-18%.

Figure 4 shows the average CH_4 uptake rates for each gas replenishments with respect to time in soil, biochar-amended soil (2% & 10%), methanotrophic-activated biochar-amended soil (2% & 10%). All the systems showed decline or steady state condition in the beginning of the tests for a period of 20-30 days reflecting adaptation stages in the microbial growth (**Figure 4**). Thereafter, the samples showed increase in the oxidation rates that follows typical growth phase in the bacteria. After two months of incubation, all the experimental sets showed a decline or steady state in the oxidation rates which was followed by a stationary phase similar to the bacterial growth curve, except 10% methanotrophic-activated biochar-amended soil which showed increased uptake rates. The reason could be that the microbes were still in their growth phase and had not reached stationary phase.

Overall, these results demonstrate that the methanotrophic-activated biochar-amended soil showed significant potential in accelerating the CH_4 removal process when compared to soil or biochar-amended soil that takes time for colonization and acclimatization in the biochar. Similarly, 10% methanotrophic-activated biochar-amended soil performed better than the 2% methanotrophic-activated biochar-amended soil in removing CH_4 from the systems which suggests higher proportion of biochar amendment is beneficial in enhancing CH_4 oxidation.

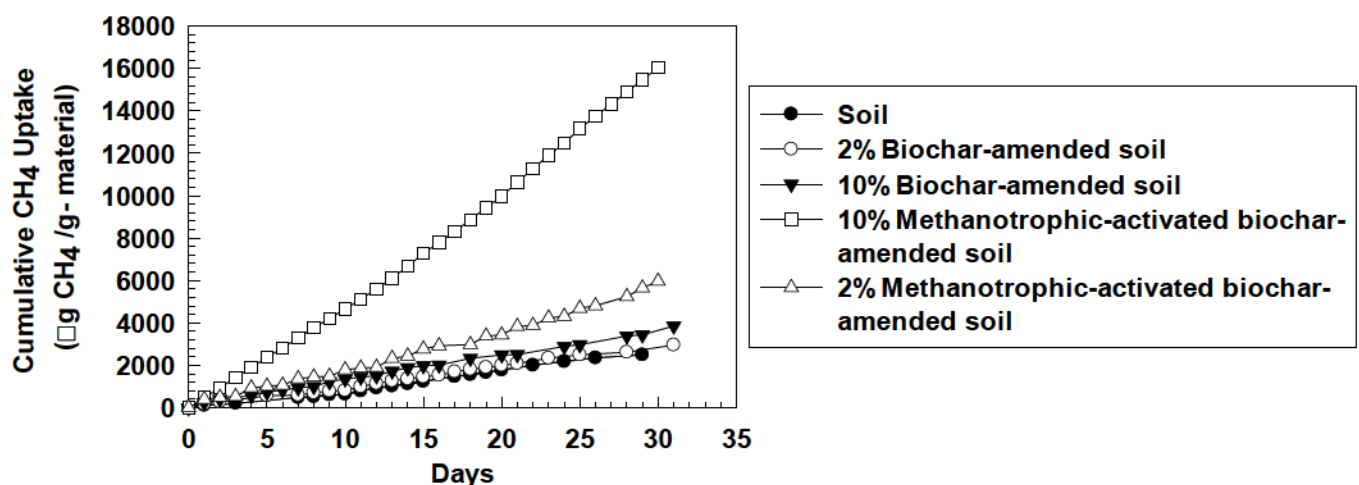


Figure 3. Phase III testing showing cumulative uptake of methane: soil, 2% biochar-amended soil, 10% biochar-amended soil (10% w/w), 2% methanotrophic-activated biochar-amended soil, and 10% methanotrophic-activated biochar-amended soil

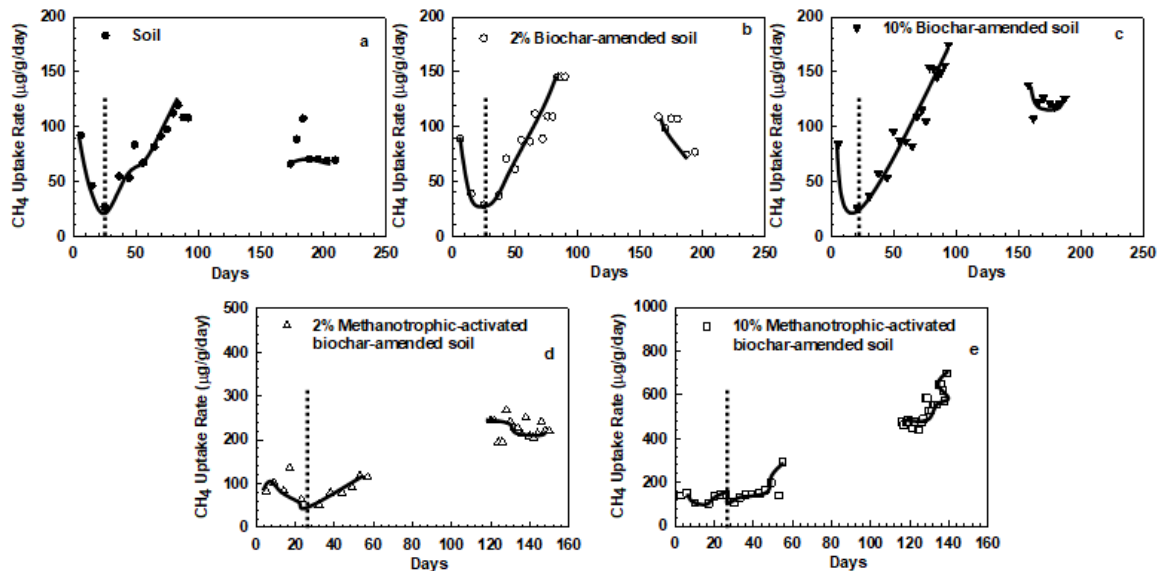


Figure 4. Average methane uptake rates for each gas replenishment with time in (a) soil, (b) biochar-amended soil (2% w/w), (c) biochar-amended soil (10% w/w), (d) methanotrophic-activated biochar-amended soil (2% w/w), and (e) methanotrophic-activated biochar-amended soil (10% w/w)

Conclusions

The biochar-amended soil and methanotrophic-activated biochar-amended soil at two different proportions (2% and 10%) were assessed to study the CH_4 uptake or removal capacity. The results demonstrate that the methanotrophic-activated biochar-amended soil had significant potential in the removal or uptake of CH_4 when compared to non-activated biochar-amended soil. Of which, the 10% methanotrophic-activated biochar-amended soil showed improved uptake of CH_4 over 2% methanotrophic-activated biochar-amended soil. The CH_4 oxidation rates at the end of the study resulted to be in the following order $518.6 \mu\text{g/g/day} > 169.2 \mu\text{g/g/day} > 116.1 \mu\text{g/g/day} > 97.4 \mu\text{g/g/day} > 88.3 \mu\text{g/g/day}$ for 10% methanotrophic-activated biochar-amended soil, 2% methanotrophic-activated biochar-amended soil, 10% biochar-amended soil, 2% biochar-amended soil and soil, respectively. Overall, this study demonstrated that when the biochar is activated with methanotrophs and amended with soil, the CH_4 removal is faster when compared to biochar-amended soil and therefore can be used to mitigate landfill CH_4 gas emissions. However, column and field-scale studies are recommended to evaluate the efficiency of methanotrophic-activated biochar-amended soil in the removal of CH_4 under dynamic field conditions.

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