Enhanced Landfill Methane Oxidation Using Activated Biochar

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ABSTRACT

Biochar, a solid porous product derived from waste biomass, has garnered profound attention from the geoenvironmental engineers in the recent years, due to its ability to absorb wide range of gaseous and liquid phase contaminants. One important application of biochar that has been explored recently is the use in landfill cover soil to enhance microbial methane oxidation. The unique properties of biochar such as high-internal porosity, high-moisture retention, and presence of recalcitrant carbon compounds offer conducive environment for the methane oxidizing microbes to proliferate and thrive in the long-term exposure to landfill methane, thereby enhancing aerobic methane oxidation and mitigating landfill methane emissions. Although biochar has shown promising potential to enhance methane oxidation, the addition of inert biochar in the landfill cover soil leads to an initial lag phase due to the time required for microbial acclimation and may result in lower methane oxidation rates in comparison to the soil alone which has already been exposed to the landfill gas. However, once the microbes are acclimated, the effect of biochar kicks in and transcends the capacity of soil alone to oxidize landfill methane. This paper investigates reduction of the initial lag phase caused by addition of inert biochar using an activated biochar. Activated biochar was prepared by soaking biochar in a methanotrophic bacterial consortium isolated from a landfill cover soil. Several series of laboratory batch and column experiments were performed with activated biochar amended soil, non-activated biochar amended soil, and unamended soil to quantify methane oxidizing potential. DNA based 16S rRNA gene amplicon sequencing was performed to characterize and compare the microbial community. The activated biochar amended soil showed higher methane oxidation rates and efficiency from the beginning of the incubation in batch and column experiments in comparison to the non-activated biochar amended and unamended soils. The cumulative methane uptake of 10% non-activated biochar amended soil was lower than the unamended soil until initial 50 days of batch incubation which increased rapidly thereafter. The carbon dioxide generation and significant increase in methylotrophic relative abundance confirmed methane oxidation. Overall, the activated biochar showed promising potential to reduce the initial lag phase and enhance microbial methane oxidation in landfill cover soil.

Keywords: activated biochar; landfill cover; methane emissions; methanotrophic bacteria; methane oxidation

INTRODUCTION

Municipal solid waste (MSW) landfills are the third-largest source of anthropogenic methane (CH_4) emissions in the US) and CH_4 is a highly potent greenhouse gas with 36 times more heat

trapping potential that that of carbon dioxide (CO_2) (USEPA 2021. Landfill gas (LFG) is composed of nearly 50% (*v/v*) methane, 50% (*v/v*) carbon dioxide (CO_2) and small amount of non-methane organic compounds (USEPA 2021). Biologic oxidation of CH_4 has been an attractive and most explored technique for mitigation of CH_4 emissions from the MSW landfills. Due to continuous exposure to CH_4 emanating from the waste, landfill cover soils are enriched with methane-oxidizing microorganisms called methanotrophs which oxidize CH_4 in the presence of oxygen (O_2) and release carbon dioxide (CO_2) (Reddy et al. 2019; Yargicoglu and Reddy 2017a; Abushammala et al. 2014; Bogner et al. 2011). However, the CH_4 oxidation capacity of landfill cover soil is affected by various environmental and physical factors (Scheutz and Kjeldsen 2004; Abushammala et al. 2014). In the recent years, attempts have been made to enhance the methanotrophic methane-oxidation capacity of landfill cover soils in the form of biocover by adding various amendments such as compost (e.g., Mor et al. 2006; Huber-Humer et al. 2011), sewage sludge (e.g., Contin et al. 2012), and biochar (Reddy et al. 2014; Yargicoglu and Reddy 2018) and improving the physical properties of the soil.

Biochar is a solid carbonaceous product produced by pyrolysis of biomass (Xie et al. 2016). Biochar has become an attractive choice for enhancing soil fertility, adsorption of contaminants and for carbon sequestration applications (Clough and Condron 2010). Because biochar has recalcitrant form of carbon, it has potential for long-term use than other organic amendments such as compost in the biocover. In addition, biochar is characterized with favorable properties such as high internal porosity, high surface area, and high moisture retention capacity which are conducive for enhancing microbial growth and activity in landfill cover soil (Yargicoglu and Reddy 2017b). Biochar amendment in landfill cover soil has shown enhanced methanotrophic activity and higher CH_4 oxidation rates in both laboratory incubations and field studies (Reddy et al. 2014, 2017a, b, 2018, 2021).

Although biochar has shown remarkable potential in enhancing microbial methane oxidation in the long-term, the biochar amendment in landfill cover soil shows an initial lag phase due to microbial adaptation resulting in lower CH_4 oxidation rates in the beginning of the incubation. Hence, the main aim of the study is to activate the inert biochar with the methane-oxidizing bacterial (MOB) consortium prepared from the enrichment of landfill cover soil. The activated biochar is then used to amend the landfill cover soil and assess its CH_4 oxidation potential through incubations in batch reactors and column reactors under simulated LFG conditions. The study also aims to characterize and compare the microbial community structure of the MOB activated biochar amended soils along with the non-activated biochar and landfill cover soil control.

MATERIALS AND METHODS

The landfill cover soil used in the study was obtained from intermediate cover from Zion Landfill, Illinois, USA. The soil was air dried, pulverized and screened through 4.75 mm sieve to remove large particles. Biochar used in the study was derived from waste pine wood (Chip Energy, IL, USA). The MOB consortium was prepared in the laboratory by enriching the landfill cover soil in modified Nitrate Mineral Salts and mixture of CH_4, and CO_2 balanced in air (Rai et al. 2019). Biochar was activated following procedure mentioned in Rai et al. (2019). In summary, the biochar pellets were soaked in the MOB consortium in a 500 L glass bottle and the headspace was supplied with CH_4 and CO_2 gas mixture balanced in air. The headspace CH_4 concentration was monitored to gauge the methanotrophic activity of the activated biochar.

Batch Incubation Tests. Nearly 10 g of test material was placed in a 125 mL serum vial and moisture content was adjusted to 40% (*w/w*) (field capacity) using deionized water. Five combinations of biocover substrates were tested in batch incubation: 1) landfill cover soil alone (SC); 2) landfill cover soil + 2% (*w/w*) non-activated biochar (S2B); 3) landfill cover soil + 10% (*w/w*) non-activated biochar (S10B); 4) landfill cover soil + 2% (*w/w*) MOB activated biochar (S2AB); and 5) landfill cover soil + 10% (*w/w*) MOB activated biochar (S10AB). Vials were hermetically sealed with butyl rubber septa and aluminum crimps. Following that, 20 mL of air was withdrawn from the headspace and replaced with same volume of mixture of 50% (*v/v*) CH_4 and 50% (v/v) CO_2 to obtain headspace concentration of ~6% CH_4 and 6% CO_2 balanced in air. The headspace concentrations of CH_4, CO_2 and O_2 were monitored regularly using gas chromatography (GC) until the CH_4 concentration dropped to less than 1% (*v/v*). When the headspace CH_4 depleted, the vials were flushed with air and replenished with ~6% CH_4 and ~6% CO_2 following similar procedure as explained above to evaluate the CH_4 oxidation rates and microbial activity of the cover substrates in the long-term. Each sample was prepared in triplicate along with the controls (with LFG and without any material). The incubation was continued for 90 days for soil and non-activated biochar amended soil samples and for 60 days for activated biochar amended soil samples.

Column Experiment Set up. Three columns made of acrylic tubing with inside diameter of 18.42 cm and height 100 cm were used in column incubation. The top and bottom were sealed with flanged lids fitted with rubber O-rings. A 25 cm thick gas distribution layer (GDL) made of pea gravel was placed at the bottom of each column. A 20 cm thick lightly compacted biocover layer was placed over the GDL. The properties of the biocover layers are summarized in Table 1. GDL and biocover layer was separated with a geotextile fabric. Three biocover samples (SC, S10B and S10AB) were tested. The moisture content in the biocovers were adjusted to ~15% (*w/w*) instead of field capacity to facilitate gas flow. The simulated LFG was supplied to the column through an inlet at the bottom of each column. Gas sampling ports were provided at 10 cm interval along the depth of the column. Atmospheric air was supplied through an inlet at the top of the column. An outlet was provided at the top of the column for outgoing gases. Flowmeters were connected at the inlet and outlet lines to measure the inflow and outflow gas fluxes. The columns were exposed to 50% (*v/v*) CH_4 and 50% (*v/v*) CO_2 at an inflow flux rate of 50 $gCH_4\ m^{-2}\ day^{-1}$ for nearly 90 days. Gas samples were extracted from the sampling ports at a regular interval to monitor the gas concentration profiles along the depth of the biocover layer.

The gas concentrations were measured using GC (SRI Instruments, CA, USA). The CH_4 oxidation efficiency was derived from the CH_4 and CO_2 concentrations using the relation shown in Eq. 1 and 2 (Gebert et al. 2011).

$$\frac{CO_{2\_LFG}+x}{CH_{4\_LFG}-x} = \frac{CO_{2\_i}}{CH_{4\_i}} \quad (1)$$

$$f_{ox} = \frac{x}{CH_{4\_LFG}} \quad (2)$$

Where, x = fraction of CH_4 oxidized; CO_{2_LFG} and CH_{4_LFG} = concentration of CO_2 and CH_4 (% *v/v*) in LFG (or inlet LFG); CO_{2_i} and CH_{4_i} = concentration of CO_2 and CH_4 (% *v/v*) measured at a depth i in the cover; f_{ox} = CH_4 oxidation efficiency (%).

Table 1. Properties of control soil and biochar amended soils

Properties	CS	S10B	S10AB
Substrate	Soil only	Soil+10% Biochar	Soil+10% Act. Biochar
Bulk Density (g/cm^3)	1.53	1.37	1.25
Total Porosity	0.49	0.52	0.56
Initial Moisture (%w/w)	16.6	16.0	15.7

Microbial Community Analysis. Samples (~1 g) were extracted from the top 0-5 cm of each of the biocover layer using a 1.0 cm diameter thin-walled sampler specifically fabricated for this purpose. DNA based 16S rRNA gene amplicon sequencing was performed on the samples obtained from the columns as well as the original samples (before incubation in column reactors) to characterize the microbial communities. Nucleic acid extraction, library preparation and sequencing were performed by the Genome Research Core (GRC) at the University of Illinois at Chicago (UIC).

RESULTS

Methane Oxidation in Batch Incubation. Methane consumed by the cover substrates during batch incubations are shown in Figure 1. The activated biochar amended soil samples (S2AB and S10AB) consumed CH_4 at a significantly higher rate than soil control and non-activated biochar amended soil samples from the beginning of the incubation and continued to oxidize higher amount of CH_4 (Figure 1a and 1b). In contrary, S10B showed lower CH_4 uptake than SC and S2B until initial 30 days of incubation (Figure 1a). The reason could be that when the soil is amended with biochar, a portion of microbially loaded soil is replaced with inert non-microbially loaded biochar lowering the microbial load in overall biochar amended soil which results in a lag phase and lower CH_4 uptake rates due to the time needed for microbial acclimation. CH_4 uptake of S2B is marginally lower than SC which shows that higher the amendment ratio, higher the replacement of microbial load, and higher the lag phase. However, once biochar amended soil is acclimated, the microbial activity spikes resulting in higher CH_4 uptake (Figure 1b). Figure 1c shows that in the long-term, biochar amended soil outperforms soil control resulting in significantly higher cumulative CH_4 uptake. On the other hand, activated biochar amended soils showed significantly higher cumulative CH_4 uptake and CH_4 oxidation rates than the non-activated biochar amended soils and soil control. The CH_4 oxidation rates followed the order of 518.6 μg/g/day (S10AB) >169.2 μg/g/day (S2AB) >116.1 μg/g/day (S10B) > 97.4 μg/g/day (S2B) > 88.3 μg/g/day (SC) by the end of the incubation. Hence, these observations suggest that biochar amendment is beneficial for the long-term enhancement of CH4 oxidation rates in landfill cover soil and biochar activation can overcome the lower microbial activity in the short-term.

Gas Concentration Profiles. Figure 2 shows CH_4 concentration in column headspace over time during column incubation. As shown in Figure 2, CH_4 concentrations in the headspace reduced gradually over time as the methanotrophs got acclimated to the column incubation conditions. The S10B (activated biochar amended soil) showed relatively higher reduction in

CH_4 concentration from the first week of incubation in comparison to S10B (non-activated biochar) and SC (soil control). It shows that the microbes in S10AB were already acclimated from prior activation process and hence were in growth phase unlike SC and S10B where the microbes needed time for acclimation. After initial lag phase or acclimation of the microbes, the CH_4 oxidation spiked resulting in rapid reduction of CH_4 concentration in the headspace which is similar to the observations in batch incubation.

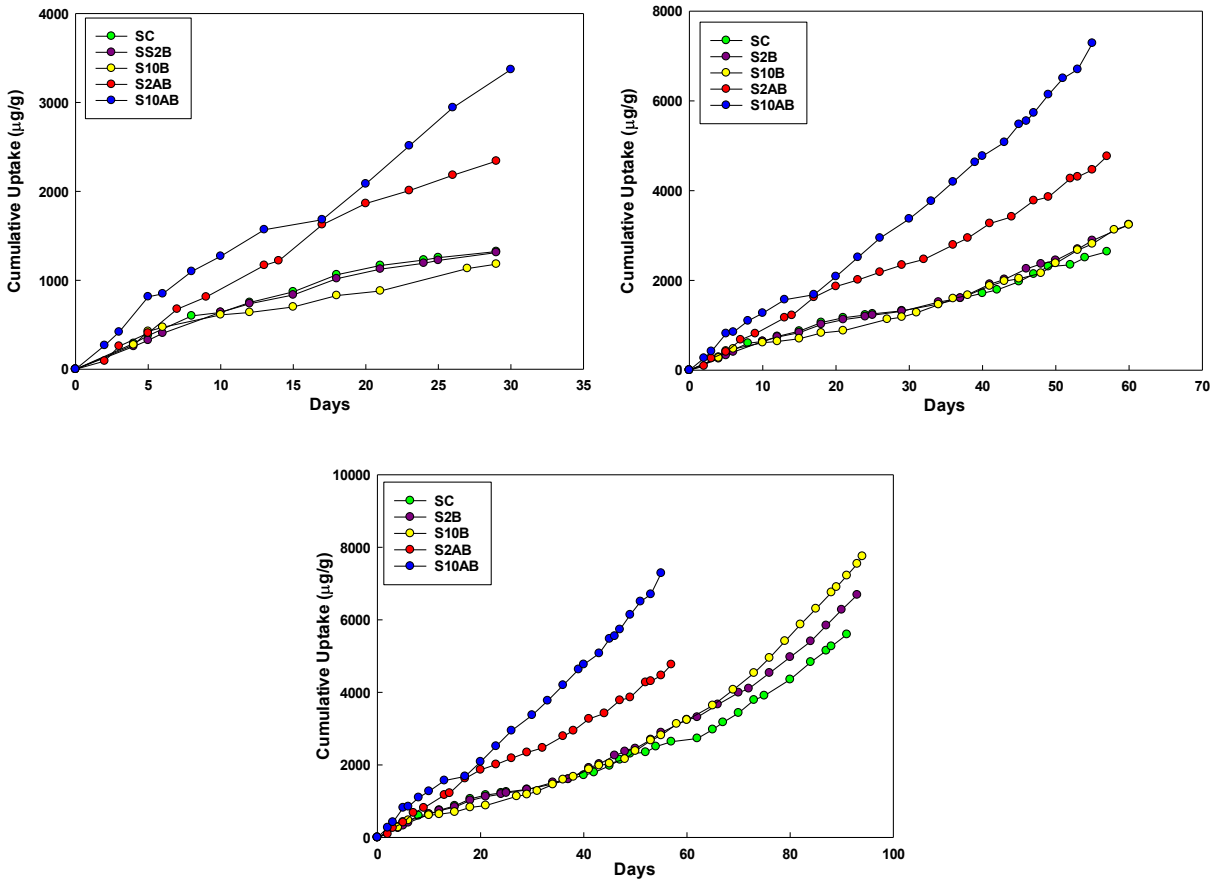

Figure 1. Cumulative methane uptake in soil control, soil +2% non-activated biochar, soil +10% non-activated biochar, soil +2% activated biochar and soil+10% activated biochar during a) 30 days, b) 60, and c) 90 days of batch incubation.

Methane Oxidation Efficiency. Calculating cumulative CH_4 uptake was not straight forward in column incubation like in batch incubation as there are many phenomena occurring at the same time such as dilution, oxidation, diffusion, and advection making the process more complicated. Therefore, oxidation potential is represented in terms of CH_4 oxidation efficiency. Figure 3 shows average CH_4 oxidation efficiency along the depth of the biocover layer in each column calculated based the CO_2/CH_4 concentration ratios (Eq. 2). S10AB showed significantly higher CH_4 oxidation efficiency (~50% at top 0-5 cm) along the depth than SC (36%) and S10B (32%). This is consistent with the observations in batch incubation where S10B showed significantly higher CH_4 uptake. Huang et al. (2019) also observed relatively higher CH_4

oxidation efficiency in biochar amended soil enriched with MOB consortium in comparison to landfill cover soil alone. Similar to the observation of batch incubation, CH_4 oxidation efficiency of S10B was not significantly higher than SC which further affirms our hypothesis that inert biochar takes longer time to acclimate resulting in lower CH_4 oxidation rates in the beginning.

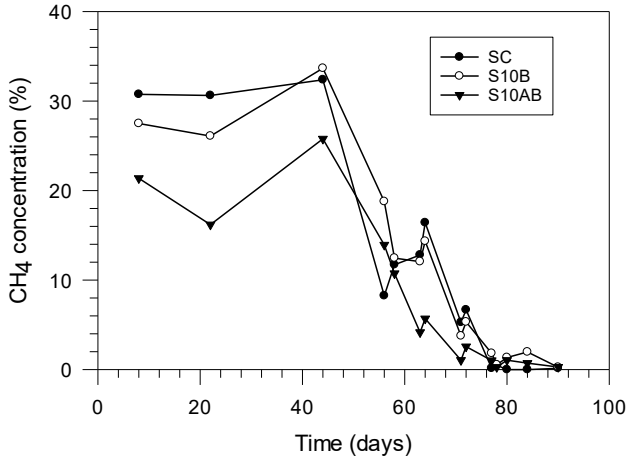

Figure 2. Headspace methane concentration with time during column incubation

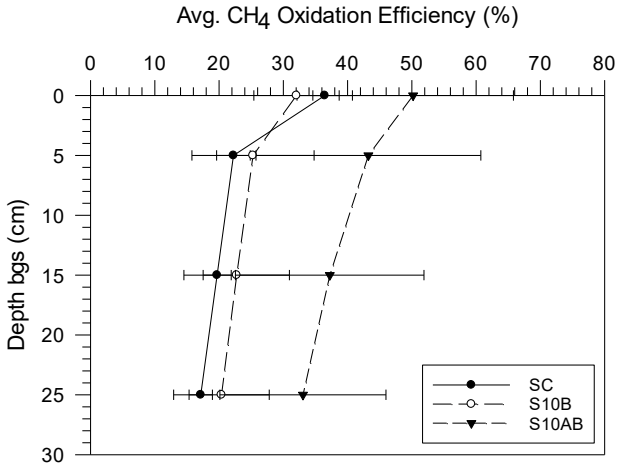

Figure 3. Average steady state CH_4 oxidation rates along the depth of the biologic layer in the columns.

Microbial Community Distribution. Samples were extracted from the biocover layer in each column and microbial community structure was characterized with the help of DNA based 16S rRNA sequencing. Figure 4 shows average abundance of methylotrophs relative to the total microbial community present in each soil sample before and after column incubation. Biochar activation was successful in loading biochar with methylotrophic communities resulting in significantly higher methylotrophic relative abundance (23.6% out of total sequences) in activated biochar (AB). Before incubation, the methylotrophic abundance ranged from 4.1% to 7.4% in the biocover samples which increased significantly after incubation in column reactors

leading to methylotrophic relative abundance ranging from 31% to 42%. Since the soil was obtained from a landfill cover and stored in the laboratory for an extended period, the methylotrophic communities were present in the soil even before column incubation but were in significantly low numbers. However, the methylotrophic abundance grew significantly upon exposure to CH_4 in column reactors. This shows the resilience of the methylotrophic communities and suggests that they can survive extended periods of CH_4 starvation.

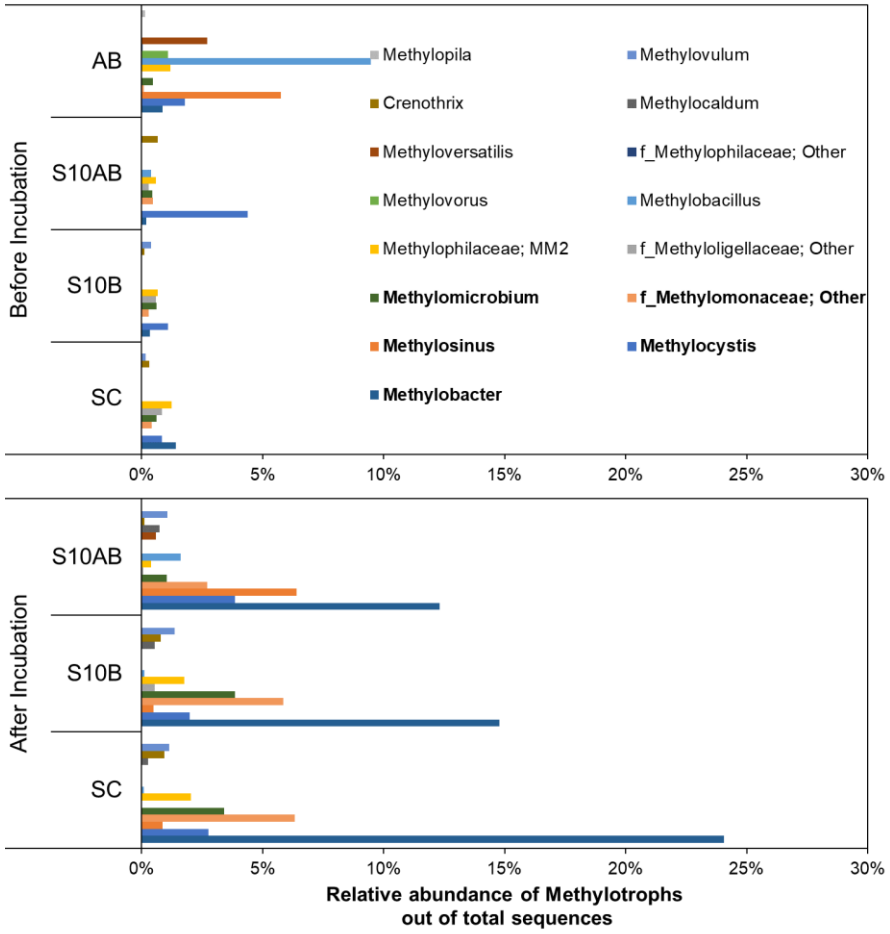

Figure 4. Average abundance of methylotrophs out of total microbial communities in the biologic layers before and after column incubation. Note: SC = Soil control, S10B = Soil + 10% biochar, S10AB = Soil + 10% activated biochar, AB = Activated biochar

The methylotrophic communities were significantly different before and after incubation (ANOSIM, $p = 0.001$). The communities in activated biochar and activated biochar amended soils were significantly different from the soil control and non-activated biochar amended soil (ANOSIM, $p = 0.029$). Methanotrophic genera *Methylobacter*, which is a Type I methanotroph, prevailed in all the samples after column incubation and in SC and S10B before incubation (Figure 4). Type II methanotrophs such as *Methylocystis* and *Methylosinus* were also prevalent in all the samples. These methanotrophs have been commonly identified in the landfill cover soil in the previous studies (Kallistova et al. 2013; Reddy et al. 2019). However, it is interesting to note

that the relative abundance of Type II methanotrophs were higher in activated biochar in relation to the non-activated biochar and soil control (Figure 5). This suggests that the biochar activation conditions favored the growth of Type II methanotrophs over Type I. Studies in the past have suggested that growth of Type I methanotrophs is favored in low CH_4 concentrations and Type II in high CH_4 concentrations (Scheutz and Kjeldsen 2004), however, in this study, the conditions were not CH_4 limiting. So, there is no clear reason why Type II methanotrophs outgrew Type I in activated biochar. The S10AB showed consistently higher CH_4 oxidation efficiency during batch and column incubation (Figures 1 and 3) which can be associated with the higher abundance of Type II methanotrophs. However, there has been no study to affirm this hypothesis. Hence, it requires further study to confirm the methane oxidizing potential of Type II methanotrophs over Type I.

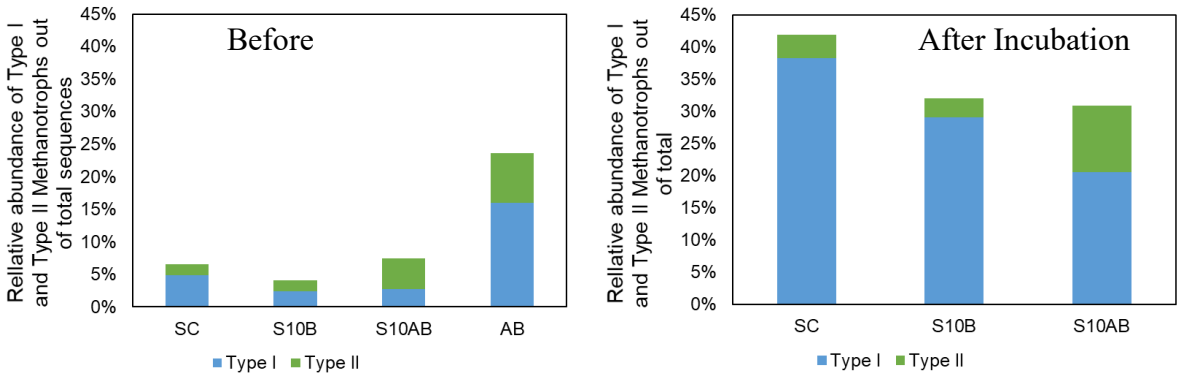

Figure 5. Relative abundance of Type I and Type II methanotrophs out of total sequences: a) Before incubation; and b) After incubation.

CONCLUSION

The study assessed the methane oxidation potential of the methanotrophically activated biochar amended landfill cover soil (10% w/w), non-activated biochar amended landfill cover soil (10% w/w) and landfill cover soil alone. Biochar activation with MOB consortium assisted in loading biochar with methane oxidizing microbes. The activated biochar when mixed with the landfill cover soil helped to expedite the microbial activity in the inert biochar. The activated biochar showed higher CH_4 oxidation efficiency from the beginning of incubation in contrary to soil control and non-activated biochar amended soil in both batch and column incubations. Biochar activation not only helped to reduce the lag phase but also resulted in higher CH_4 uptake and oxidation efficiency. Non-activated biochar on the other hand showed similar CH_4 oxidation efficiency as that of soil control during the time of incubation. Microbial communities that are commonly prevalent in landfill cover soils were observed affirming the occurrence of methane oxidation. However, a relatively higher abundance of Type II methanotrophs were observed in the activated biochar and activated biochar amended soil in comparison to the soil control and non-activated biochar amended soil. The study suggests that there could be relation between Type II methanotrophic abundance and methane oxidation rates, however, the same needs to be verified with further specific studies isolating Type II methanotrophs. Overall, the study shows that biochar activation with MOB consortium could be a promising technique to expedite and enhance microbial methane oxidation activity in the biochar amended landfill cover soil. This

activated biochar amended soil cover system can be used as a supplement to existing gas collection systems or in an old landfill to enhance the CH_4 mitigation efficiency.

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