ASSESSMENT OF POTENTIAL BIOFILTER MATERIALS TO MITIGATE METHANE EMISSIONS

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Laboratory and field studies have previously demonstrated the ability of volcanic pumice soil to mitigate both high and low CH_4 emissions through the activity of both type I and type II aerobic methanotrophs or methane oxidising bacteria (MOB). However, the limited availability of volcanic pumice soil necessitates the assessment of other potentially suitable, economical, and widely available biofilter materials. We mixed a small inoculum (of volcanic soil) with potential biofilter materials, viz. in situ soil (isolated from a dairy effluent pond bank area), pine biochar, garden waste compost, and fresh and weathered pine bark mulch. These materials were incubated at 25°C with periodical feeding of CH_4 and O_2 to support methanotroph growth and activity and the efficiency of CH_4 removal was monitored over 6 months. All materials (except fresh pine bark mulch) supported the growth and activity of methanotrophs. However, the efficiency of CH_4 removal in all the materials fluctuated between no or low CH_4 removal (0-40%) and high CH_4 removal phases (> 90%), indicating disturbances in the methanotroph community. Among these, soil and biochar consistently removed at an average of > 80% CH_4 and provided a more resilient media to changes in the community. Amendment of soil and biochar with micro-quantities of macro- and micro-nutrients (nitrate mineral salts) enhanced the stabilisation with CH_4 removal of up to 99%. This study demonstrated that (1) other soils and cheaply available materials can be used as a biofilter material by spiking with an active methanotroph community, and (2) nutrient additions enhance the growth and activity of MOB in the biofilter materials.

Introduction:
Methane is the largest agricultural GHG emitted in New Zealand and its emissions increased by 8.2% from 26834.7 to 29038.5 Gg CO_2-e between 1990 and 2012. Sources of this CH_4 include enteric fermentation of grazing animals (~84%), manure management (~2.5 %), solid waste disposal (~11.2 %), coal mining and natural gas (~2.2 %) (MfE, 2014).

Methane can be converted to CO_2 by a specific group of naturally occurring bacteria, called methanotrophs. The aerobic methanotrophs or methane oxidising bacteria (MOB) are present naturally in many New Zealand soils (pasture, forest and landfill) (Tate, 2015; Tate et al., 2012). Previous Landcare Research/Massey University studies on CH_4 oxidation indicated that the volcanic pumice soil is an ideal material for removing both low and high concentrations of CH_4 (Pratt et al., 2012a,b,c, 2013; Syed et al., 2014; Tate et al., 2007, 2012). Recent study using molecular techniques indicated that the volcanic soil had a healthy community of most of the sub-groups of type I and type II aerobic methanotrophs favouring the removal of CH_4 (Syed et al., 2014). Currently there is no other mitigation technology available that can mitigate CH_4 emissions without the production of CO_2 as a by-product. In

fact, few technologies produces N_2O emissions during the process, which is 295 times more potent than CO_2 (Haubrichs and Widmann, 2006; Menard et al., 2012). Methane mitigation using soil biofilters is considered to be the cleanest technology with no net production of N_2O or any toxic by-products.

Scaling up this technology for use nationally to mitigate emissions is limited by the availability of volcanic pumice soil and associated transportation costs. This study was therefore initiated to test different materials that are cheaper and more widely available that can be used as alternative biofilter media. The objectives of this study were 1) to test the efficacy of cheaply and widely available materials as alternative biofilter media, 2) characterise the aerobic methanotroph community present in these materials, and 3) study the effect of nitrate mineral salts (nutrients) to enhance the growth and activity of methanotrophs.

Materials and Methods:

The alternative biofilter materials tested were (i) on-farm soil (isolated from the area adjacent to effluent storage), (ii) garden waste compost (3–5 months old), (iii) biochar from pine bark (pyrolysis at 450°C), and (iv) pine bark mulch (weathered and fresh). These materials were spiked with 20% of the active volcanic soil (see next section for details) and CH_4 oxidation was measured in fed-batch conditions for a period of 6 months at constant temperature (25°C). Moisture loss during the study period (1–1.5 g of H_20 for every 5 weeks – data not shown) was compensated by periodical spraying of about 1–1.5 ml distilled water onto the material. Physico-chemical properties of the materials are listed in Table 1

Biofilter material	Dry bulk density (g cm^{-3})	Porosity (%)	Total C (%)	Total N (%)	NO_3^- - N (mg/kg)	NH_4^+ - N (mg/kg)
On-farm soil	0.63	75	4.67	0.48	683	224
Compost	0.44	80	14	1.35	1060	201
Biochar	0.19	85	86	0.19	1.44	20
Pine mulch (Fresh)	0.13	89	45	0.26	4.06	69
Pine mulch (Weathered)	0.13	89	50	0.26	5.73	65
Volcanic pumice soil	0.42	75	4.17	0.36	27	34

Table 1 Physico-chemical properties of the materials tested.

Laboratory fed-batch experiments

Preliminary experiments were performed to select the best way to inoculate/spike the alternative materials, whether by direct mixing or by suspending in buffer (data not shown). The direct mixing method was chosen as it was effective and can easily be used on a large scale. Direct mixing of the inoculum (20%) with other alternative biofilter materials (80%) was therefore established as the effective approach (data not shown). The total volume of the materials tested was kept constant at 100 ml; 20 ml of inoculum (volcanic pumice) was mixed with 80 ml of the material tested separately (in triplicates) in different air-tight

1800 ml AGEE^{TM} jars. The CH_4 removal ability of the materials (without inoculum) was also studied. For moisture content regulation, a 40-ml container half-filled with water was kept in the jars. Ports were fitted on the AGEE^{TM} jars for feeding CH_4 and for sampling purposes. All the materials were air dried and mixed with known amounts of water to adjust moisture content to satisfactory levels to support CH_4 oxidation (see table 2). The pH of the materials varied from 2.78 to 7. The pH was not adjusted to optimum conditions (5.5–6.5) to simulate natural working conditions of the materials.

Initially 10 ml of 60% (CH_4 in CO_2) was injected to supply methane at 3400 ppm, and then gradually increased to 10 000 ppm and 20 000 ppm over the study period. Methane and O_2 were regularly fed at the start of each fed-batch period, which lasted for 24 hours. Oxygen was supplied by opening the lid of the jar and passively letting the fresh air to diffuse for about 20 minutes, as previously suggested by (Pratt et al., 2012b). Gas samples containing CH_4, CO_2 and N_2O were analysed using gas chromatography (GC) (Schimadzu auto GC-2010) using flame ionisation (FID), thermal conductivity (TCD) and electron capture (ECD) detectors, respectively. GC was calibrated over the following gas standard ranges CH_4 (0–25 000 ppmv), CO_2 (0–50 000 ppmv) and N_2O standards (0–2000 ppbv). Methane removal was calculated by using the formula: $(C_0–C_t)/C_0 \times 100$; where Ct is concentration (ppm) time t and C_0 is concentration (ppm) at time 0.

Addition of nutrients to biofilter materials

Another fed-batch experiment as described above was set up to assess the impact of nutrient supply on methane oxidation. Soil and biochar biofilter materials were used with additional supply of 12ml of NMS (nitrate mineral salts) media. The final amounts of constituents in the material are as follows KNO_3 (12 mg), Na_2HPO_4 (864 µg), KH_2PO_4 (336 µg), Tetra sodium EDTA (12 µg), $ZnSO_4.7H_2O$ (0.84 µg), $MnCl_2.4H_2O$ (0.36 µg), H_3BO_3 (3.6 µg), $CoCl_2.6H_2O$ (2.4 µg), $CuCl_2.2H_2O$ (0.12 µg), $NiCl_2.6H_2O$ (0.24 µg), Na_2Mo_4, 2H2O (0.36 µg), $FeSO_4.7H_20$ (0.06 µg), $MgSO_4.7H_20$ (2.4 µg) & $CaCl_2.2H_2O$ (0.24 µg).

Materials – chemical and physical analysis

Moisture content was determined by oven drying the samples for 18 h at 105°C. Moisture content (% dry wt) was calculated as the percentage of H_2O before and after drying. Before soil pH measurement, samples were air dried for a period of 14 h, and were analysed by following the procedures described by Blakemore et al. (1987). The particle density, dry and wet bulk density and porosity of the materials were calculated following the techniques described by Gradwell (1972). Total C and N were measured by combustion in a FF-2000 CNS analyser (LECO Corporation, St Joseph, MI, USA). Ammonium (NH_4^+) and nitrate (NO_3^-) were extracted with 2 M KCl using a 1:10 material: extractant ratio and a one hour end-over-end shaker followed by filtration, as described by (Blakemore et al., 1987)

Materials – DNA analysis

Samples were extracted in duplicate using a Mobio ^{TM} Powersoil DNA extraction kit (Mobio Laboratories, Carlsbad, CA, USA) according to the manufacturer's instructions. Three pmoA primer-sets designed by Kolb et al. (2003) MBAC (A189F/Mb601R) – targeting *Methylobacter* and *Methylosarcina*, MCOC (A189F/Mc468R) – *Methylococcus*, MCAP (A189F/Mcap630R) – *Methylocapsa*; and two 16SrRNA primer sets designed by Chen et al. (2007) – Type IF/IR – targeting type I MOB (*Methylobacter*, *Methylosarcina*, *Methylococcus*, *Methylocaldum*, *Methylomicrobium*, *Methylomonas*, *Methylosphaera*, and unclassified *Methylococcales*), and Type IIF/IIR – type II MOB (*Methylocystis*, *Methylosinus*, *Methylocella*, *Methylocapsa*, and unclassified *Methylocystaceae)* were used to amplify conserved sequences of aerobic methanotroph community.

Quantitative PCR standards were prepared by cloning purified assay-specific amplified genes into the *E. coli* host using a commercial kit (Topo™ TA, Invitrogen) by following manufacturer's instructions. Amplified portions of plasmid DNA were quantified and serially diluted from 1/100 to 1/1000000 using sterile PCR grade water and were used as standards. Each qPCR reaction volume (10 µL) consisted of 5 µL ssofast™ qPCR master mix, 0.6 µL each of 10 nM forward and reverse primers, 2 µL of sample DNA, and sterile PCR grade water made up to final volume of 10 µL. Sample DNAs were diluted 1/25 times to reduce the effect of inhibitors in the sample. Assay-specific standards (for calibration curve) and negative controls were run along with the samples. Reactions in duplicates were carried out in a Roche Light cycler 480™ machine with the following thermal profile: initial denaturation at 94°C for 15 secs; 40 cycles of denaturation at 95°C for 5 secs; annealing at assay-specific temperature (MBAC, MCOC, MCAP, type I 16SrRNA and type II 16SrRNA – 58, 58, 55, 65 and 65°C, respectively) for 25 secs; and data acquisition at 82°C (16SrRNA type I & II at 65°C) for 4 secs. Melt curve analysis was carried out post-qPCR by acquiring fluorescence data by continuous melting of samples from 65°C to 95°C for 30 secs. In addition, the amplified products from qPCR were run on 2% TBE gel to confirm formation of assay specific product size. Gene copy numbers of the samples were calculated by plotting linear regression of crossing point (C_p) values and logarithmic gene copy number values of the standards (calculations adapted from Lee et al. (2008)). The r^2 values of the plots ranged from 0.9893 to 1.

Results and Discussion:

Performance of the materials

Methane removal (%) of the biofilter materials (spiked with 20% active volcanic soil (Figure 1) and the those without the spike (Figure 2) showed that all the inoculated biofilter materials (except fresh mulch) removed CH_4 satisfactorily up to 99% at some stage during the study period. All the materials (both with and without inoculum) went through a no or low CH_4 removal phase and high CH_4 removal phase during the study period. This disturbance (lower limits) was extreme in the materials without inoculum. Interestingly, inoculated soil and soil (without inoculum) followed a similar CH_4 removal trend (with latter removing lower amounts of CH_4). Similarly, inoculated compost and compost (without inoculum) followed a similar trend line as evident from Figures 1 and 2. This indicates these phase changes were probably due to competition between microbial communities or biological changes, rather than being from differences in physical or chemical properties of the materials.

Inoculated soil started removing >95% CH_4 from day 1 until day 66, when CH_4 removal dropped to 66%. The disturbance phase lasted until day 144, but after that the CH_4 removal increased and remained stable, with CH_4 removal of up to 99%. Inoculated compost, on the other hand, had an initial lag period, where it was removing low levels of CH_4 until Day 86. After day 86, CH_4 removal increased up to 99% until day 145, where it again fluctuated and went into disturbances phases during final stages of the study period. On the final day of the study (day 217), inoculated compost was removing 73% of the CH_4. Like inoculated soil, the biochar (with inoculum) also started very well, with few disturbances on day 26 and 38. Overall, inoculated biochar removed more than 80% of CH_4 during the study period. Although the high doses of CH_4 affected the CH_4 removal ability of the biochar, overall more than 80% of CH_4 was removed during the study period. In biochar – unlike in soil and compost – less disturbances/fluctuations were evident, probably because biochar had no native methanotroph population (and microbial community) to compete with (see Table 3).

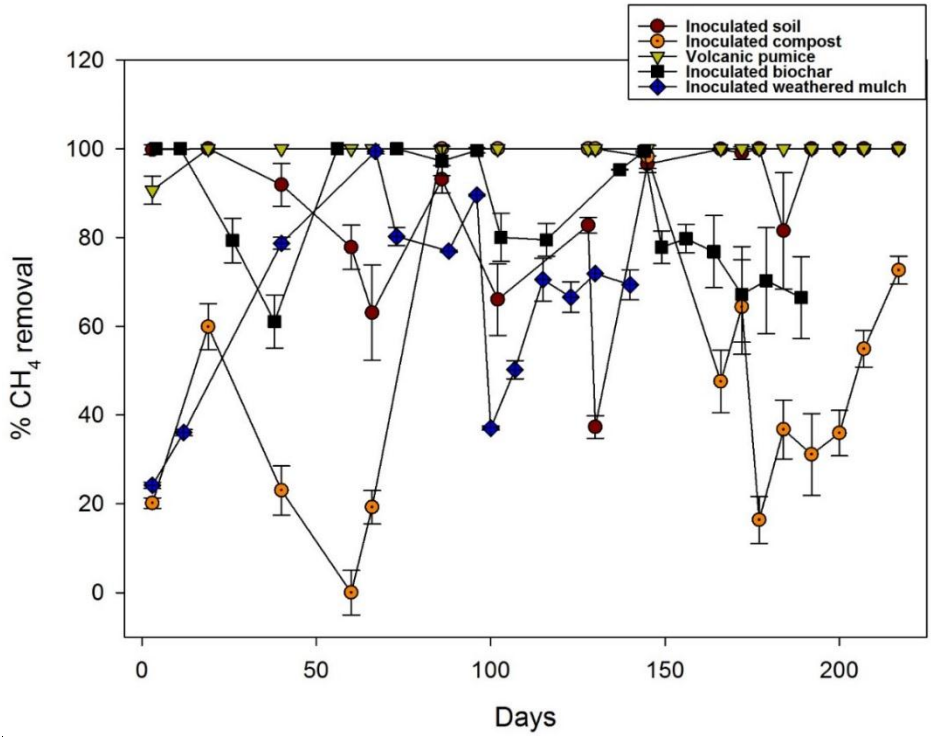

Figure 1. CH_4 removal of the materials inoculated with volcanic pumice soil. Error bars represents the standard deviation from the mean of replicates. Each data point represents the % CH_4 calculated at the end of a fed-batch period on a particular day of study.

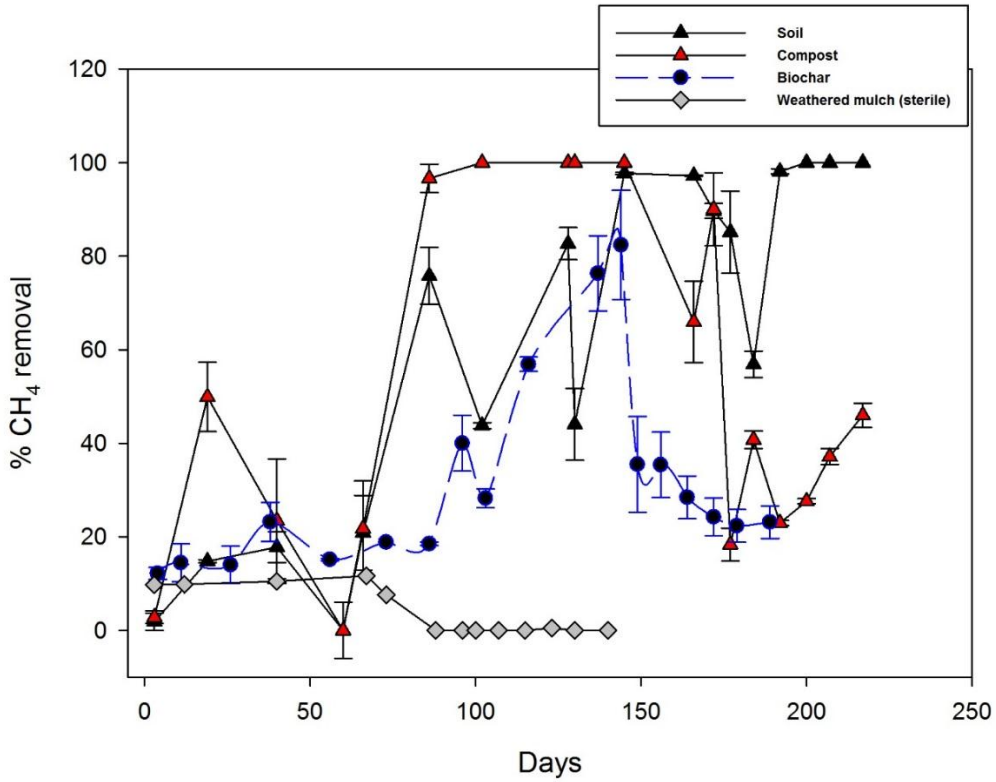

Figure 2. CH_4 removal of the pure materials or control (with no inoculum). Error bars represents the standard deviation from the mean of replicates. Each data point represents the % CH_4 calculated at the end of a fed-batch period on a particular day of study.

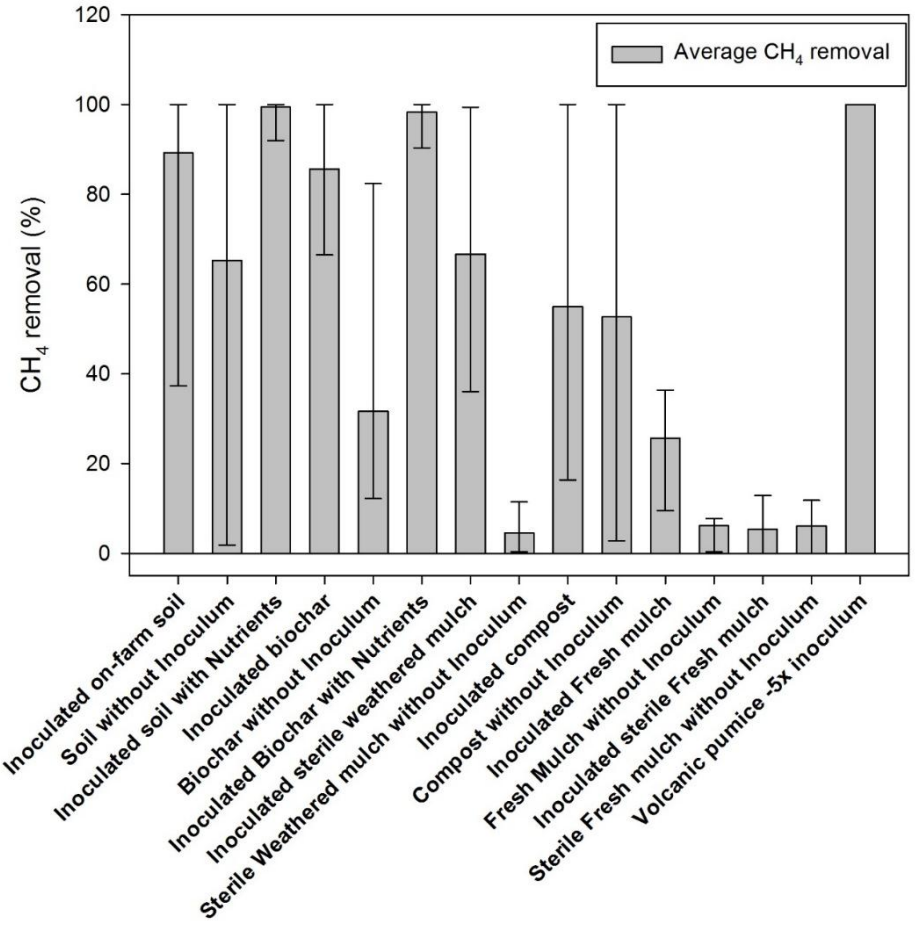

Figure 3. Average CH_4 removal (%) by all the biofilter materials tested. Error bars represents the maximum and minimum CH_4 removed during the study period.

Figure 3 shows the average CH_4 removal by each material over the study period, For instance, inoculated soil removed an average of 89% CH_4, with a minimum and maximum removal of 37 and 100%, whereas the soil without inoculum removed an average of 65% CH_4, with a minimum and maximum CH_4 removal of 1.85% and 100%. The average CH_4 (%) removals by the inoculated materials – soil, biochar, sterile weathered mulch, and compost were 89, 86, 67, and 55 respectively. On the other hand, the average CH_4 (%) removal by the pure materials (without inoculum) – soil, biochar, sterile weathered mulch, and compost were 65, 32, 5, and 53 respectively. Of all the materials tested, inoculated soil and biochar performed best.

Ambient levels of N_2O emissions were measured in the gas samples taken from all the materials. Concentrations of N_2O ranged between 330 and 370 ppbv. Moisture content of all the materials remained c. 40–80% dry weight, except for biochar and mulch, where the moisture content levels were a little higher. Regardless, no drying or clogging of the material was evident, suggesting the materials were moist enough to support CH_4 oxidation. In addition, no significant change in pH (initial and final) was evident in the materials (see Table 2).

Materials	Moisture		pH	
	Initial	Final	Initial	Final
Inoculated soil	31.5	44.1	5.62	5.56
Soil without Inoculum	29.6	46.2	5.68	5.54
Inoculated soil with nutrients	31.3	40.6	5.14	5.66
Inoculated compost	48.4	76.2	7.36	7.13
Compost without Inoculum	51.2	73.4	7.36	7.28
Volcanic pumice	40.3	57.3	5.99	6.11
Inoculated biochar	56.9	138.1	6.7	6.48
Biochar without Inoculum	84.7	175.0	6.84	6.7
Inoculated biochar with nutrients	77.4	61.7	6.37	6.61
Inoculated fresh mulch	88.7	69.5	5.77	5.15
Fresh mulch without inoculum	112.8	179.5	5.56	4.94
Inoculated Sterile weathered mulch	110.3	69.7	3.38	3.32
Sterile weathered mulch without inoculum	111.4	120.9	2.74	2.57
Inoculated sterile fresh mulch	42.8	38.6	4.13	4.69
Sterile fresh mulch without Inoculum	48.2	107.9	3.58	3.96

Table 2. Initial and final moisture content and pH measurements of all the materials tested

Aerobic methanotroph community

Results from qPCR (see Table 3) indicate the materials (particularly soil and compost) had a native methanotroph population along with other microbial communities. The fluctuations or variability due to the competition between methane oxidising and non-methane oxidising bacteria were less evident in the inoculated materials. This could be because the methanotrophs with higher starting population numbers might have competed more successfully for available nutrients (other than C) with the non-methane bacteria present in the materials. Nevertheless, there could be many other factors (nutrients, inhibitors, etc.) responsible for this variability, but these are unknown at this stage.

Type I and type II gene copy numbers (except for *Methylococcus*) increased during the study period for soil, compost, biochar, and weathered mulch (Table 3), indicating that the conditions were favourable for methanotrophs growth and activity. The methanotroph community differed among the materials.

Like volcanic pumice, the inoculated on-farm soil had both type I ($5.24\pm0.05 \times 10^8$ gene copies) and type II ($2.02\pm0.06 \times 10^8$ gene copies) communities, but with a higher type I population. While there was no significant difference ($P = 0.65$) between the methanotroph communities in the soil and volcanic pumice, the methanotroph populations of compost were significantly different ($P < 0.005$) from the volcanic pumice. Gene copies belonging to the type I community significantly increased from $4.8\pm0.14 \times 10^8$ on day 1 to $10.68\pm0.37 \times 10^8$ on day 217 in compost. The higher type I population was strongly represented by members from the *Methylobacter* ($7.43\pm0.03 \times 10^8$ gene copies) sub-group that were actively engaging

in CH_4 oxidation. On the other hand, the type II population increased only slightly. This could be due to the presence of high concentrations of organic nutrients, or to the presence of inhibitory compounds. Biochar had a balanced composition of both type I and type II population, with type II gene copies slightly higher than in the volcanic pumice soil. Regardless of the material type, gene copies of *Methylococcus* (from the type I community) did not increase in number during the study period. This finding is supported by the fact that *Methylococcus* typically prefers low CH_4 concentrations (e.g., a few 100 ppm).

Materials	Type I		Type II		Methylobacter		Methylococcus		Methylocapsa	
	Day 0	*Day final*	*Day 0*	*Day final*	*Day 0*	*Day final*	*Day 0*	*Day final*	*Day 0*	*Day final*
Inoculated soil	4.87 ± 0.09	5.24 ± 0.05	0.75 ± 0.01	2.02 ± 0.06	0.52 ± 0	1.21 ± 0.08	0.31 ± 0.02	0.14 ± 0.00	2.81 ± 0.11	2.49 ± 0.08
Inoculated compost	4.8 ± 0.14	10.68 ± 0.37	0.79 ± 0.02	0.82 ± 0.03	0.38 ± 0.02	7.09 ± 0.17	0.45 ± 0.01	0.26 ± 0.00	2.07 ± 0.08	-
Volcanic pumice	6.78 ± 0	5.36 ± 0.05	1.39 ± 0.05	2.32 ± 0.03	1.13 ± 0.06	1.24 ± 0.02	0.38 ± 0.00	0.15 ± 0.01	2.98 ± 0.21	2.32 ± 0.04
Soil without Inoculum	4.43 ± 0.09	4.73 ± 0	0.46 ± 0	1.39 ± 0.01	0.35 ± 0.0	0.52 ± 0.00	0.33 ± 0.01	0.08 ± 0.00	3.16 ± 0.11	1.19 ± 0.14
Compost without Inoculum	4.25 ± 0.52	12.68 ± 0.20	0.39 ± 0.01	0.56 ± 0.02	0.29 ± 0.01	7.43 ± 0.03	0.76 ± 0.00	0.32 ± 0.02	2.59 ± 0.08	-
Biochar with Inoculum	1.88 ± 0.06	5.46 ± 0.03	1.21 ± 0.05	3.22 ± 0.15	0.51 ± 0.01	1.21 ± 0.00	0.33 ± 0.03	0.21 ± 0.02	2.2 ± 0.03	3.48 ± 0.11
Biochar without Inoculum	0.14 ± 0.0	0.63 ± 0.05	0.03 ± 0	0.79 ± 0.03	0.01 ± 0.0	0.17 ± 0.01	0.14 ± 0.02	0.02 ± 0.00	0.05 ± 0.00	0.82 ± 0.02
Sterile weathered mulch with inoculum	1.17 ± 0.03	5.19 ± 0.07	0.52 ± 0.01	1.7 ± 0	0.46 ± 0.01	1.08 ± 0.12	0.24 ± 0.01	0.06 ± 0.01	1.22 ± 0.09	1.44 ± 0.03
Sterile weathered mulch without inoculum	0.02 ± 0	0.04 ± 0	0.03 ± 0.0	0.06 ± 0	0.29 ± 0.01	0.51 ± 0.02	0.07 ± 0.02	0.03 ± 0.01	0.81 ± 0.00	1.63 ± 0.02

Table 3 Gene copy number (x 10^8) per gram of dry material. Table includes the data of initial and final days of the study period.

Effect of nutrient addition (nitrate mineral salts)

Inoculated soil and biochar amended with nutrients removed all the CH_4 supplied (92 and 99% respectively) with only small fluctuations reflected in CH_4 removal. This indicates that the CH_4 removal potential of soil and biochar can be accelerated with the addition of nutrients (Figure 4).

It is important to note here that the inoculated soils and biochar amended with nutrients took less incubation time to reach a higher CH_4 removal efficiency, than inoculated soils and biochar without added nutrients. This indicates that faster acclimatisation can be expected by adding micro quantities of nutrients. For instance, soil amended with nutrients took about 23 days, whereas the soil without nutrients took about 145 days. Even though sufficient N levels

were present in the soil, other micronutrients stimulated the higher methanotroph gene copy numbers in the nutrient-amended materials.

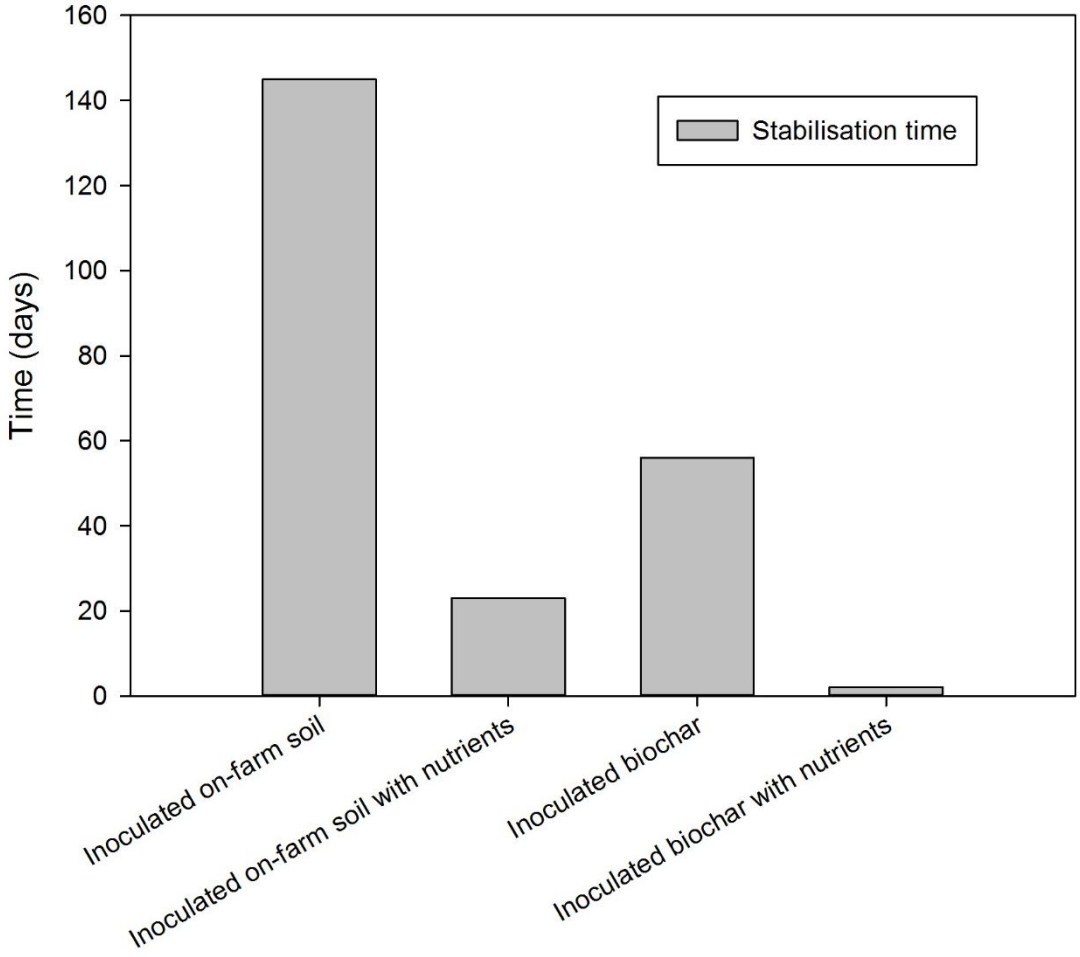

Figure 4 Comparing inoculated soil and biochar – with and without nutrients. Stabilisation time indicates the number of days required for a material to reach a stable CH_4 removal efficiency of more than 80%.

Conclusion:

This study indicates that in addition to the active volcanic soil, other biofilter materials tested here can be used as alternatives by spiking them with a source of active population of methanotrophs (volcanic pumice soil). Soil and biochar tend to be more stable and resilient than other materials tested. To reduce the acclimatisation/stabilisation time significantly in the materials, nitrate mineral salts can be added. The quantitative PCR technique used in this study provided information about the aerobic methanotroph community at the genera level, particularly the composition of type I and type II in different materials. Other techniques like DGGE and T-RFLP can be used to identify any novel species present in these materials. Further studies are needed to assess the feasibility of these materials at small plot and field scales.

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