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Functional green wall development for increasing air pollutant phytoremediation: substrate development with coconut coir and activated carbon

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Highlights

- Particle size of coconut media did not alter removal efficiency for any pollutants.
- Adding activated carbon to the media increased the removal efficiency for VOCs.
- Gas removal efficiency plateaued as activated carbon concentrations approached 50%.
- The addition of activated carbon negatively influenced biofilter PM removal.

Abstract

Functional green walls are gaining attention due to their air cleaning abilities, however the air cleaning capacity of these systems may be improved through substrate modification. This experiment investigated the capacity of several green wall media to filter a range of air pollutants. Media, consisting of differently sized coconut husk-based substrates, and with different ratios of activated carbon were evaluated through the use of scaled down model 'cassettes'. Tests were conducted assessing each substrate's ability to filter particulate matter, benzene, ethyl acetate and ambient total VOCs. While the particle size of coconut husk did not influence removal efficiency, the addition of activated carbon to coconut husk media improved the removal efficiency for all gaseous pollutants. Activated carbon as a medium component, however, inhibited the removal efficiency of particulate matter. Once the substrate concentration of activated carbon approached ~50%, its gas remediation capacity became asymptotic, suggesting that a 50:50 composite medium provided the best VOC removal. In full-scale botanical biofilter modules, activated carbon-based substrates increased benzene removal, yet decreased particulate matter removal despite the addition of plants. The findings suggest that medium design should be target pollutant dependent, while further work is needed to establish plant viability in activated carbon-based media.

Keywords

Air quality; biofilter; VOC; PM; bioremediation

1 Introduction

There is a growing need to enhance indoor air quality and maintain it at acceptable levels through energy efficient technologies [1, 2]. In recent decades, significant research has demonstrated the potential of potted-plants to remove a range of volatile organic compounds (VOCs) [3-9], with the mechanism of removal largely attributed to microbial degradation of pollutants that diffuse into the potted-plant substrate [4, 5, 7, 8]. The efficacy of potted-plants notwithstanding, their application for VOC removal *in situ* may be less efficient than demonstrated in many laboratory studies, due to pollutant removal capacity overestimates stemming from the use of small test chambers with high concentrations of pollutants [10].

Green wall technology, specifically active botanical biofiltration, builds upon the remediation capacities of potted-plants through the use of active airflow to the substrate, and greater plant density for a given floor area [11]. In these systems, the volume of polluted air to which the system is exposed is increased by actively drawing air through the substrate, which is kept moist by regular irrigation. In doing so, polluted air is drawn through the porous substrate, which supports a microbial population capable of VOC degradation [12]. In this process, gaseous pollutants are removed in three steps: firstly, they are transferred from the gas phase to the liquid film within the biofilter; secondly, pollutants diffuse within the film; and finally, pollutants diffuse to substrate microbial cells where they are degraded, or are otherwise adsorbed onto the packing material of the biofilter [13]. It is therefore advantageous to use relatively porous materials with large surface areas to increase

liquid film area, reduce the diffusion pathway length between film and adsorption site, and to increase the number of adsorption sites [14].

Studies of other vegetated filtration systems have demonstrated that media plays a critical role in their functionality, as the substrate not only provides the physical support for plants, but facilitates the primary removal processes for pollutants. Green wall systems designed specifically for pollution removal have focused on the use of use coco-coir [15, 16]. However, it is unclear how this media would perform under varying pollutant loading of different pollutants. Prodanovic et al. [16] investigated the processes that govern pollutant removal performance of coir media in green walls and suggested that a combination of coir with adjunct substrates might prove to be the best option for optimal application in green walls for pollutant removal.

Previous studies have highlighted activated carbon as an excellent adsorbent for VOCs in botanical [3, 17] and microbial biofilters [18-22]. While activated carbon is known to be an effective substrate in microbial biofilters, its application in botanical biofilters requires it to also provide conditions that support plant health. Aydogan and Montoya [3] trialed a number of novel substrates for VOC removal and found a substrate consisting of wetted activated charcoal removed formaldehyde efficiently, but could not sustain long term plant health. Wang and Zhang [17] developed a botanical air filtration substrate composed of a 50:50 mix (by volume) of shale pebbles and activated charcoal, recording high removal rates for formaldehyde and toluene, however it was unclear which substrate components were responsible for the VOC removal. Furthermore, activated carbon-based botanical biofilters have not previously been assessed for their particulate matter (PM) filtration capacity, thus further research is needed before such systems can be comprehensively evaluated for practical use in air cleaning systems that target multiple pollutants.

The addition of activated carbon to the plant growth substrate in a botanical biofilter system may substantially enhance these systems' potential to efficiently remove gaseous pollutants. Research is, however, required to assess the quantitative effects of the addition of activated carbon. The research presented here aimed to optimize the pollutant removal capacity of an existing botanical biofilter system through substrate modifications. This was achieved by characterizing the benzene, ethyl acetate, ambient TVOC and PM single pass removal efficiency (SPRE) performance of three sizes of coconut husk biofilter substrates. Then, using the best performing substrate size fraction with the incorporation of activated carbon adsorbents, further possible improvements in pollutant removal were tested. Finally the best performing substrate identified was tested in a full-scale botanical biofilter with plants, using the species *Nephrolepis exaltata bostoniensis,* as this species has previously been identified as an efficient phytoremediator of PM [23] and VOCs [7, 24].

2 Methods

2.1 Test cassettes

To test the effectiveness of different substrates on reducing VOC and PM, substrate cassettes were designed to facilitate the use of a large number of fully independent replicates (Figure 1). Previous work has shown that repeated exposure of the plant / microbe system to VOCs enhances draw down rates [25], and thus would introduce severe carry over effects if samples were used more than once. Further, it

has been demonstrated that the performance of air cleaning media at repeated doses of VOCs cannot directly reflect their performance at typical indoor concentrations [25].

Cassettes were constructed from PVC piping (85 x 85 mm, 482.1 cm^3). Media were encased within a loose weave high-density polyethylene (HDPE) membrane within the PVC housing unit. A diameter of 85 mm was chosen to match the air intake inlet of a green wall module that has previously been tested for air pollutant remediation [23, 26, 27], while an 85 mm depth corresponds to the approximate shortest horizontal airflow path length through these green wall units, thus this design reflected airflow that followed the path of least resistance through the central outlet at the front face of the green wall unit; resulting in a conservative estimate of system performance.

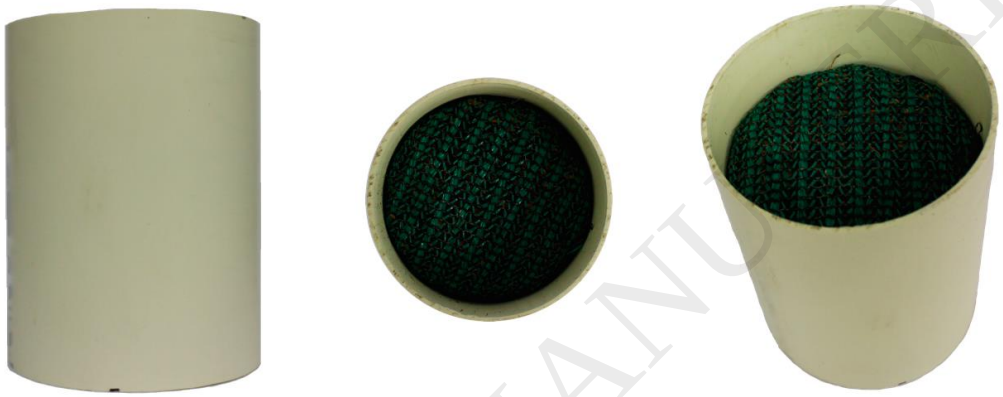

Figure 1. Cassettes that contained the test substrates.

2.2 Medium combinations tested

2.2.1 Coconut husk-based media

Three different sized fractions of coconut husk-based media were trialed, with each treatment independently replicated 6 times (Figure 2). These consisted of a fine fraction (coir fibers with a diameter of ~0.5 mm), a medium fraction (particles of 5–15 mm) and a coarse fraction (particles of 8–35 mm). Coconut husk has been used in several functional green wall studies, with the literature thus far indicating that it is a functional substrate for active green walls and is capable of serving as packing media in biofilters. Coconut husk used in biofilters typically has a water content of 72.5 %, is 95% organic matter, has a specific surface area of 0.75 m^2/g, and has a water holding capacity of 5.5g[H20]/g dry material. All media were packed to a density equivalent to that used in green wall modules. Media were tested for air pollutant removal after saturation to field capacity and draining overnight.

Figure 2. The different coconut-based media. Pictured from left to right: fine, medium and coarse grades.

2.2.2 Carbon based media

Using the results from *Section 2.2.1*, the highest performing coconut husk substrate was used for a series of trials that incorporated differing proportions of granular activated carbon (GAC; EA1000 4 mm; Activated Carbon Technologies Pty Ltd, Melbourne, Australia). This GAC is specifically made for the removal of atmospheric VOCs, and is manufactured from steam-activated coal, producing a large surface area and high degree of microporosity [28]. Typical analysis provided by the manufacturer for the activated carbon indicates the apparent density is 0.45-0.50 g/mL, moisture as packed is 2%, surface area is 1000m^2/g min, and carbon tetrachloride activity is 65% min. The following ratios of coarse coconut husk to GAC by volume were assessed: 0:100, 10:90, 20:80, 30:70, 40:60, 50:50, 60:40; with the coarse coconut husk and GAC having bulk densities of ~0.20 g/cm^3 and ~0.52 g/cm^3 respectively. Each ratio was replicated 4 times. Prior to cassette construction, the GAC was rinsed thoroughly with water to remove residual fine particles. Before testing, all substrate media used in the experiments were watered to field capacity (the maximum volume of water the substrate can hold) and left to drain overnight.

2.2.3 Full-scale botanical biofilters

In order to produce practical outcomes for the horticultural infrastructure industry, the air cleaning potential of the optimized system was tested to indicate how efficiently VOCs and PM could be removed by complete biofilter-modules containing the modified substrate. Additionally, these trials incorporated any effects caused by plant interactions with the substrate.

The most efficient substrates identified in *Sections 2.2.1* and *2.2.2* were used in full-scale active green wall modules containing plants (Figure 3). These experiments utilized the biofilter modules previously described by Irga et al. [26]. For these experiments, all green wall modules utilized the species *Nephrolepis exaltata bostoniensis* as the botanical component.

Figure 3. A full-scale green wall module containing *Nephrolepis exaltata bostoniensis.*

2.3 Experimental set up

The experiments used a flow-through chamber set up to assess air pollutant SPREs (Figure 4). The flow-through procedure used a sealed Perspex chamber (0.6 X 0.6 X 0.6 m; 216 L), with one removable side, thus allowing cassette or green wall module placement in the chamber. Ducting from one side of the chamber led to a secondary chamber in which air pollutants were generated. Air pollutants flowed through the fitted ducting with active airflow provided by an in-duct axial impeller (FANTECH TEF-100 fan 16 W), before flowing through the biofilter. A second fan within the chamber was used to create a homogenous concentration of pollutants, and limited precipitation of particles before exhaust into another ducting system that led to an additional chamber that housed air pollutant concentration monitoring instruments. Air was exhausted to waste through a vacuum exhaust after sampling. Vacuum pressure was adjusted such that the pressure drop across the cassettes or green wall modules approximated that which occurs when the system is running unrestricted (~24.5 Pa [29]). The pressure drop of all substrate types was quantified individually to determine the required vacuum pressure (see *Section 2.4*).

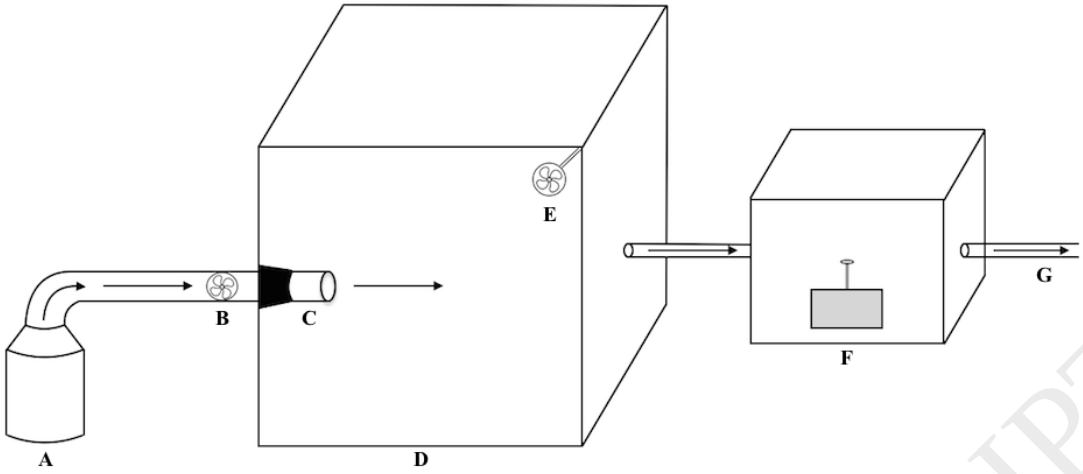

Figure 4. Flow-through chamber set up used to assess single pass removal efficiencies. A = pollutant generation chamber; B = axial impeller; C = cassette holding substrate (or active botanical biofilter); D = Perspex chamber; E = dispersal fan; F = pollutant detecting instrument; G = vacuum exhaust.

Trials for each pollutant were run independently, i.e. with a single pollutant type per run. Media were tested for their SPRE of a high dose and ambient concentration of PM, as well as vapor phase ethyl acetate, benzene and ambient total volatile organic compounds (TVOCs).

High dose PM was generated by burning 2 µL of filtered retail-grade diesel fuel (Shell) absorbed onto a 0.75 cm^2 536:2012 80 gsm square of paper in the pollutant generation chamber, providing a particle concentration and size distribution similar to some polluted environments [30] (for particle size distribution details, see Table 1S). Trials for each replicate were recorded for 8 minutes, which was sufficient time for the PM concentration to return to ambient levels for all treatments. Ambient PM trials were run using the same method, without generating any PM, therefore assessing each substrate's capacity to filter ambient PM from the laboratory atmosphere (see Table 2S). The average particle density and size distribution of the filtered airstream was measured with a laser nephelometer (Graywolf PC- 3016A, Graywolf Sensing Solutions, Connecticut, USA; counting efficiency: 50% at 0.3 µm; 100% for particles >0.45 µm (as per ISO 21501-4) with a concentration limit of 4,000,000 particles / ft^3 at 5% coincidence loss). To ensure data independence, average PM concentration was recorded for five mutually exclusive PM fractions: $PM_{0.3\text{-}0.5}$, $PM_{0.5\text{-}1.0}$, $PM_{1.0\text{-}2.5}$, $PM_{2.5\text{-}5.0}$, and $PM_{5.0\text{-}10.0}$.

Media were also tested for their SPREs of gaseous ethyl acetate and benzene. Both of these VOCs are problematic in indoor environments [31, 32], and were chosen to assess how the system treats relatively hydrophilic VOCs (ethyl acetate: solubility at 25°C = ~80.3g/L [33]) and relatively hydrophobic VOCs (benzene: solubility at 25°C = ~1.71g/L [34]). Trials were additionally conducted with ambient total VOCs (TVOCs) to assess the removal efficiency at low-level (500-600 ppb) concentrations. VOC removal was tested using the flow-through chamber method previously described, with benzene and ethyl acetate generated by placing 4.0 mL of the liquid chemical into a 10 mL sealed glass vial and extracting 2.5 mL of the vapor saturated headspace with a gas chromatograph syringe, before injection into the pollutant generation chamber of the flow through system. Each injection put through either 1.275×10^{-5} or 1.253×10^{-5} mol of gaseous benzene and ethyl acetate respectively. The concentration of the effluent gas was monitored with a

photoionization detector (ppbRAE 3000, RAE Systems, San Jose, CA, USA), which has a detection resolution of 1 ppbv of VOC concentrations ranging from 1 ppbv to 10000 ppbv. Ambient laboratory air TVOCs were measured and assessed in a similar manner without any VOC generation. In these trials, the labs ambient air with an average TVOC concentration of 585.12 ± 52.67 ppbv was continuously flowing through the chamber.

Blank (empty chamber) control data for all PM and VOC treatments were assessed to ensure that the flow through system without media did not affect PM or VOC concentrations. All test cassettes and full-sale botanical biofilters used the experimental set up described above to test their SPREs of air pollutants. For trials that tested the SPREs of full-scale botanical biofilters, these modules were placed within the flow-through chamber, in the location denoted 'C' in Figure 4.

2.4 Performance evaluation and substrate characteristics

All biofilter trials were compared to a control specific to each pollutant, which was obtained using the same process without any biofilter in the chamber. This procedure was replicated ≥ 10 times for each pollutant to provide an accurate measure of the generated pollutant concentrations (see Tables 1S-3S). The SPRE for each pollutant treatment was calculated as the difference between air pollutant concentration within the duct with and without the application of the biofilter treatments.

In addition to the pollutant removal characteristics of the media, the air filled porosity, substrate water holding capacity and pressure drop were determined for each treatment. Air filled porosity is the proportion of a medium that is filled with air and thus indicates the degree of aeration of the medium [35], and is therefore an important consideration for a medium subject to active airflow. Air filled porosity was measured as the volume of water displaced by a known volume of saturated substrate.

Substrate water holding capacity is important for plant health, but may also affect pollutant filtration [36]. Water holding capacity was measured as the difference in mass between cassettes that were watered to field capacity and allowed to drain for 1 day, and the cassettes' corresponding mass after drying at 60 °C for 1 week to remove all free water. Pressure drop is the resistance to airflow across each cassette. The pressure drop across each treatment cassette was measured with a Sensirion digital sensor (SDP610 125 Pa) placed between the fan and the cassette. Values were recorded every second over a ~2 minute period, providing an average pressure drop value for each substrate treatment.

2.5 Data analysis

To compare PM SPRE across the three different sized coconut husk-based particles, two separate one-factor PERMANOVAs (PAST Ver 3.15) were conducted. One-factor ANOVAs (IBM SPSS Statistics Ver 21) were conducted to compare the SPREs of ethyl acetate, benzene, and ambient TVOCs amongst the different coconut husk-based treatments, and also for the coconut husk-based treatments to compare pressure drop, air filled porosity and water-holding capacity.

To assess the influence of GAC concentration as a predictor for the SPRE of VOCs, independent non-linear logarithmic loss function regression analyses (IBM SPSS Statistics Ver 21) were conducted. Three independent general linear model regression analyses (IBM SPSS Statistics Ver 21) were conducted to determine if the percentage of GAC significantly influenced the variation in pressure drop, air filled porosity and water holding capacity.

The best performing GAC-based substrate and the best performing coconut husk-based substrate were compared in full-scale botanical biofilter modules for air pollutant removal. The SPRE of ethyl acetate and benzene between treatments were compared using ANOVA. To compare the PM filtration performance between the treatments, a multivariate PERMANOVA was used, with the SPRE of the mutually exclusive PM fractions as independent response variables.

3 Results and Discussion

3.1 Coconut husk-based substrates

The coconut husk-based substrate results for the SPRE of the tested pollutants are presented in Figure 5. There were no significant differences in the SPRE of PM amongst the differently-sized coconut husk-based substrates for both the high dose PM treatment (*pseudo-F* = 2.813, $p = 0.060$) and the ambient PM treatment (*pseudo-F* = 0.897, $p = 0.509$). ANOVA revealed that there were no significant differences in the SPRE of ethyl acetate ($F = 1.249$, $p = 0.315$), benzene ($F = 0.731$, $p = 0.498$), and ambient TVOCs ($F = 0.727$, $p = 0.5$) amongst the coconut husk treatments. It should be noted in the following figures that SPREs < 0 indicate that the treatments were releasing PM into the outlet duct.

Whilst no differences were observed for pollutant removal across the substrates, significant differences in pressure drop were recorded (Table 1; $F = 27.852$, $p < 0.000$). Post-hoc Tukey HSD tests showed that the coarse substrate had a significantly lower pressure drop than the fine and medium substrates ($p < 0.000$ for both comparisons). Further, significant differences amongst the water holding capacities of the different coconut husk-based substrates were found (Table 1; $F = 37.980$, $p < 0.000$). Post-hoc Tukey HSD tests found all treatments to have significantly different water holding capacities relative to each other, with the coarse substrate's water content significantly lower than both other media ($p < 0.000$ for both comparisons), and the fine medium significantly higher than the medium substrate ($p = 0.043$). Additionally, air filled porosity was significantly different between treatments (Table 1: $F = 134.756$, $p < 0.000$). Post-hoc Tukey HSD revealed that the coarse substrate had a significantly higher air filled porosity than both the fine and medium substrates ($p < 0.000$ for both comparisons).

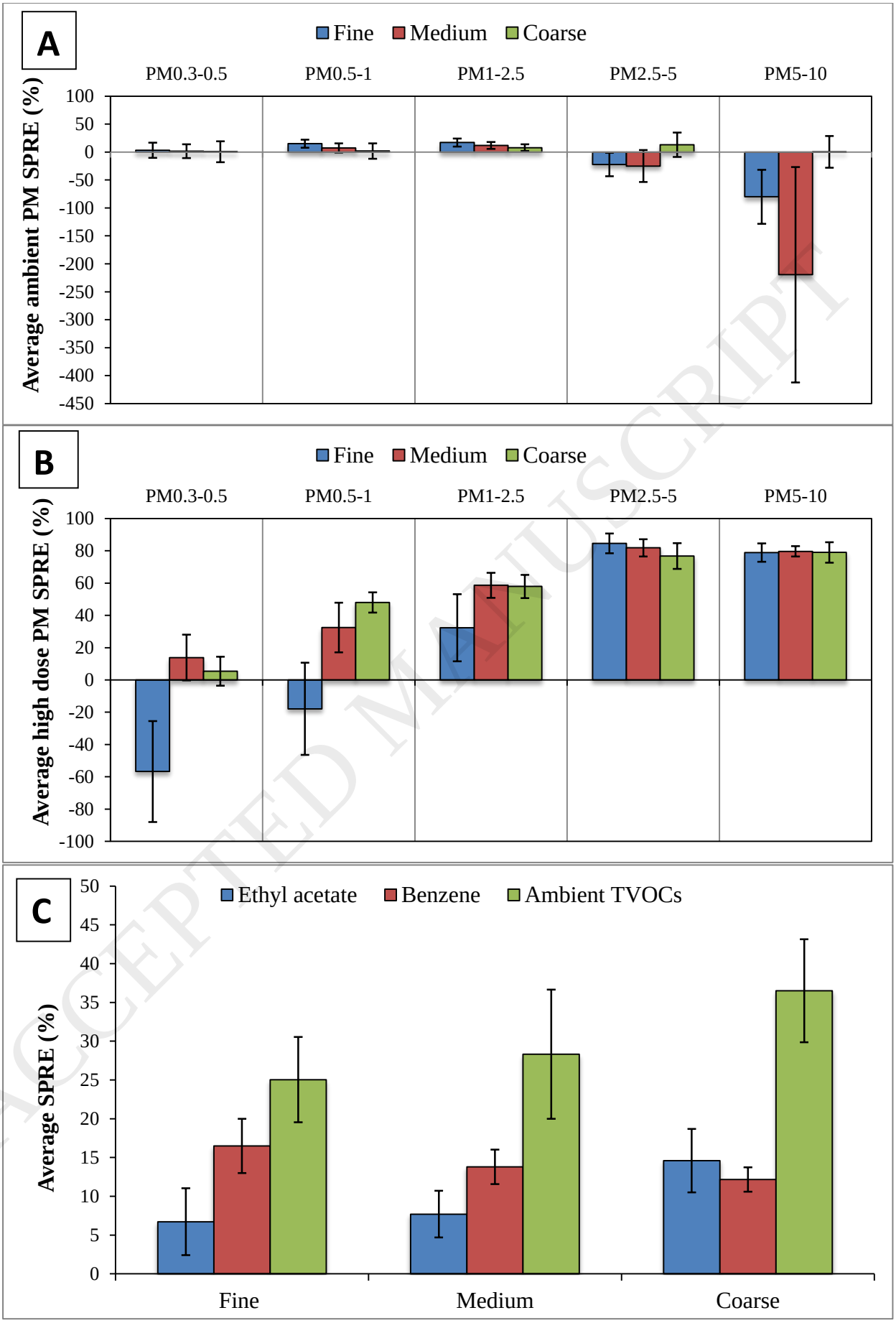

Figure 5. Average SPREs (%) recorded by the fine, medium and coarse coconut husk-based media treatments (*n* = 6). A = ambient PM SPRE; B = High dose PM SPRE; C = VOC SPRE. Error bars represent standard error of the mean. No significant differences in the SPRE of the high dose PM treatment, ambient PM treatment, ethyl acetate, benzene and ambient TVOCs.

Unexpectedly, the fine and medium particle size coconut fibre substrates appeared to emit some PM during the trials (Fig 5), with some $PM_{2.5–10}$ emitted in the ambient PM trial, and $PM_{0.3\text{-}1}$ released in the high dose SPRE trial. It should be noted that the ordinate scales of these figures are in units of percentage of the initial dose, so the absolute % values of PM cannot be compared between figures 5a and b. Whilst we cannot determine why different PM fraction sizes were emitted between these two trials, clearly the release of PM from a system designed for indoor air treatment is detrimental to its overall performance. Although it is likely that the release of these particles would decline with longer-term use of the biofilter's ventilation system, we must nonetheless present these findings as further evidence that the smaller fraction coconut fibre substrates are inferior for practical use.

Table 1. The water holding capacity, pressure drop and air filled porosity of the fine, medium and coarse coconut husk-based substrates. Values represent averages ± standard error of the mean (*n* = 6).

Substrate	Water holding capacity (%)	Pressure drop (Pa)	Air filled porosity (%)
Coarse	41.03 ± 1.26*	52.87 ± 0.31*	53.27 ± 0.98*
Medium	50.82 ± 1.40*	55.29 ± 0.19	31.34 ± 0.85
Fine	55.64 ± 1.45*	55.50 ± 0.31	28.24 ± 1.57

* indicates statistically significant at $p < 0.000$.

These findings indicate that the coarse coconut husk material was the best performing substrate, due to its significantly lower pressure drop and equivalent pollutant removal performance. The pressure drop findings are unsurprising due to the significantly higher air filled porosity of the coarse medium. Although particle size does not theoretically affect porosity for well-sorted particles [37], the larger variability in size and shape of the coarse media resulted in a larger air filled porosity. A lower pressure drop is desirable as it allows a greater volume of air to be processed by the biofilter, while media with higher pressure drops require greater mechanical ventilation energy to process equivalent volumes of air. Similarly, the water holding capacity is an important metric for plant growth, and although the coarse substrate had a significantly lower water holding capacity than the other coconut husk-based substrates, it's capacity has been shown to be sufficient to maintain plant health with a manageable watering regime [38]. The apparent release of PM by several treatments was very surprising, and is discussed in the following section.

Due to the favorable properties of the coarse coconut husk-based media, it was selected as the base substrate for the subsequent GAC trials.

3.2 Granular activated carbon and coconut-based media

All treatments showed highly variable SPREs for both the ambient and high dose PM concentrations. It is possible that this variability could be reduced with the addition of plants due to their functional role in increasing PM filtration efficiency

[23]. Significant differences amongst media with different portions of GAC were observed for their high dose PM SPREs for several independently-sized PM fractions (Figure 6; PERMANOVA: *pseudo-F* = 3.621, $p < 0.000$), with the location of this difference due to the apparent release of PM by the 60% GAC treatment relative to the 0% treatment. No significant differences amongst the media were observed for ambient PM SPREs (Figure 6; PERMANOVA: *pseudo-F* = 1.954, $p = 0.0518$).

Despite a lack of significant differences among treatments for ambient PM SPRE, there were several instances where the PM SPRE of the GAC treatments was negative, indicating that these substrates were generating PM above ambient concentration. This was particularly evident in the 30% and 40% GAC treatments, which generated considerable concentrations of the $PM_{0.3\text{-}0.5}$, $PM_{2.5\text{-}5}$ and $PM_{5\text{-}10}$ fractions. The nature of this PM release is currently unknown, although it is possible that these particles may be water droplets, which are known to be detected with laser nephelometry [39]. Alternatively, GAC pellets consist of compressed fine particles and it is possible that some became aerosolized under active airflow. Further work that characterizes the composition of these particles is needed to make this distinction. This marks an important finding, as previous studies that have highlighted GAC as an effective filter for VOC removal have not assessed PM release (e.g. [17]).

A series of non-linear logarithmic loss function regression analyses indicated that the concentration of GAC significantly predicted the SPRE of ethyl acetate (Figure 7A; $F = 65.466$, d.f. = 1 and 22, $R^2 = 0.748$, $p < 0.000$) benzene (Figure 7B; $F = 29.582$, d.f. = 1 and 22, $R^2 = 0.573$, $p < 0.000$) and ambient TVOCs (Figure 7C; $F = 5.528$, d.f. = 1 and 22, $R^2 = 0.201$, $p = 0.028$).

A series of general linear model regressions found that the percentage of GAC in the media did not significantly influence substrate pressure drop (Table 2; $R^2 = 0.099$, $p = 0.173$), air filled porosity (Table 2; $R^2 = 0.013$, $p = 0.713$) or water holding capacity (Table 2; $R^2 = 0.246$, $p = 0.061$), while the low R^2 values in every case indicated that the percentage of GAC in the media accounted for very little variability in these three dependent variables.

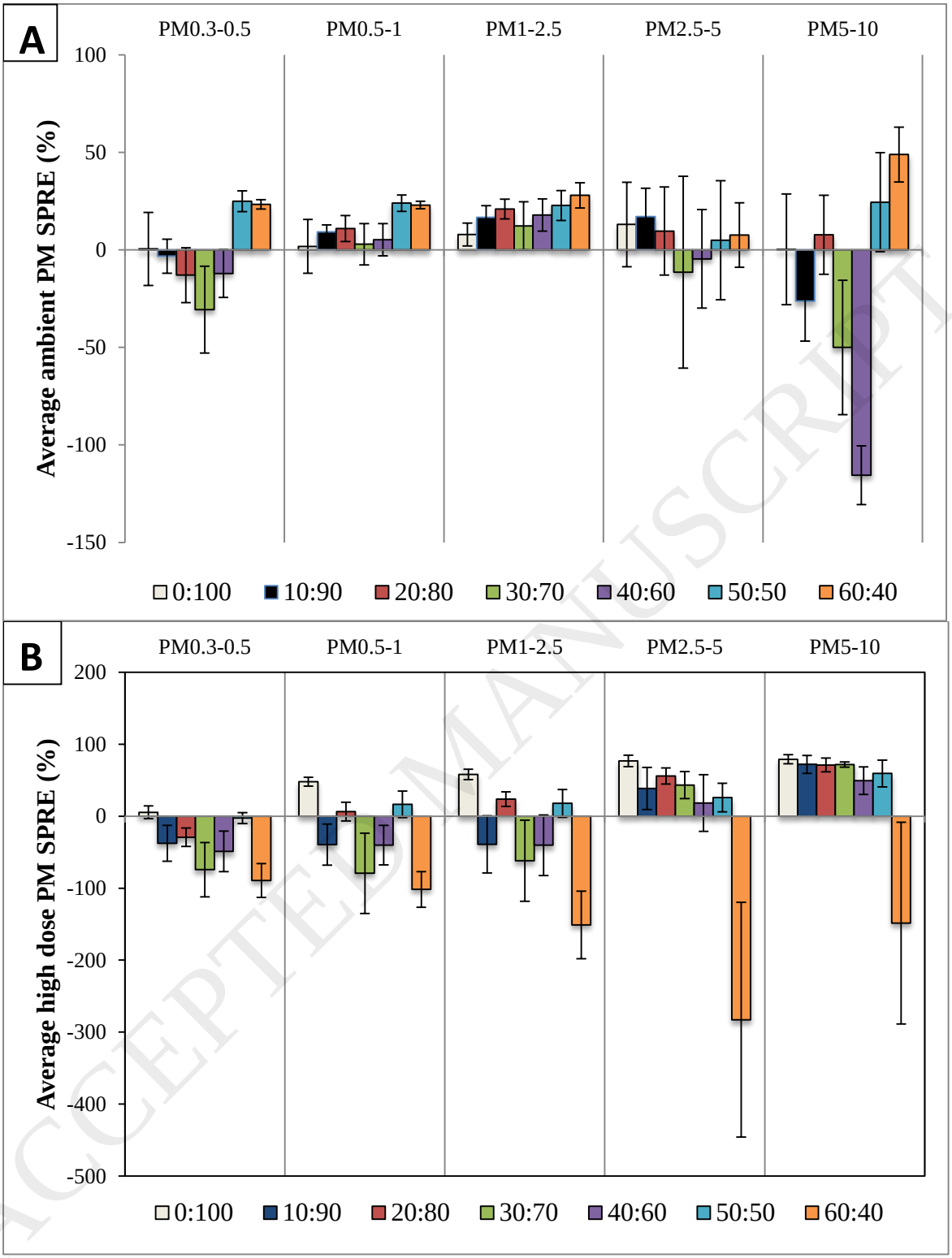

Figure 6. Average PM SPRE (%) across a range of independent PM sizes media with different concentrations of GAC (*n* = 4). Figure legends represent the ratio of GAC to coconut husk; A = ambient PM SPRE; B = high dose PM SPRE. Error bars represent standard error of the mean.

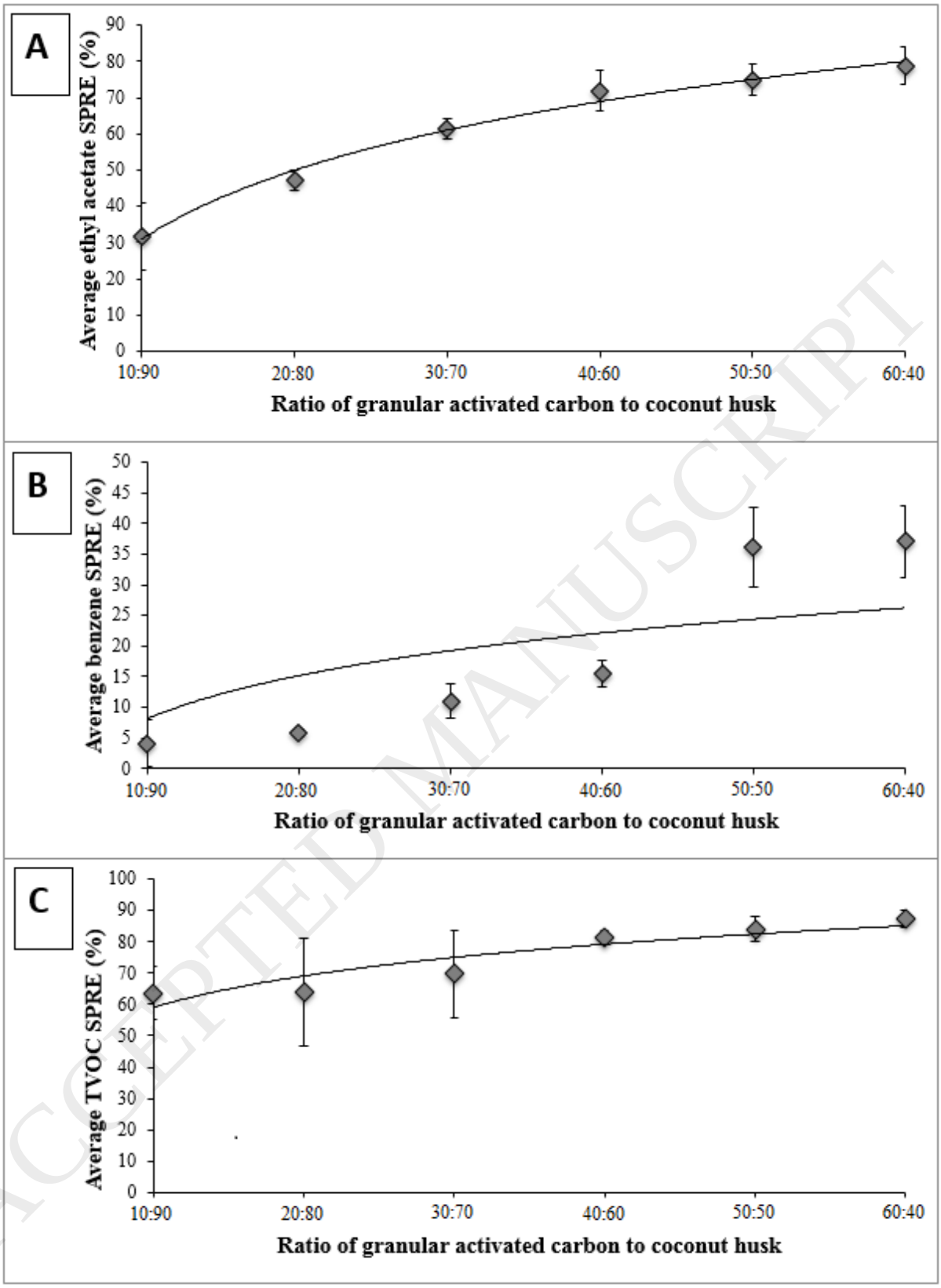

Figure 7. Average SPRE (%) across media containing different ratios of GAC to coconut husk (n = 4). A = ethyl acetate SPRE; B = benzene SPRE; C = Ambient TVOC SPRE. Error bars represent standard error of the mean.

Table 2. The water holding capacity, pressure drop and air filled porosity of substrates with varying concentrations of granular activated carbon. Values represent averages ± standard error of the mean (n = 4).

GAC to coarse coconut husk ratio	Water holding capacity (%)	Pressure drop (Pa)	Air filled porosity (%)
0:100	41.03 ± 1.26	52.65 ± 0.38	52.17 ± 1.08
10:90	46.63 ± 1.73	51.35 ± 0.39	49.77 ± 2.06
20:80	46.45 ± 1.07	50.64 ± 0.36	51.60 ± 1.24
30:70	45.63 ± 0.88	51.41 ± 0.13	45.10 ± 2.20
40:60	43.42 ± 0.49	51.30 ± 0.47	51.23 ± 0.92
50:50	42.16 ± 0.48	53.16 ± 0.36	51.81 ± 1.09
60:40	41.59 ± 0.96	53.05 ± 0.25	49.73 ± 1.86

* no regression analyses were statistically significant at $p = 0.05$.

The addition of higher proportions of GAC improved the ethyl acetate, benzene and ambient TVOC SPREs. As the GAC to coconut husk ratio in the media approached ~50%, the SPRE of these gases plateaued, suggesting that the addition of GAC above this level provides no additional performance benefit. This concentration of GAC was also used by Wang and Zhang [17], who achieved high removal efficiencies for toluene and formaldehyde. The current results have further highlighted the value of GAC in biofilter media to remove both hydrophilic and hydrophobic VOCs.

The limitation of GACs capacity to adsorb gaseous pollutants at 50% by volume may result from the rate at which the gaseous pollutants transfer to the aqueous phase, which must occur before the pollutants can be adsorbed onto the GAC [40]. These observations correspond with those of Darlington et al. [1], who recorded greater toluene, ethyl benzene and *o*-xylene biofiltration rates, at lower temperatures, which decreased microbial activity but increased the solubility of the tested compounds, suggesting that the transition from the gas phase to the solubilized water phase is the rate limiting step rather than microbial activity. The current observation of the higher SPRE for the more soluble VOC ethyl acetate relative to benzene, supports this conclusion. Although a dry medium may remove this limiting step, water is essential for plant growth, and therefore testing dry media would be of no practical value. There is insufficient time in SPRE trials for significant microbial metabolism to occur, thus making VOC removal likely a solely physiochemical property of the substrate (which may, nonetheless, be affected by microbial properties)**.**

Although these findings highlight the potential of certain botanical biofilter substrates to filter and / or adsorb various air pollutants, it is possible that the cassette results would vary when applied to full-size biofilters that are able to distribute pollutants through their larger media volume via a plenum. Furthermore, the interaction between plant and substrate should be assessed to determine the system's realistic air cleaning potential.

3.3 Full scale tests

This section compared the SPRE of ethyl acetate, benzene and a high dose PM treatment between two full-scale green wall modules: one containing a substrate of coarse coconut husk only, and the other containing a composite substrate consisting of a 50:50 ratio of coarse coconut husk to GAC (by volume).

The contact time between pollutant and filtration materials ranged between 11.2 and 11.3 minutes. Significant differences in benzene SPRE were observed between treatments (Figure 8; ANOVA, $F = 117.39$, d.f. = 1, 6, $p < 0.000$), with the composite substrate biofilter recording an average of 25.66% higher benzene removal efficiencies than the coarse coconut husk substrate treatment.

The SPRE of ethyl acetate was exceptionally high across both treatments, with both biofilters removing ~78% of the VOC on a single pass. There was no significant difference between the treatments (Figure 9; ANOVA, $F = 0.003$, d.f. = 1, 6, $p = 0.961$).

Multivariate PERMANOVA found significant differences between the treatments for the SPRE of a range of PM sizes (Figure 9; *pseudo-F* = 5.699, $p = 0.033$).

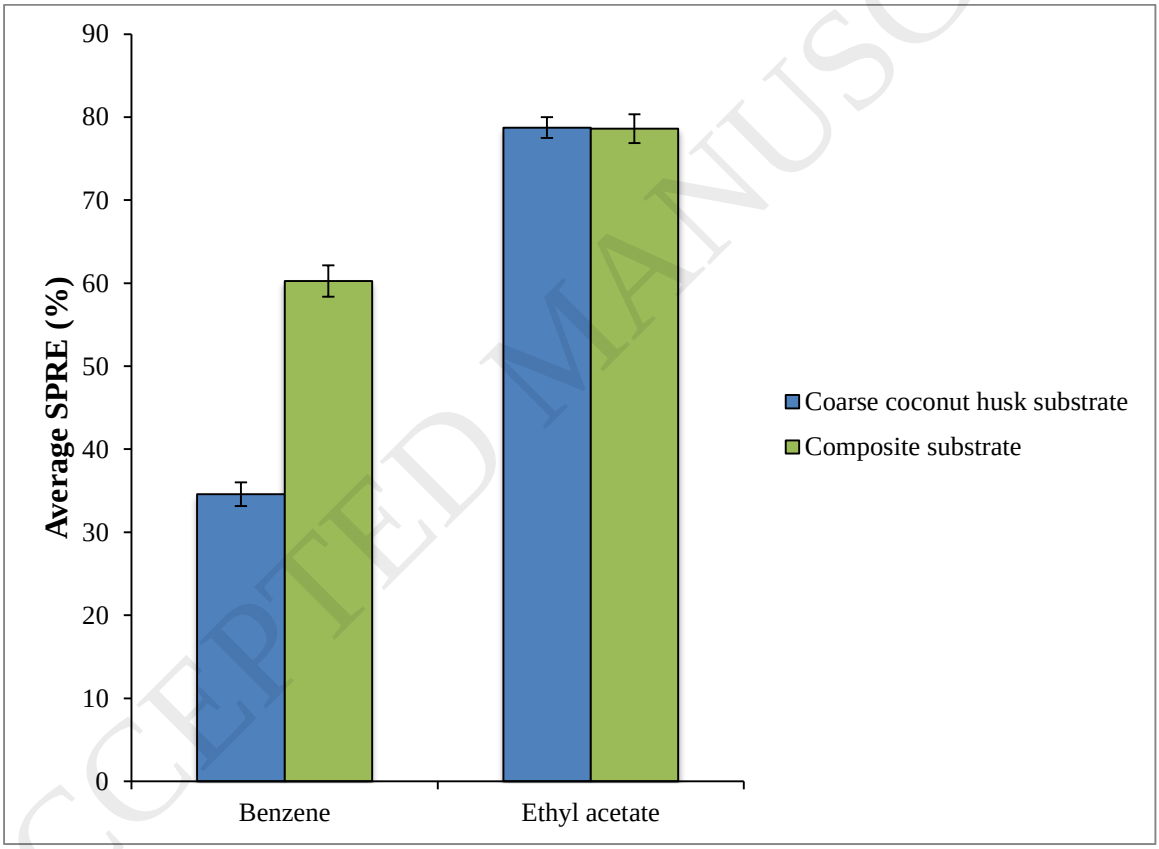

Figure 8. Average SPRE (%) of VOCs by botanical biofilters (n = 4). Error bars represent standard error of the mean.

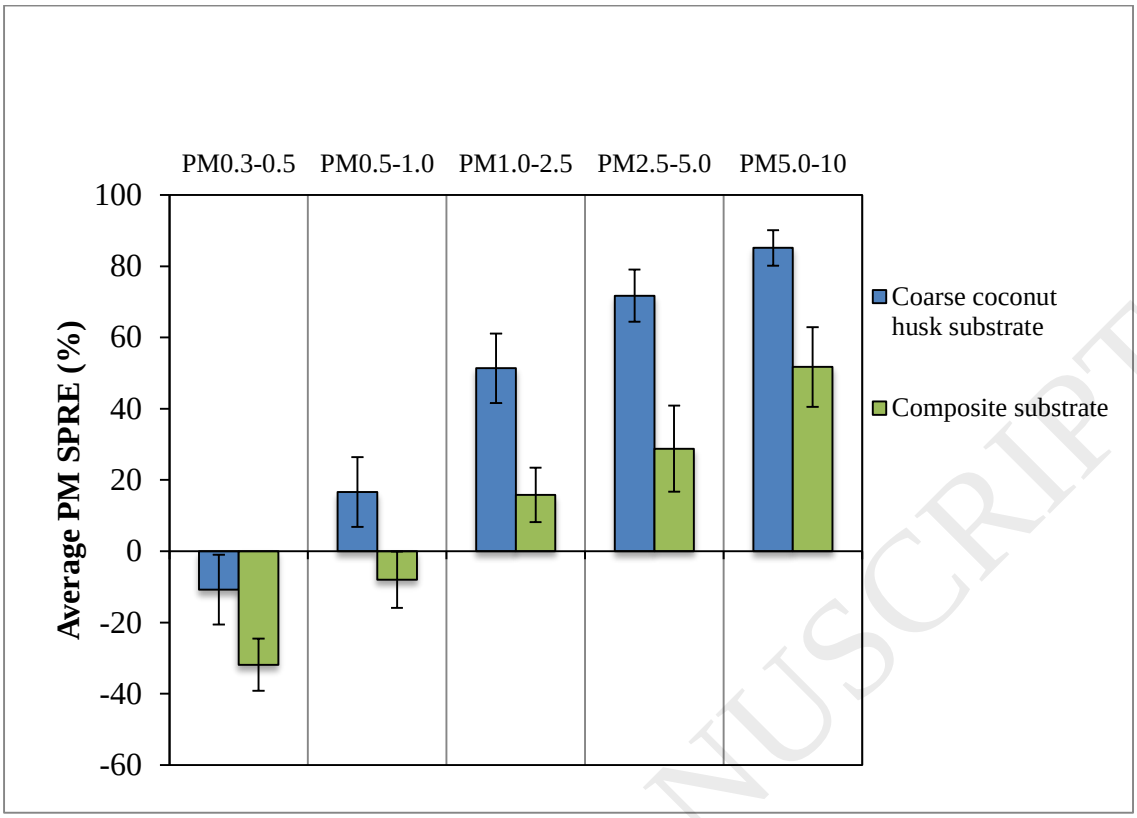

Figure 9. Average ambient PM SPRE (%) across a range of independent PM sizes media with different percentages of GAC (n = 4). Error bars represent standard error of the mean.

Both substrates demonstrated similar SPREs for ethyl acetate, despite differences between these substrates when trialed in cassette format. The removal rates observed indicate that active biofilter ethyl acetate removal may be dependent upon an interaction effect between the plants and substrate, with the coarse coconut husk substrate removing this VOC more efficiently with plants present. It is possible that the plant roots may provide hydrophilic adsorbent sites for ethyl acetate, thereby increasing SPRE. Plant roots release a considerable proportion of the plant's total fixed carbon [41, 42]. While this process assists the plants by promoting beneficial interactions with the soil microbial community to prevent pathogenic infection and increase water and nutrient uptake [43], it also alters the rhizospheric chemical composition [44] and can increase the bioavailability and plant uptake of soil contaminants [45-47]. Tu et al. [48] found that phytic acid and oxalic acid were the primary low molecular weight organic acids released from the roots of *N. exaltata bostoniensis*. It is possible that the presence of these chemicals will increase ethyl acetate dissolution into the rhizosphere due to the interaction of the polar functional groups of these molecules. It is also possible that the plant root exudates may have had a stronger influence on the SPRE of ethyl acetate than the presence of GAC, however this trend may not be seen to the same extent with benzene as a result of the strongly nonpolar structure of this VOC. Consequently the presence of plants has a strong impact on the removal efficiency of different VOCs. Although no study has tested the relative effects of different plant species on their SPRE for any VOCs, several studies using potted-plants in static chambers have revealed differences between species. For example Kim et al. [49] reported differences in formaldehyde

removal efficiencies amongst 86 tested species, with ferns recording the highest removal rates, followed by herbs and woody foliage plants. These patterns are surprising due to clear evidence that VOC removal is driven by microorganisms in the root zone [8], suggesting that different plants may be encouraging different substrate microbial communities, thus affecting their VOC removal rates. As expected from the cassette trials, coconut husk biofilters were more effective at removing PM than GAC-containing units. This was most likely due to the co-detection of PM released from the GAC substrate filters.

The application of GAC as a substrate component improved the benzene SPRE of the biofilter, with a removal rate of 60.24%. While previous studies have suggested that the biofiltration of VOCs is limited by the rate at which they transfer into the aqueous phase [1, 50], it is possible that the combined effects of active airflow and highly efficient adsorbents can overcome this limitation even for hydrophobic VOCs such as benzene. The presence of water in the substrate possibly also increased the capacity of GAC to filter hydrophobic compounds [51]. Although GAC has both hydrophobic and hydrophilic adsorption sites [52], the interactions between the water and GAC allows water molecules to cluster in the hydrophilic micropores of GAC that would otherwise hinder its ability to adsorb hydrophobic compounds [36]. Consequently a hydrophobic pollutant, such as benzene, can generate a larger driving force for adsorption in the aqueous phase [36]. It is noteworthy that the coarse coconut husk substrate recorded a higher benzene SPRE than that recorded for the non-botanical coarse coconut husk cassette, however it is not known if this was due to a functional role of the botanical component or was simply a result of the larger module and/or plenum.

The addition of GAC in the composite substrate treatment reduced the capacity of the system to filter PM. Reduced PM removal was also a consistent characteristic of cassettes containing GAC substrates, and despite the presence of plants that are known to improve PM removal efficiency [23], the full scale composite substrate botanical biofilter still performed comparatively poorly for PM filtration, and in some cases, appeared to emit PM. This is an important finding as other studies that have solely tested the VOC removal of GAC based substrates have suggested that it is an optimal substrate choice [17]. With the current findings, it is likely that a composite substrate should be used with caution or in conjunction with additional PM filtration system components. However, if the system was run *in situ* for an extended period of time, it may be possible that PM will be emitted at only the initial run of the system, and this release would decline over longer-term use.

It is clear that different media have different remediation capabilities and that some media remediate particular pollutants more efficiently than others. The medium traits that influence pollutant remediation also have important ramifications for plant health. While the high adsorbent capacity of GAC is beneficial in VOC remediation, GAC is also efficient in removing several botanically-important nutrients from solution, such as nitrates [53], ammonium [54] and phosphates [55]. Although Aydogan and Montoya [3] found that whilst a substrate of 100% wetted activated carbon was their best performing media for formaldehyde removal, this medium did not sustain long-term plant growth, and was therefore impractical as a botanical biofilter substrate. Wang and Zhang [17] however sustained plant health over their 300-day trial using a 50:50 mix of activated carbon and shale pebbles. At the date of writing, the 50% GAC substrate module tested in the current work has effectively supported plant growth for 280 days without subsequent fertilization. These findings suggest that GAC concentrations above a threshold may not provide conditions that

sustain plant health. Green wall plant health is paramount, and further studies are thus needed before the viability of a range of plant species grown in such a substrate can be confidently established.

These results indicate a high air cleaning potential for all active green wall substrate treatments, and demonstrate that the application of GAC as a substrate component can improve the removal efficiency for certain pollutants. The use of GAC in active biofilter media should thus be target pollutant dependent, and tested for PM emissions if they may be a problem in a specific application.

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Table 3. The water holding capacity, pressure drop and air filled porosity of the fine, medium and coarse coconut husk-based substrates. Values represent averages ± standard error of the mean (*n* = 6).

Substrate	Water holding capacity (%)	Pressure drop (Pa)	Air filled porosity (%)
Coarse	41.03 ± 1.26*	52.87 ± 0.31*	53.27 ± 0.98*
Medium	50.82 ± 1.40*	55.29 ± 0.19	31.34 ± 0.85
Fine	55.64 ± 1.45*	55.50 ± 0.31	28.24 ± 1.57

* indicates statistically significant at $p < 0.000$.

Table 2. The water holding capacity, pressure drop and air filled porosity of substrates with varying concentrations of granular activated carbon. Values represent averages ± standard error of the mean (n = 4).

GAC to coarse coconut husk ratio	Water holding capacity (%)	Pressure drop (Pa)	Air filled porosity (%)
0:100	41.03 ± 1.26	52.65 ± 0.38	52.17 ± 1.08
10:90	46.63 ± 1.73	51.35 ± 0.39	49.77 ± 2.06
20:80	46.45 ± 1.07	50.64 ± 0.36	51.60 ± 1.24
30:70	45.63 ± 0.88	51.41 ± 0.13	45.10 ± 2.20
40:60	43.42 ± 0.49	51.30 ± 0.47	51.23 ± 0.92
50:50	42.16 ± 0.48	53.16 ± 0.36	51.81 ± 1.09
60:40	41.59 ± 0.96	53.05 ± 0.25	49.73 ± 1.86

* no regression analyses were statistically significant at $p = 0.05$.