The botanical biofiltration of VOCs with active airflow: is removal efficiency related to chemical properties?

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Abstract

Botanical biofiltration using active green walls is showing increasing promise as a viable method for the filtration of volatile organic compounds (VOCs) from ambient air; however there is a high level of heterogeneity reported amongst VOC removal efficiencies, and the reasons for these observations have yet to be explained. Comparisons of removal efficiencies amongst studies is also difficult due to the use of many different VOCs, and systems that have been tested under different conditions. The current work describes a procedure to determine whether some of these differences may be related to the chemical properties of the VOCs themselves. This work used an active green wall system to test the single pass removal efficiency (SPRE) of nine different VOCs (acetone, benzene, cyclohexane, ethanol, ethyl acetate, hexane, isopentane, isopropanol and toluene) and explored which chemical properties were meaningful predictor variables of their biofiltration efficiencies. Ethanol was removed most efficiently (average SPRE of 96.34% ± 1.61), while benzene was least efficiently removed (average SPRE of 19.76% ± 2.93). Multiple stepwise linear regression was used to determine that the dipole moment and molecular mass were significant predictors of VOC SPRE, in combination accounting for 54.6% of the variability in SPREs amongst VOCs. The octanol water partition coefficient, proton affinity, Henry's law constant and vapour pressure were not significant predictors of SPRE. The most influential predictor variable was the dipole moment, alone accounting for 49.8% of the SPRE variability. The model thus allows for an estimation of VOC removal efficiency based on a VOC's chemical properties, and supports the idea that system optimization could be achieved through methods that promote both VOC partitioning into the biofilter's aqueous phase, and substrate development to enhance adsorption.

Keywords: Active green wall; botanical biofilter; potted-plant; green building; sustainability; living wall.

Highlights:

- Nine VOCs were tested for their removal efficiency through an active green wall.
- The average removal efficiency for the VOCs ranged from 19.76 to 96.34%.
- A model to estimate removal efficiency based on chemical properties was developed.

- Dipole moment and molecular mass were significant predictors of VOC removal rate.
- The model allows estimation of VOC removal based on a VOC's chemical properties.

1. Introduction

Volatile organic compounds (VOCs) are an important class of air pollutants present in many indoor environments (Cakmak et al., 2014; Wang et al., 2013a; Wolkoff, 2013), where their concentration is often much higher than in the corresponding outdoor environment (United States Environmental Protection Agency, 2017). Several hundred VOCs have been reported in the indoor environment (Meciarova and Vilcekova, 2016) and exposure to certain VOCs has been associated with a broad range of symptoms including asthma and allergic disorders (Garrett et al., 1999; Krzyzanowski et al., 1990; Norbäck et al., 1995; Rumchev et al., 2002; Venn et al., 2003), while some VOCs, such as benzene, can have carcinogenic effects (Mehlman, 2006).

Decades of research has shown that potted-plants are capable of reducing the concentration of several VOCs in both laboratory chamber and building air (Aydogan and Montoya, 2011; Deng and Deng, 2018; Godish and Guindon, 1989; Hörmann et al., 2018; Irga et al., 2013; Kim et al., 2016; Orwell et al., 2004; Wood et al., 2006), and their potential for the removal of ambient VOCs has been assessed to address growing concerns about indoor air quality (Irga et al., 2018). It is likely that the VOC removal mechanism of such systems is primarily through microbial degradation of the VOCs by the rhizospheric microbial community, with limited removal from stomatal uptake and microbial degradation within the phyllosphere, and an unknown contribution from abiotic chemical interactions between VOC and substrate (Torpy et al., 2015). It is probable that the precise contribution of each removal mechanism varies with the type of VOC tested, as well as the biotic and abiotic system components (Pettit et al., 2018a).

To increase the volumetric efficiency of botanical systems with the aim of developing more effective air cleaning systems, active green wall biofilters have been developed. These systems utilise plants which are grown in a vertical alignment, in conjunction with mechanically assisted airflow that promotes the movement of polluted air through the system's plant growth substrate and plant foliage, thus increasing the volume of polluted air that is treated by the system and promoting pollutant adsorption to the plant's growth substrate (Pettit et al., 2018a). While these systems share many characteristics with conventional non-botanical biofilters, their application differs considerably: conventional biofilters generally treat target VOCs in industrial applications with the effluent air exhausted to the external environment, while active botanical biofilters have generally been used to recirculate the air within a building, thus treating a range of indoor VOCs, which are often in very low concentrations (Llewellyn et al., 2000).

While several VOCs, mostly from the BTEX (benzene, toluene, ethylbenzene and xylene) group as well as formaldehyde (Kim et al., 2018), have been exhaustively tested for their botanical biofiltration potential, considerably different removal rates for different VOCs have been documented. This is true, both amongst (for example see (Irga et al., 2013; Orwell et al., 2004; Setsungnern et al., 2017; Treesubsuntorn et al., 2013)) and within (Cornejo et al., 1999; Mosaddegh et al., 2014; Wood et al.,

2002; Yang et al., 2009) studies depending on the tested VOCs, suggesting that VOC removal rates are strongly VOC dependent. This is unsurprising as VOCs can have immensely diverse functional groups (Lewis, 2018). No study has thus far explicitly explored the role of chemical properties for their associations with the quantitative rate of VOC removal by botanical biofilter systems. If active green wall pollutant drawdown occurs through substrate adsorption and microbial degradation (which is firstly dependent on VOC transfer to the aqueous phase), it is thus likely that specific chemical properties associated with each VOC will influence the capacity of these systems to remove different types of VOC. This may influence system design and allow selective applications associated with specific target VOCs. Investigating this issue through the current literature remains difficult, as the immense variance amongst experimental VOC application and system design amongst studies prevents unconfounded comparisons (see Pettit et al., (2018a)). This study thus assessed an active green wall system's capacity to filter a range of common VOCs and investigated which chemical properties influenced removal efficiencies.

2. Methods

2.1 Active green wall description and trial VOCs

A modular active botanical biofilter ('The Breathing Wall', Junglefy Pty Ltd; Banksmeadow, NSW, Australia; Figure 1) was used to assess VOC removal (see Pettit et al., (2017) for a detailed description). Summarily, each biofilter module has a front face (0.5 x 0.5 m) containing 16 holes from which plants grow. Fan-driven, untreated air enters the biofilter through an inlet in the module's rear face, where it is distributed across a coconut husk-based growth media via an internal plenum, before flowing out through the holes in the front face, passing through the plant foliage.

As different plant species are known to influence VOC removal efficiency (Kim et al., 2010), to eliminate the influence of plant effects all tested active green wall modules contained a single plant species, *Syngonium podophyllum*. This species is widely used in indoor greening systems, and the VOC removal efficiency of this plant species has been extensively documented in both potted-plant (Chun et al., 2010; Yang et al., 2009; Zhou et al., 2011), and hydroculture applications (Irga et al., 2013).

Prior to trials, each module was watered with 2 L of water 24 h before the pollutant dose was applied and left to drain; thus providing the active green wall modules with a moisture content representative of their *in situ* application.

The substrate (growth media) of the green wall modules was comprised of coconut husk coir. This media is favourable as it is low-cost and has been shown to support strong plant growth in practical applications. Furthermore, this substrate is capable of filtering a range of particulate matter size fractions (Pettit et al., 2017) and does not produce harmful bioaerosols (Irga et al., 2017). This media has an air filled porosity of 53.27% and a water holding capacity of 41.03% (Pettit, 2018b). The pH of the media was 4.68, which was established by mixing the dry substrate with deionized water in a 1:5 ratio and measuring the pH of the suspended substrate with an inoLab Level 2 pH meter.

2.2 Trial VOCs

The VOCs acetone, benzene, cyclohexane, ethanol, ethyl acetate, hexane, isopentane (2-methyl-butane), isopropanol and toluene were tested for their removal efficiency through the active green wall modules. Thus the VOCs tested included ketones, aromatic compounds, alcohols, esters, linear and cyclic alkanes, and thus represent VOCs with diverse chemical properties (Table 1). All trial VOCs were supplied by Sigma-Aldrich Pty Ltd (Castle Hill, Australia) and had minimum purities of 95%. The chemical variables statistically tested for their effect on removal efficiency were molecular mass, dipole moment, vapor pressure, proton affinity, octanol water partition coefficient, and Henry's law constant. These chemical properties were postulated as having the potential to influence VOC interactions with substrate adsorbents, the water film, and the rhizosphere / root zone, thus influencing the potential of these VOCs to be removed as they pass through the system. Water solubility was excluded as a predictor variable due to the inability to quantify the solubility of miscible chemicals as a ratio scale variable.

Table 1. Chemical properties of the VOCs used in the single pass removal trials. * data sourced from U.S. National Library of Medicine (2018); † data sourced from Wróblewski et al., (2006); § data sourced from Nelson Jr et al., (1967); ¶ data sourced from Haynes (2014); # data sourced from Scharpen et al., (1968).

VOC	Molecular mass (amu)*	Dipole moment (D)§	Vapour pressure (mm Hg at 25°C)*	Henry's law constant (atm-m^3/mol at 25 °C)*	Proton affinity (kJ/mol) ¶	Octanol/water partition coefficient Log K_{ow}*	Purity of test VOC
Acetone	58.08	2.88	231	3.97×10^{-5}	812	-0.24	≥99.8%
Benzene	78.11	0.00	94.8	5.56×10^{-3}	750.4	2.13	≥99.9%
Cyclohexane	84.16	0.331#	96.9	0.150	686.9	3.44	99.5%
Ethanol	46.07	1.69	59.3	5.00×10^{-6}	776.4	-0.31	99.5%
Ethyl acetate	88.11	1.78	93.2	1.34×10^{-4}	835.7	0.73	99.8%
Isopentane	72.15	0.130	689	1.40	No available data	2.72	>99.5%
Isopropanol	60.10	1.66	45.4	8.10×10^{-6}	793	0.05	>99.7%
Hexane	86.18	≤0.100	153	1.80	676.76 †	3.90	≥95%
Toluene	92.14	0.360	28.4	6.64×10^{-3}	784	2.73	99.8%

2.3 Experimental set up and sampling procedure

To assess the VOC single pass removal efficiency (SPRE) of the active green wall, experiments were conducted in a flow-through chamber (Figure 1). The flow-through set up involved a 216 L (0.6 x 0.6 x 0.6 m) Perspex chamber with air inlet and air outlets on opposite sides of the chamber. One side of the chamber was removable and resealable with metal clips, thus allowing active green wall modules to be placed into the chamber. A ducting system within the chamber connected the chamber's air inlet to the rear face of the green wall module. The chamber's air inlet led to a VOC injection port, through which a spiked dose of the VOC was introduced. The pollutant flowed from the injection port via an internal impeller housed within the ducting, through the green wall module. The volumetric airflow through the green wall modules was 0.65-0.68 m^3/min, which was measured with a Digitech Thermo-anemometer QM1646 embedded within the ducting between the impeller and the green wall module. In each trial, a proportion of the pollutant was filtered by the active green wall module, with the filtered air exiting the chamber through the air outlet. The outlet air flow was ducted to a down-flow sampling chamber that housed a photoionization detector (PID; ppbRAE3000, RAE Systems; San Jose, CA, USA) that logged the concentration of each VOC each second (the resulting concentrations of each VOC are shown in Supplementary Material). Air was then exhausted from the sampling chamber to a vacuum pump. A fan within the Perspex chamber encouraged air circulation, reducing pollutant retention within the chamber prior to sampling. With the system operating, VOC concentration was recorded for 10 minutes after generating the pollutant, allowing the VOC concentrations to return to ambient levels at the end of each trial. Control data was collected for each VOC, which involved determining the removal efficiency of the flow through system with no biofilter present.

Photon flux density was quantified with an Apogee MQ-200 Quantum Sensor (Apogee Instruments Inc., Utah, USA) and throughout the trials, biofilters were exposed to 6 µmol m^{-2} s^{-1}, which is representative of indoor light levels and thus their *in situ* application. Additionally, relative humidity (RH) and temperature were monitored over each trial period with a TSI multifunction ventilation meter 9565-P (TSI inc., Minnesota, USA) to ensure that large deviations from temperature or considerable increases in relative humidity did not affect PID measurements. The average inlet temperature and RH was 21°C and 41.6 % respectively, and by the end of each green wall trial, the average outlet temperature remained unchanged, while the average RH was 55.1 %. A period of ventilation between trials limited any cumulative effects resulting from humidity build up.

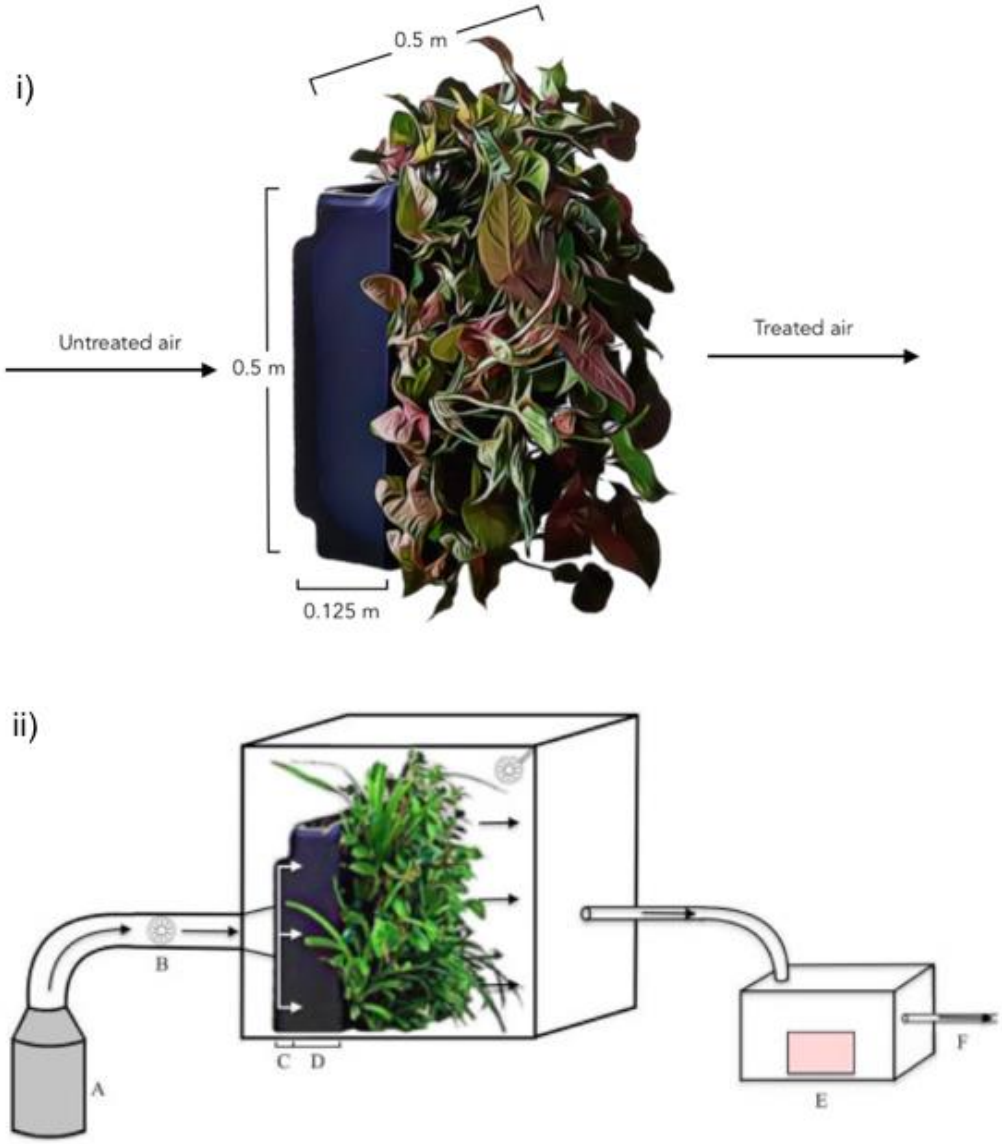

Figure 1. i) The active green wall module used in this study; ii) Single pass flow-through chamber: A = VOC injection port; B = axial impeller; C = plenum within green wall module; D = coconut husk growth media; E = photoionization detector; F = vacuum exhaust. Figure adapted from Pettit et al. (2017).

2.4 Comparisons amongst multiple VOCs

Each VOC was independently tested to assess whether the specific chemical properties of each VOC influenced SPRE. Each VOC was contained in a 10 mL vial that contained 4 mL of the liquid chemical. After an equilibration period, the vials' headspaces became saturated with the gaseous chemicals. The VOC was then drawn out of the vial's headspace with an air tight gas chromatography syringe. The gaseous VOC was then injected into the pollutant generation chamber.

As each different VOC has a different vapor pressure, there were different concentrations of gas in each vial's head space. Thus, the amount of gas extracted from the vial's headspace was adjusted for each VOC to ensure that an equivalent molar quantity of each VOC was injected into the pollutant

generation chamber, thus eliminating the possibility of dose-dependent SPREs confounding the findings. Thus, for each trial, 1.275 x 10^{-5} moles of each gaseous VOC were tested, as per (Pettit et al., 2018b).

Each VOC was trialed 10 times with an active green wall module in the chamber and 10 times without any active green wall module in the chamber (control). VOC concentration from the photoionization detector was plotted as a function of time, and the area under the curve was calculated, representing the amount of VOC that passed through the biofilter. By comparing the difference in quantitative VOC retention between the treatments, the SPRE of the active green wall was calculated for each VOC.

2.5 Data analysis

A one-way PERMANOVA (PAST Ver 3; (Hammer et al., 2001)) based on a Euclidean distance matrix was used to test for differences in the SPRE amongst the VOCs. Subsequent tests with Bonferroni corrected *p*-values were used to make pairwise comparisons between the SPREs of each VOC. Multiple linear stepwise regression (IBM SPSS Statistics Ver 25) was used to determine which chemical properties were meaningful predictors of SPRE by the active green wall. Predictor variables included molecular mass, dipole moment, vapour pressure, Henry's law constant, proton affinity and the octanol water partition coefficient.

3. Results and Discussion

3.1 VOC removal rates

The SPREs of different VOCs by the active green wall are shown in Figure 2. PERMANOVA revealed that there were significant differences in the SPREs amongst the tested VOCs (pseudo-F = 24.8, $p < 0.000$, n = 10). Ethanol was the most efficiently removed VOC (average SPRE = 96.34%) and had a significantly higher SPRE than acetone, benzene, cyclohexane, hexane, isopentane and toluene (Table 2). Acetone was also removed efficiently, with an average SPRE of 72.72%, which was significantly higher than that of benzene, cyclohexane, hexane and toluene. Additionally, both benzene and toluene had significantly lower SPREs than ethyl acetate, hexane and isopropanol, while cyclohexane had a significantly lower SPRE than that of ethyl acetate and isopropanol.

It is clear that different VOCs are filtered through the green wall system with different efficiencies, with the average SPRE for each of the chemicals ranging from 19.76 % to 96.34 %. This large disparity amongst VOC SPREs reflects the diversity in chemical properties amongst the VOC chemical class and their interaction with the specific filtration medium used, confirming the necessity to assess how phytoremediation systems remove each target VOC, rather than using a single VOC to represent the entire class of pollutants. The efficient removal of alcohols in this study and the relatively poor removal of aromatics and alkanes reflects trends observed in the non-botanical biofiltration of VOCs: Deshusses and Johnson (2000) found that the maximal removal performance was highest for alcohols followed respectively by esters, ketones, aromatics and alkanes. The authors suggested that both

Henry's law constant and the octanol water partition coefficient were useful predictors of removal efficiency, with the VOCs Henry's law constant linked to VOC specific removal rates in several other studies (Cheng et al. 2016c; Vikrant et al. 2017; Zhu et al. 2004). Interestingly, our study found that the dipole moment associated with each VOC is a more significant predictor of VOC removal rate through active botanical biofilters.

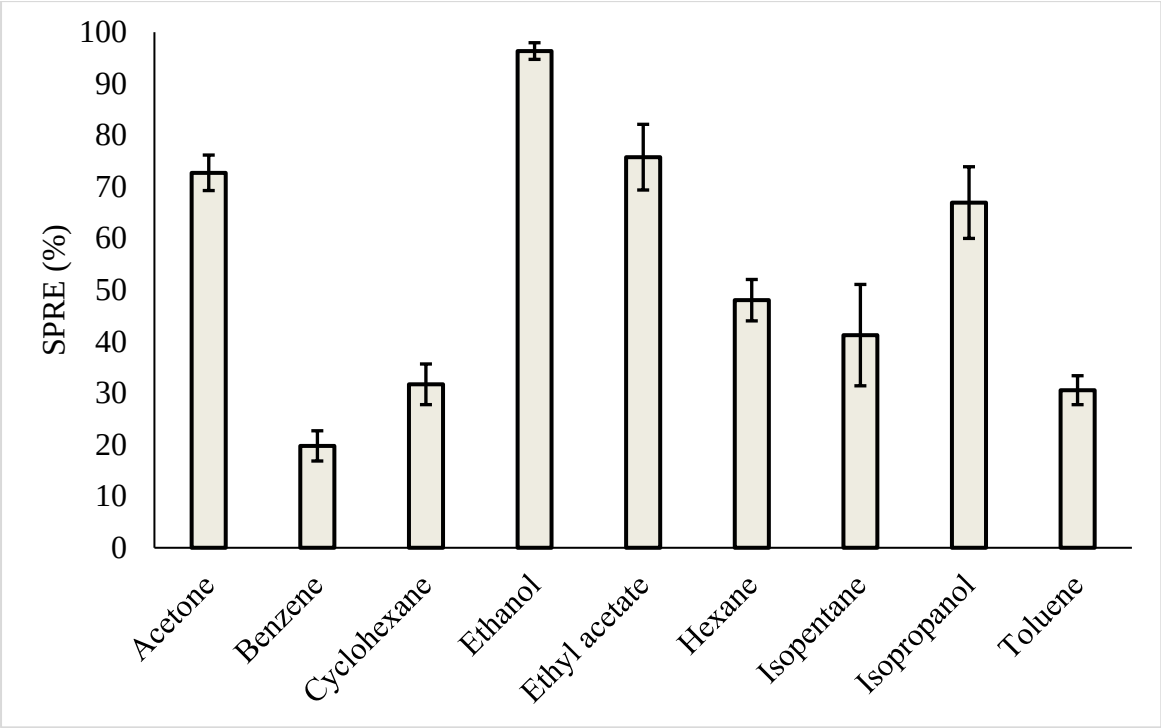

Figure 2. Average SPREs of an active green wall across different VOCs. Error bars represent standard error of the mean (*n*=10).

Table 2. Active green wall VOC SPRE pairwise comparisons. Data shown are the Bonferroni adjusted *p*-values. * indicates significant differences at $p < 0.05$.

VOC	Acetone	Benzene	Cyclohexane	Ethanol	Ethyl acetate	Hexane	Isopentane	Isopropanol
Benzene	0.011*							
Cyclohexane	0.011*	1						
Ethanol	0.007*	0.007*	0.007*					
Ethyl acetate	1	0.011*	0.018*	0.122				
Hexane	0.018*	0.011*	0.09	0.004*	0.212			
Isopentane	0.154	1	1	0.007*	0.230	1		
Isopropanol	1	0.004*	0.014*	0.097	1	1	0.979	
Toluene	0.004*	1	1	0.004*	0.004*	0.018*	1	0.004*

3.2 Predictive modelling of VOC SPRE

Multiple stepwise linear regression was used to identify the chemical properties that were the strongest predictors of SPRE amongst the different VOCs. This analysis indicated that the dipole moment and molecular mass were statistically significant predictors of VOC SPRE, accounting for 54.6% of the variability in SPRE (R^2 = 0.546, F = 69.393, p < 0.000, Table 3). The octanol water partition coefficient, proton affinity, Henry's law constant and vapour pressure were not significant predictors of SPRE in the model. The most influential individual predictor variable was the dipole moment, accounting for 49.8% of the SPRE variability, with compounds that have a higher dipole moment demonstrating higher SPREs. Molar mass accounted for an additional 6.8% of the SPRE variation, with smaller molecular weight VOCs being filtered more efficiently.

Table 3. Regression coefficients of VOC SPRE predictive model.

	B	**SE of *B***	**β**
Constant	77.044	16.249	-
Dipole moment	14.423	3.059	0.511*
Molecular mass	-0.497	0.183	0.294*

Note: R^2 = 0.546; * indicates p < 0.05.

The work provides the first model that allows quantitative predictions of the SPRE of VOCs through an active botanical biofilter. It has previously been hypothesised that VOC SPRE is dependent on the rate of dissolution into the aqueous phase (Darlington et al., 2001), a property which is strongly linked to Henry's law constant (Guieysse et al., 2008). While dipole moment, Henry's law constant and octanol water partition coefficient are all associated with water solubility, the dipole moment was the strongest predictor in a model with all factors acting as competing variables. Nonetheless, with a considerable proportion of the SPRE variability remaining unexplained by our model, along with the variance displayed amongst the SPRE values recorded for individual VOCs, it is likely that inherent variation in the system's biological material (i.e. the botanical component) may account for substantial residual SPRE variation.

Initial experiments using active botanical biofilters detected relatively similar removal rates for toluene, ethylbenzene and *o*-xylene (Darlington et al., 2001), however these VOCs are structurally similar, with similar chemical properties, so differences might not be expected amongst this VOC subgroup. Alternatively, Wang and Zhang (2011) found different single pass removal efficiencies for toluene and formaldehyde through their dynamic botanical air filtration system, particularly with low moisture levels in the filtration bed and high airflow rates. The present experiment has further explored differences in VOC SPRE, extending testing to nine diverse VOCs, thus confirming that differences in removal rates are strongly dependent upon the properties of the VOC.

While several experiments have observed differences amongst the removal rates of chemically diverse VOCs in trials using potted-plants (Pettit et al., 2018a), the use of active airflow in our experiment allows a greater volume of air to be treated and promotes substrate adsorption processes rather than

relying primarily upon microbial degradation or stomatal uptake for removal. Further, potted-plant experiments are typically carried out over hours or days, where microbial metabolism and plant mediated VOC removal will be sufficient to create concentration gradients in VOC concentrations that will facilitate diffusion of VOCs to the active sites in the substrate, and thus removal. In the current experiment the very short VOC–substrate exposure time would have been insufficient to allow these interactions to occur on a major scale, thus increasing the reliance on absorption and adsorption as rate-limiting steps in VOC removal. It is possible that the only removal mechanism in these short-term experiments may have been absorption into the aqueous layer and adsorption to substrate particles. It is thus likely that the chemical properties associated with each VOC were the primary factors that influenced dissolution in to the aqueous phase and substrate adsorption rates and consequently, the removal efficiency. Additionally, Mikkonen et al. (2018) identified potentially VOC degrading bacteria within the irrigation water and this presents an additional VOC removal pathway that is yet to be quantified.

As non-botanical biofilters are generally tested to treat a specific VOC, or a limited range of VOCs, an induction period is generally necessary to allow the native microbial community to acclimatise to these VOC specific conditions. Alternatively, for botanical biofilters, which treat the relatively low levels of complex mixtures of VOCs commonly found indoors, it is unlikely that such systems would be exposed to VOC concentrations above the threshold required to induce microbial acclimatisation. Nonetheless, it has been hypothesised that botanical biofilters contain a unique microbial community, supported by the root system of the plant, which is capable of degrading a range of VOCs in low concentrations (Guieysse et al. 2008). It follows that the addition of plants to biofilters (Mikkonen et al. 2018; Pettit et al. 2018b), and appropriate plant species selection (irga et al. 2019) and planting densities (Liddy et al. 2005) can enhance VOC removal efficiency.

Whilst there are limited studies that have tested the SPRE of other VOCs through active botanical biofilters, it is of interest to test the predictive model developed here for the estimation of the SPRE of VOCs that were not tested in this study. Darlington et al. (2001) tested the SPRE of toluene, ethylbenzene and *o*-xylene (TEX) through a botanical biofilter comprised of mosses (*Plagiomnium cuspidatum* and *Taxiphyllum deplanatum*). The authors reported the ratio of VOC concentration effluent to influent. Extrapolating these ratios to SPREs (see (Guieysse et al., 2008): SPRE = ([VOC inlet] – [VOC outlet]) / [VOC inlet]) suggests that average removal efficiencies of ~30–35% for each VOC across a range of temperatures and air fluxes were recorded by Darlington et al. (2001). These values are well within the 95% confidence intervals of the SPRE predicted by the current model (toluene = 36.44%, ethylbenzene = 32.78% and xylene = 33.22%). Whilst these findings suggest that our model may be of value, differences in biofilter volume, temperature, volumetric airflow and plant species in Darlington et al.'s (2001) system may confound this comparison.

3.3 Implications

The current findings offer promising development opportunities for biofilter system optimisation, with the importance of VOC dipole moment suggesting that methods that promote both

dissolution into the aqueous phase and adsorption to substrate particles being likely means of improving VOC SPRE. VOC removal is a stepwise process: VOCs must firstly solubilise into the water phase in biofilter systems before they can undergo substrate adsorption or microbial degradation (Halecky et al., 2016). Without these effects, dissolved VOCs will leave the water phase with continual VOC loading once the water reaches the VOC saturation point (as per its Henry's law constant).

One possible method for increasing water partitioning may be to increase the volumetric airflow across the system, thus increasing partial pressure and thus VOC dissolution into the aqueous phase. This however, will simultaneously reduce pollutant retention time, which may in turn adversely influence system SPRE. Alternatively, modifications to the irrigation water may be used to increase VOC solubility, such as reducing its temperature (Darlington et al., 2001). The use of surfactants could be used to increase the solubility of chemicals with low dipole moments and large molecular masses. While the use of surfactants offers a promising and simple system enhancement, it is critical that appropriate materials are used in concentrations that do not compromise plant health, rhizospheric microbial health and do not pose a human health risk. Tween 20 (polysorbate 20) is a favourable non-ionic surfactant that has been previously used in a biotrickling filter with a polyurethane sponge packing material to improve the removal efficiency of ethylbenzene from 67% to 86% (Wang et al., 2013b). Additionally, Yang (2008) found that irrigation water supplemented with Tween 20 increased the moisture retention of a peat-based growth substrate (Fafard 3B) and increased growth of the plant species *Impatiens hawkerii*, while simultaneously reducing irrigation requirements, indicating that if Tween 20 was used, plant health may be promoted. Furthermore, Cheng et al. (2016b) found that Tween 20 was able to be biodegraded by the microbial community present within their biofilter. While this is evidence of non-toxicity to certain members of the microbial community, it is important to consider how the availability of preferred carbon sources, including those from both VOCs and surfactants, may shift the microbial community and impact a system's ability to remove the range of different VOCs present in most *in situ* applications.

An alternative or additional approach for increasing the SPRE of low dipole moment VOCs is through the use of varied substrate components that are capable of adsorbing a range of VOCs (Cheng et al., 2016a) with considerably different dipole moments. Alternative components for botanical biofilter media may include the use of activated carbon or zeolite, as these are widely used in conventional biofilters for their adsorptive capacity (Devinny et al., 1999), however as the active botanical biofilter effluent is released indoors, it is necessary to comprehensively evaluate substrate additions to ensure they do not emit harmful bioaerosols (Darlington et al., 2000; Irga et al., 2017) or compromise particulate matter removal (Pettit, 2018b).

There are a limited number of studies investigating the botanical biofiltration of multiple VOCs simultaneously, however it is likely that there may be interactions that would influence removal efficiency. Although this work evaluated the removal of different VOCs individually, it has been shown that a complex mixture of VOCs exist within most indoor environments (Meciarova and Vilcekova, 2016). Potted-plant experiments that have assessed the simultaneous removal of multiple VOCs have found that this may improve or hinder the rate of microbial degradation. For example Yu et al. (2001) suggested that competitive inhibition limited the rate of simultaneous benzene and toluene degradation. Alternatively, Orwell et al. (2006) suggested that toluene and *m*-xylene have a positive interaction on

removal rates as exposure to either of these VOCs can induce increased activity of the catechol 1,2 di-oxygenase enzyme, which is used to degrade both VOCs. It is thus likely that the indefinite combinations of VOCs in *in situ* environments have the potential to influence microbial degradation in variable ways. There is also capacity for VOC interactions to influence the rate at which pollutants both absorb into the aqueous phase and adsorb to substrate media. These are all areas in need of further research to better understand the performance of such systems *in situ*. Recent work has revealed that *Hedera helix* in a static system is capable of removing several compounds at the same time, including heptane, 3-methylhexane, toluene, ethylbenzene, and *m*- and *p*-xylene (Dela Cruz et al., 2019). Notably, the VOC removal efficiency was greater when the epigeous plant parts were absent than when they were present, with the authors suggesting that in such a system, the above ground plant components may have reduced the rate of diffusion into the substrate (Dela Cruz et al., 2019).

The current work has thus determined that the chemical properties of VOCs play a major role in determining the rate at which they are filtered by an active botanical biofilter, with the dipole moment the most important determinant. We thus propose that this characteristic could be used to predict the SPREs of VOCs that were not tested here, and that performance enhancements to biofilter systems that are specifically aimed at low dipole moment-VOC reduction should focus on mechanisms by which the aqueous dissolution and substrate adsorption of VOCs could be increased.

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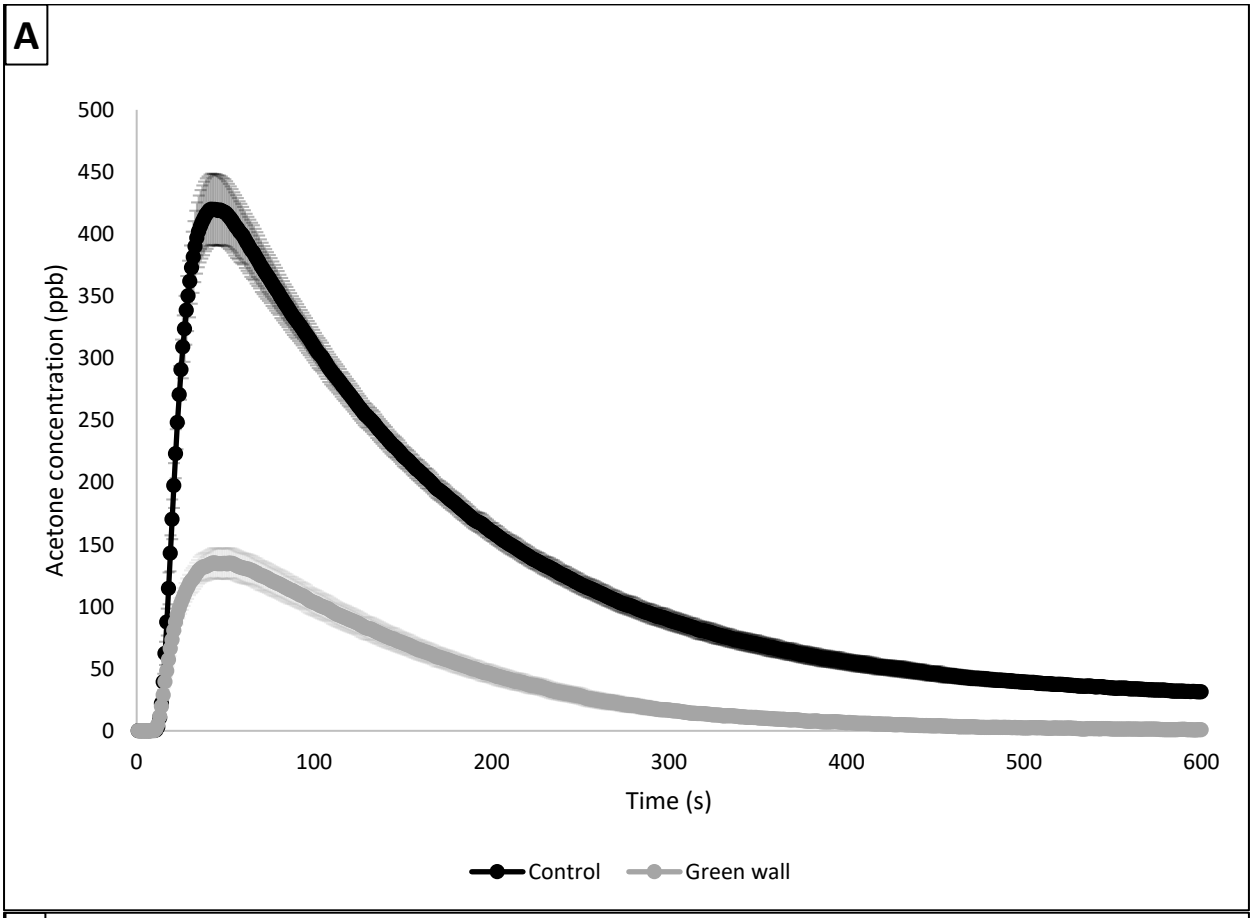
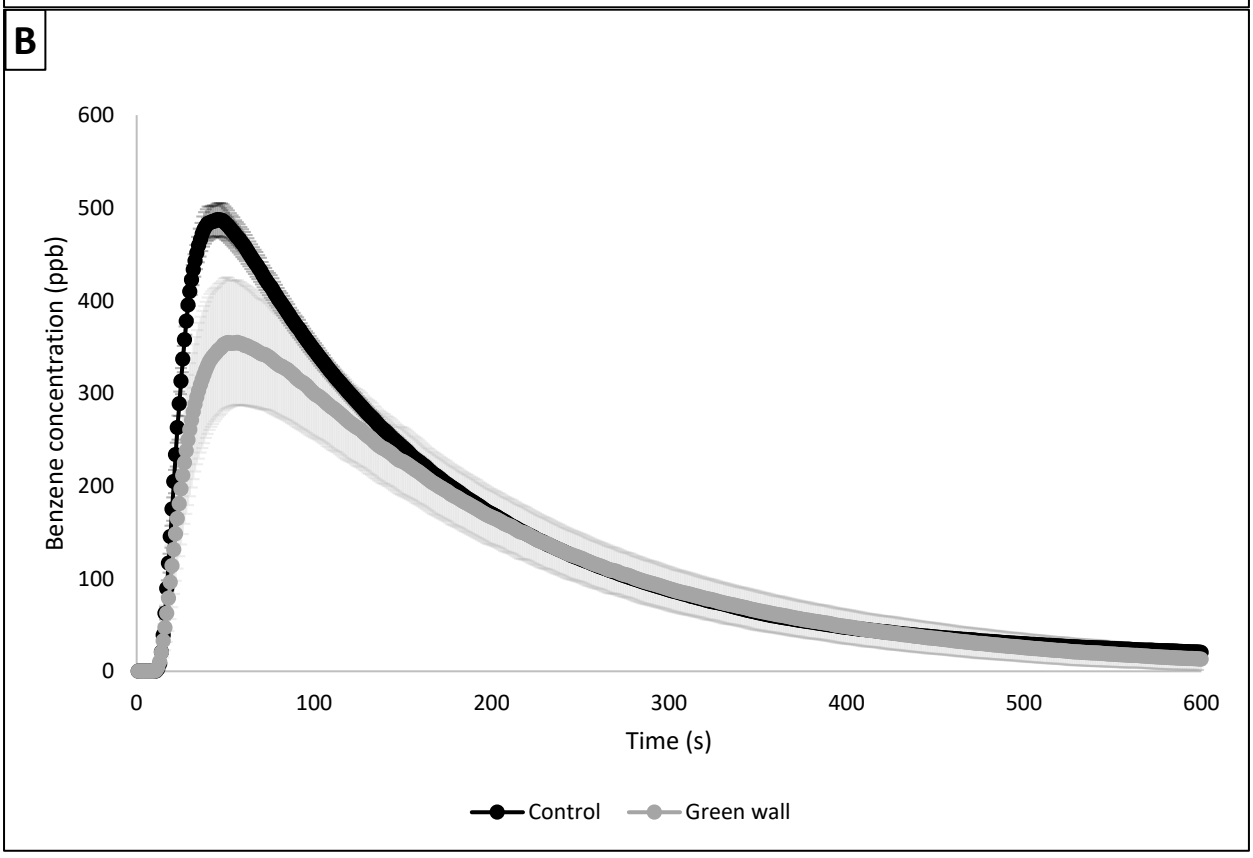
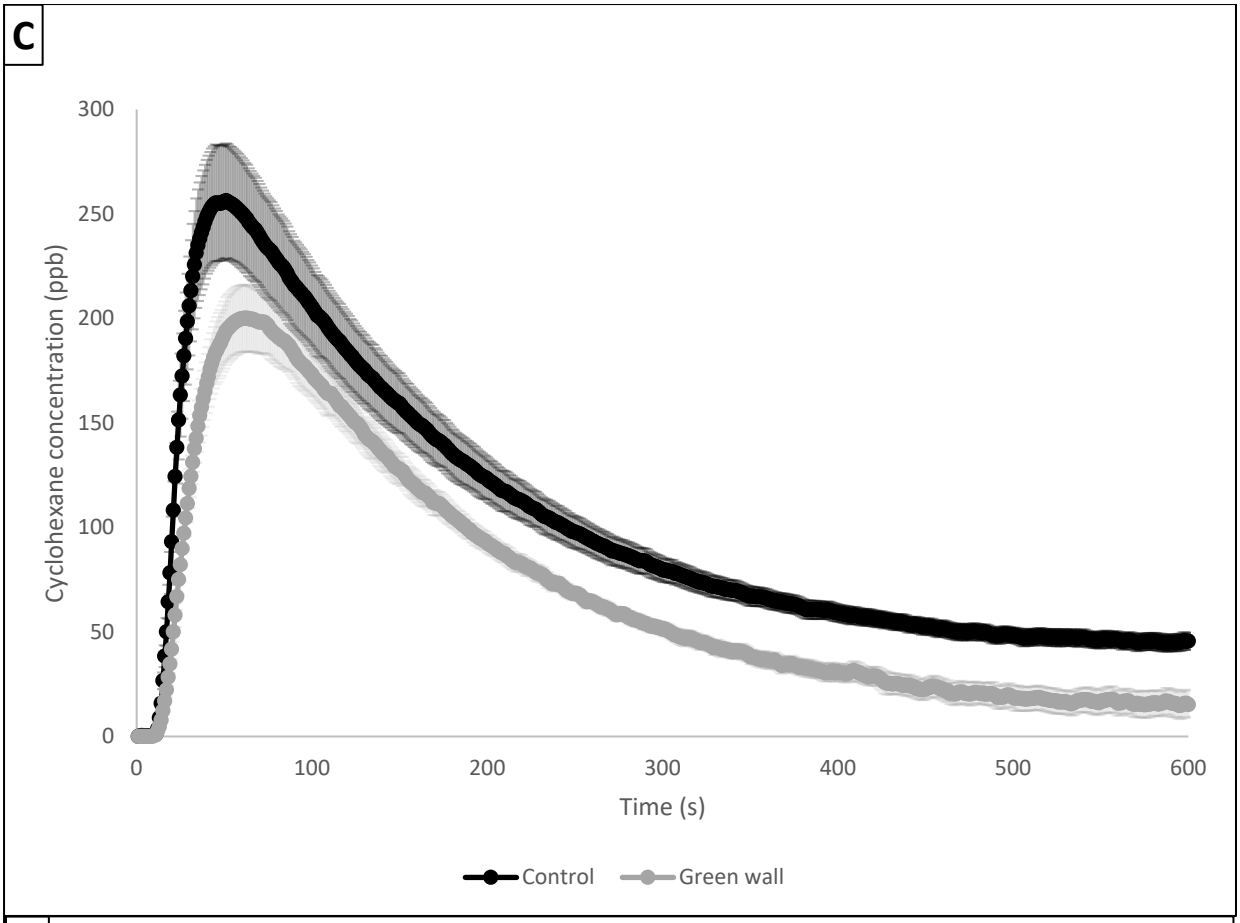
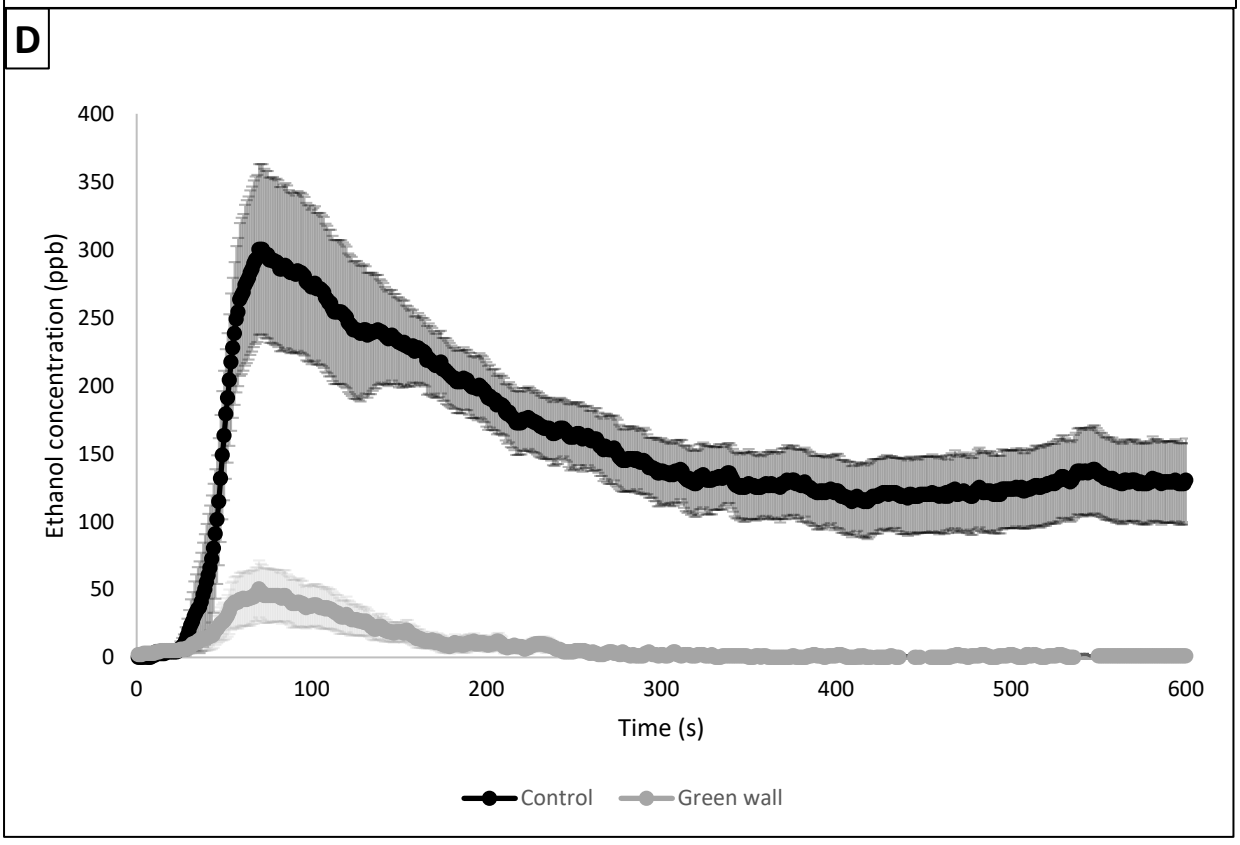
Supplementary material






C
300
250
200
150
100
50
0
Cyclohexane concentration (ppb)
0
100
200
300
400
500
600
Time (s)
Control
Green wall

580


D
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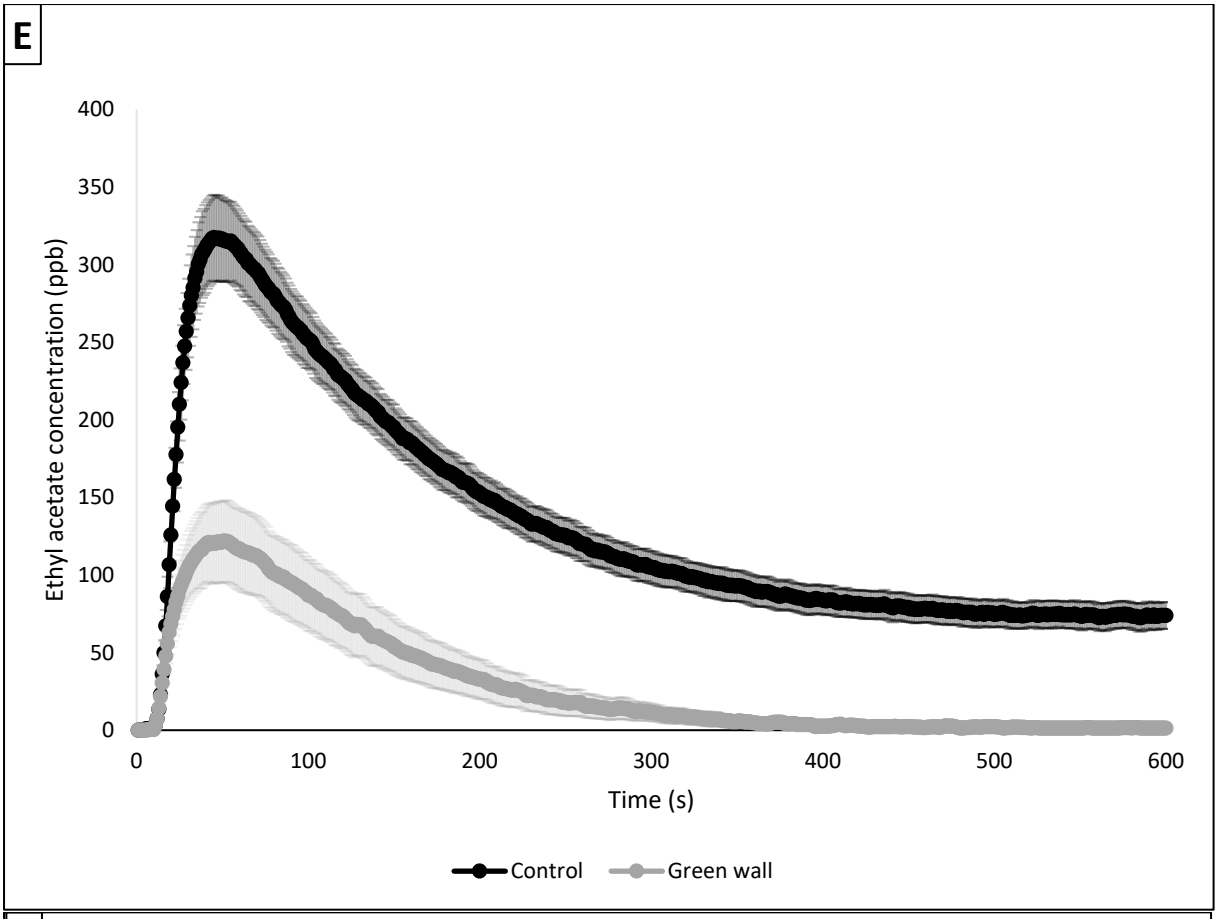
350
300
250
200
150
100
50
0
Ethanol concentration (ppb)
0
100
200
300
400
500
600
Time (s)
Control
Green wall

581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Ethyl acetate concentration (ppb)
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350
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200
150
100
50
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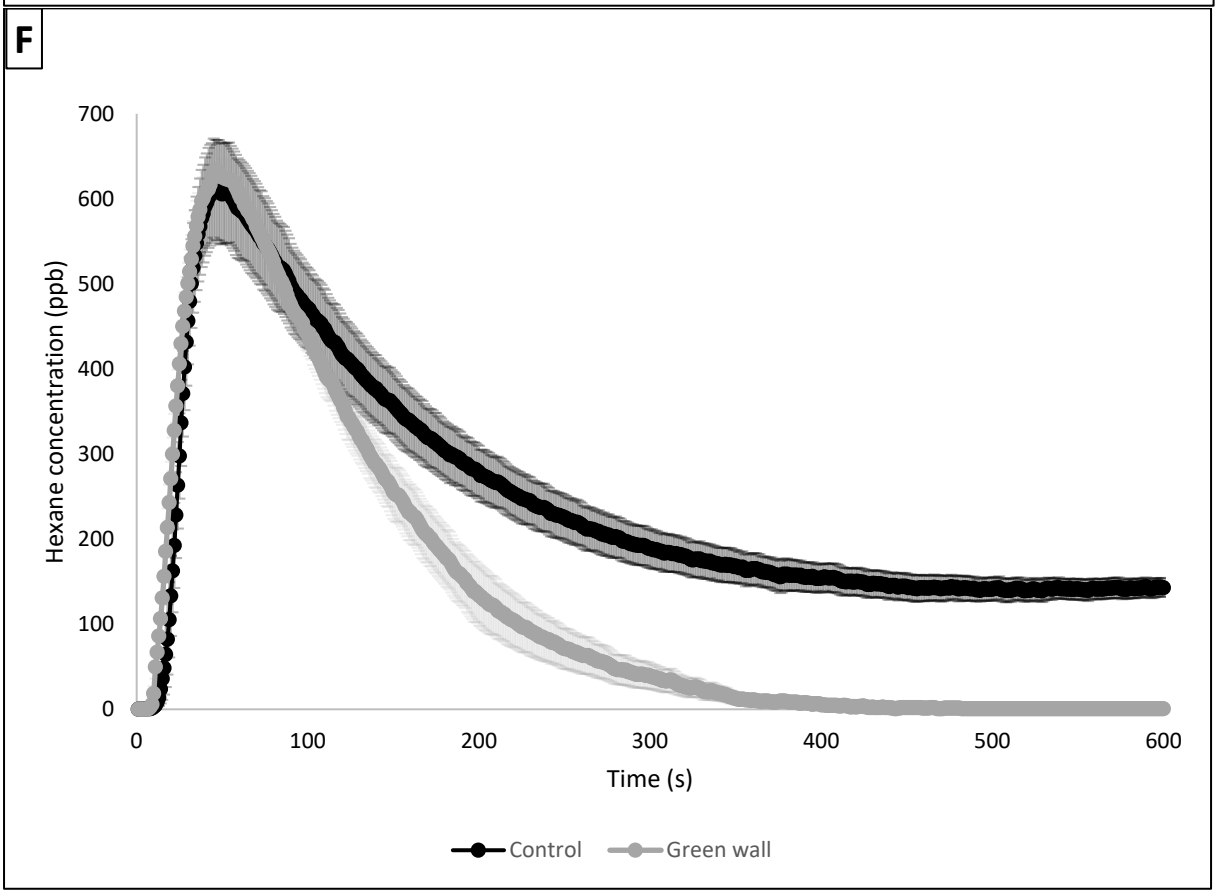
0
100
200
300
400
500
600
Time (s)
Control
Green wall

582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Hexane concentration (ppb)
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600
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200
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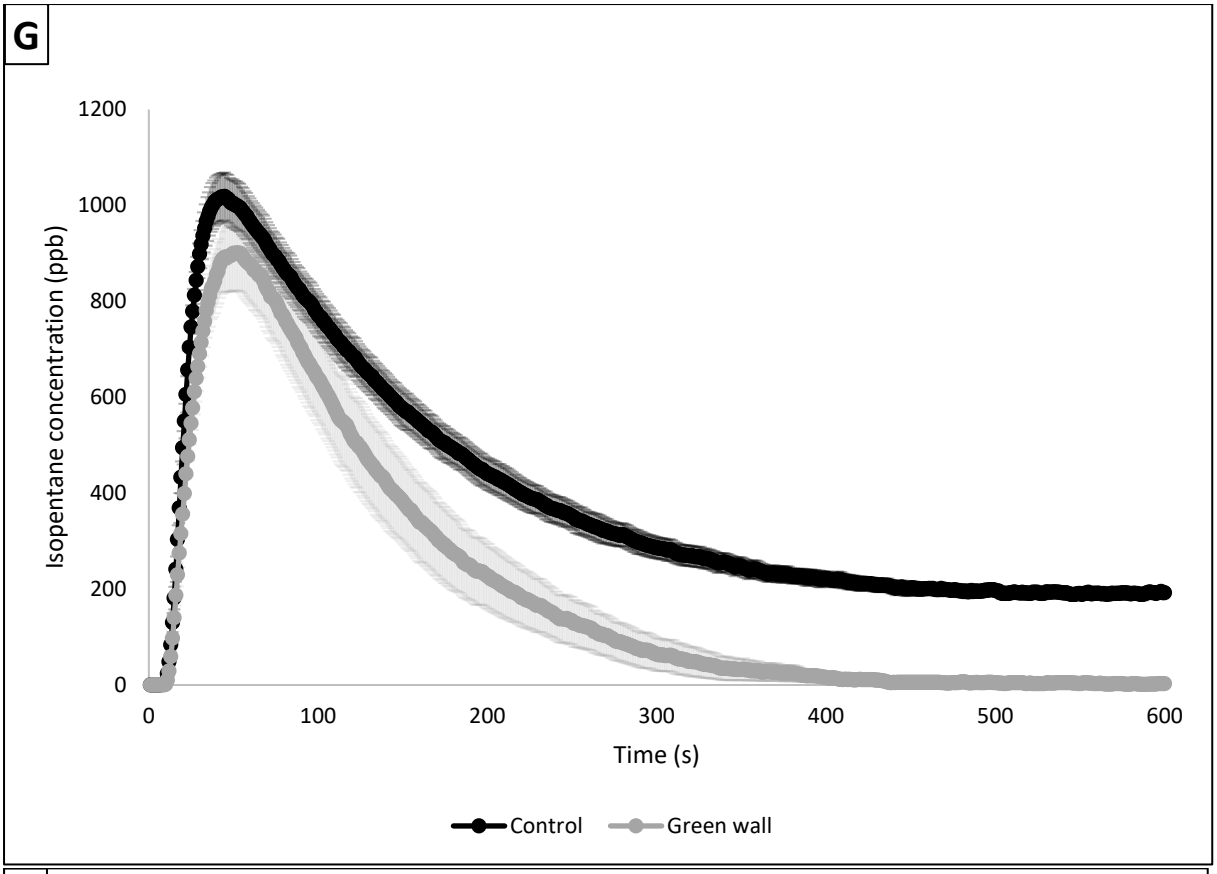
0
100
200
300
400
500
600
Time (s)
Control
Green wall

583


G
1200
1000
800
600
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200
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Isopentane concentration (ppb)
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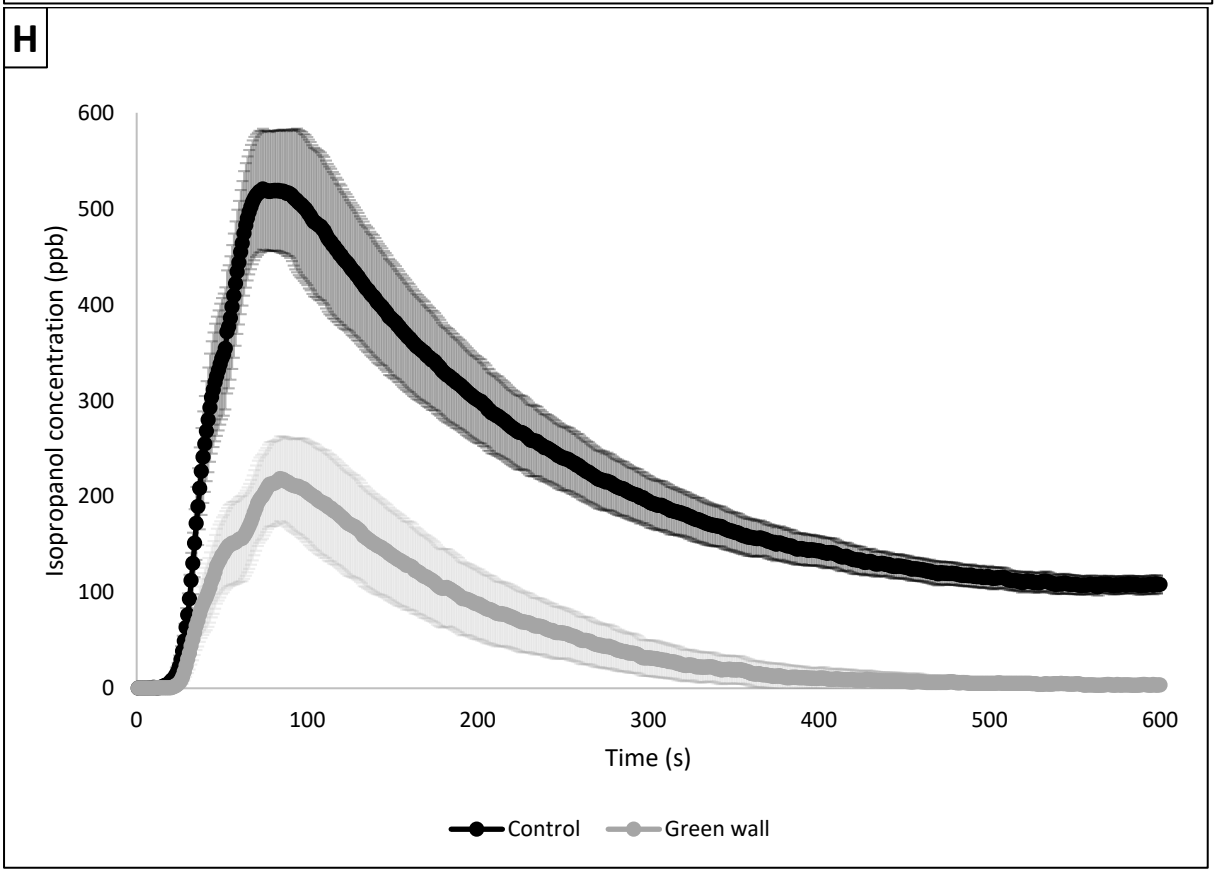
100
200
300
400
500
600
Time (s)
Control
Green wall

584


H
600
500
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200
100
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Isopropanol concentration (ppb)
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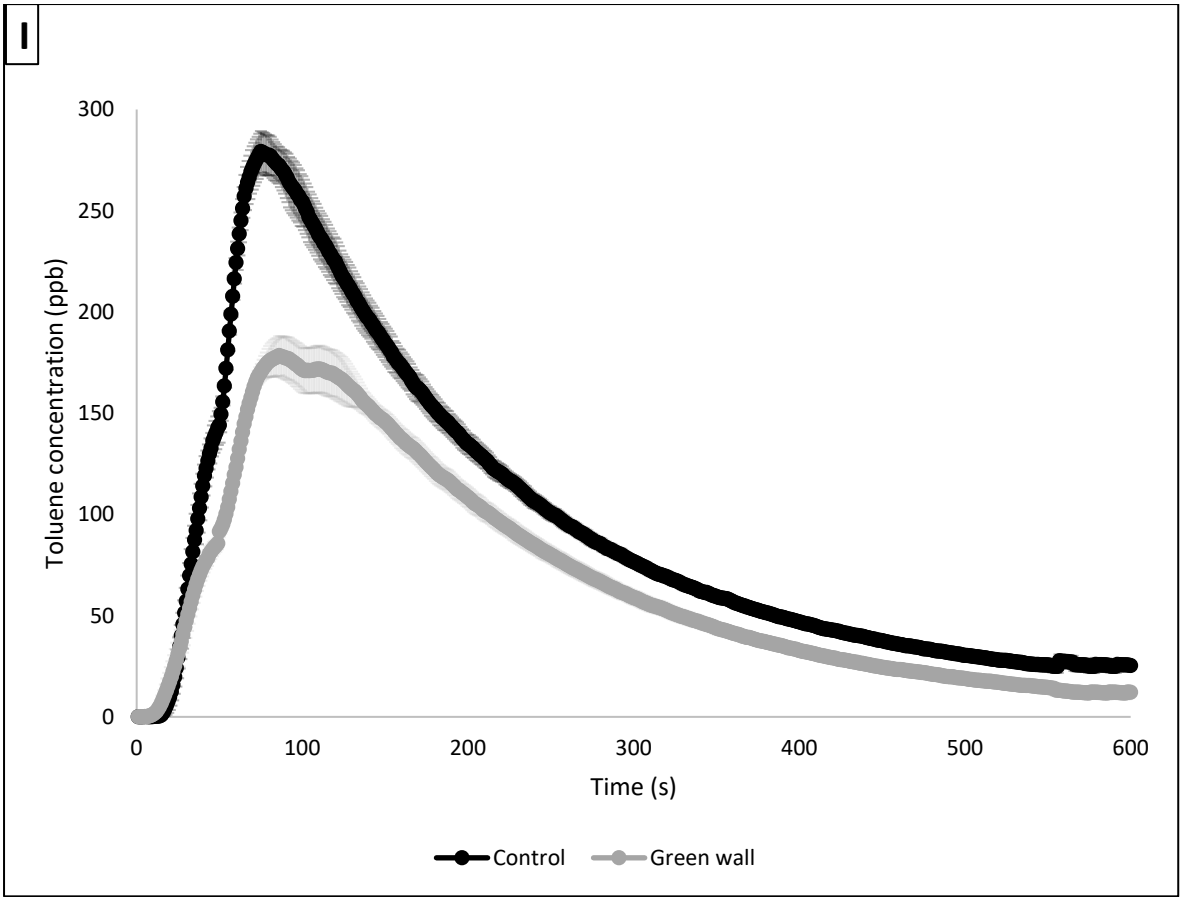
100
200
300
400
500
600
Time (s)
Control
Green wall

585
586



Supplementary material 1. The average concentration of each VOC for the control (empty chamber) and green wall treatments detected in the flow through system determined through photo ionisation detection analysis. Error bars represent SEM. A = acetone; B = benzene; C = cyclohexane; D = ethanol; E = ethyl acetate; F = hexane; G = isopentane; H = isopropanol; I = toluene.