Botanical Biofilters for the Phytofiltration of Urban Air Pollutants

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Thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy under the supervision of Dr Fraser Torpy and Dr Peter Irga

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November 2021

Certificate of Original Authorship

I, Thomas Pettit, declare that this thesis, is submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Life Sciences at the University of Technology Sydney. This thesis is wholly my own work unless otherwise reference or acknowledged. In addition, I certify that all information sources and literature used are indicated in the thesis. This document has not been submitted for qualifications at any other academic institution. This research is supported by the Australian Government Research Training Program.

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Acknowledgements

I would like to thank my two supervisors, Dr Fraser Torpy and Dr Peter Irga. I could not have asked for better supervisors and I am forever grateful for the time and effort you have invested in me to help me develop as a scientist and as a professional. You have given me the greatest opportunities that a PhD student could ask for and have made the years fun and enjoyable as well. I would like to thank the entire Plants and Environmental Quality Research Group for their support, camaraderie and help.

I would like to extend my thanks to all of my co-authors who I worked with on these manuscripts. These great people include Nic Surawski, Robert Fleck, Miranda Bettes, Lilian Hoch, Nicholas James, and Ailis Chapman.

A huge thank you goes out to Junglefy, in particular Jock Gammon and Mark Daniels. Your provision of amazing green walls has been critical for this research to occur.

I would like to thank Matt Brennan from Transurban for supporting this research and supporting active green wall projects on Transurban roads.

Thank you to the Royal Society of New South Wales who have shown interest in this work and awarded me with the Royal Society of NSW Scholarship to support my work.

Thank you to the University of Technology of Sydney and the Australian Government Research Training Program who have both supported me and my research over the years.

Format of Thesis

This thesis is submitted as a *thesis by compilation*. This thesis consists of seven chapters. Chapters 1-6 represent separate articles, all of which have been peer-reviewed, accepted and published in scientific journals. As such, parts of this thesis are presented verbatim to their published form; consequently, some repetition occurs in regards to themes and style. To prevent unnecessary duplication, a single reference list has been provided at the end of the thesis.

This thesis is a compilation of my own work with guidance from my supervisors and additional assistance from others. I conceptualized my research, designed the experiments including choice of methods and instrumentation, conducted all data collection and analysis, and wrote the manuscripts. My supervisors and co-authors proof-read and edited the final peer reviewed manuscript versions. Publication details and contributions of co-authors are detailed below.

List of peer-reviewed publications contributing to this thesis

Chapter 1:

Pettit, T., Irga, P.J. and Torpy, F.R., 2018. Towards practical indoor air phytoremediation: a review. *Chemosphere*, *208*, pp.960-974.

Pettit, T., Irga, P. and Torpy, F., 2020, October. The evolution of botanical biofilters: developing practical phytoremediation of air pollution for the built environment. In *1st International Conference on Climate Resilient Built Environment iCRBE*. World Energy and Environment Technology Ltd-WEENTECH.

Chapter 2:

Pettit, T., Bettes, M., Chapman, A.R., Hoch, L.M., James, N.D., Irga, P.J., Torpy, F.R. and Plants and Environmental Quality Research Group, 2019. The botanical biofiltration of VOCs with active airflow: is removal efficiency related to chemical properties?. *Atmospheric Environment*, *214*, p.116839.

Chapter 3:

Pettit, T., Irga, P.J. and Torpy, F.R., 2019. The *in situ* pilot-scale phytoremediation of airborne VOCs and particulate matter with an active green wall. *Air Quality, Atmosphere & Health*, *12*(1), pp.33-44.

Chapter 4:

Pettit, T., Irga, P.J., Surawski, N.C. and Torpy, F.R., 2019. An Assessment of the Suitability of Active Green Walls for NO2 Reduction in Green Buildings Using a Closed-Loop Flow Reactor. *Atmosphere*, *10*(12), p.801.

Chapter 5:

Pettit, T., Torpy, F.R., Surawski, N.C., Fleck, R. and Irga, P.J., 2021. Effective reduction of roadside air pollution with botanical biofiltration. *Journal of Hazardous Materials*, *414,* p.125566.

Chapter 6:

Pettit, T., Irga, P.J. and Torpy, F.R., 2020. The botanical biofiltration of elevated air pollution concentrations associated the Black Summer wildfire natural disaster. *Journal of Hazardous Materials Letters*, *1*, p.100003.

Co-author contribution

The contribution of each co-author is stated in the preface to each chapter. Co-authors have provided their signatures to confirm their contribution in their respective publications as stated in the preface of each chapter:

Miranda Bettes:	Production Note: Signatures removed prior to publication.	13/04/2021
Ailis Chapman:	Production Note: Signatures removed prior to publication.	14/04/2021
Robert Fleck:	Production Note: Signatures removed prior to publication.	14/04/2021
Lilian Hoch:	Production Note: Signatures removed prior to publication.	13/04/2021
Peter Irga:	Production Note: Signatures removed prior to publication.	19/04/2021

Nicholas James:	Production Note: Signatures removed prior to publication.	13/04/2021
Nic Surawski:	Production Note: Signatures removed prior to publication.	14/04/2021
Fraser Torpy:	Production Note: Signatures removed prior to publication.	14/04/2021

Other peer reviewed publications published during my candidature but not forming part of this thesis

Pettit, T., Irga, P.J., and Torpy, F.R., 2018. Functional green wall development for increasing air pollutant phytoremediation: Substrate development with coconut coir and activated carbon. *Journal of Hazardous Materials*, *360*, pp.594-603.

Irga, P.J., Pettit, T., and Torpy, F.R., 2018. The phytoremediation of indoor air pollution: a review on the technology development from the potted plant through to functional green wall biofilters. *Reviews in Environmental Science and Bio/Technology, 17*(2), pp.395-415.

Torpy, F.R., Pettit, T. and Irga, P.J., 2018. Applied horticultural biotechnology for the mitigation of indoor air pollution. *Journal of People, Plants, and Environment*, *21*(6), pp.445-460.

Leonard, R.J., Pettit, T.J., Irga, P., McArthur, C. and Hochuli, D.F., 2019. Acute exposure to urban air pollution impairs olfactory learning and memory in honeybees. *Ecotoxicology*, *28*(9), pp.1056-1062.

Irga, P.J., Pettit, T., Irga, R.F., Paull, N.J., Douglas, A.N. and Torpy, F.R., 2019. Does plant species selection in functional active green walls influence VOC phytoremediation efficiency?. *Environmental Science and Pollution Research*, *26*(13), pp.12851-12858.

Fleck, R., Gill, R.L., Pettit, T., Irga, P.J., Williams, N.L.R., Seymour, J.R. and Torpy, F.R., 2020. Characterisation of fungal and bacterial dynamics in an active green wall used for indoor air pollutant removal. *Building and Environment*, *179*, p.106987.

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Pettit, T., Irga, P.J., Torpy, F.R., Shagol, C.C. and Kim, K.J., 2020. Technological aspects of the removal of air pollutants by phytosystems. In *From Biofiltration to Promising Options in Gaseous Fluxes Biotreatment* (pp. 263-281). Elsevier.

Irga, P.J., Shagol, C.C., Kim, K.J., Pettit, T. and Torpy, F.R., 2020. Plant–microbe interaction within phytosystems used for air treatment. In *From Biofiltration to Promising Options in Gaseous Fluxes Biotreatment* (pp. 245-262). Elsevier.

Irga, P.J., Pettit, T., Shagol, C.C., Kim, K.J. and Torpy, F.R., 2020. Phytosystems implementation: examples of application in practice. In *From Biofiltration to Promising Options in Gaseous Fluxes Biotreatment* (pp. 283-299). Elsevier.

Kim, K.J., Shagol, C.C., Torpy, F.R., Pettit, T. and Irga, P.J., 2020. Plant physiological mechanisms of air treatment. In *From Biofiltration to Promising Options in Gaseous Fluxes Biotreatment* (pp. 219-244). Elsevier.

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List of Abbreviations

ANOVA: Analysis of variance

CADR: Clean air delivery rate

CO_2: carbon dioxide

df: Degrees of freedom

HDPE: High density polyethylene

HSD: honestly significant difference

HVAC: Heating, ventilation and air conditioning

GAC: Granular activated carbon

MERV: Minimum efficiency reporting value

NASA: National Aeronautics and Space Administration

NO: Nitrogen oxide

NO_x: Oxides of nitrogen

NO_2: Nitrogen dioxide

O_3: Ozone

PERMANOVA: Permutational analysis of variance

PM: Particulate matter

PM_x: Particulate matter, where x denotes the maximum aerodymanic diameter of the particles in μm.

ppb: Parts per billion

ppm: Parts per million

PVC: Polyvinyl chloride

SPRE: Single pass removal efficiency

TSP: Total suspended particles

TVOCs: total volatile organic compounds

VOCs: volatile organic compounds

WHO: World Health Organisation

Abstract

Air quality is of emerging importance due to the rapid growth of urban populations that are exposed to air pollution in both indoor and outdoor environments. As a potential solution, active green walls or botanical biofilters have been developed to assist in the removal of air pollutants directly from environments where people live. Through the use of active airflow, these vertically orientated, botanical systems pass a contaminated airstream through the plant growth substrate and foliage to filter air pollutants. The work presented here explores the capacity of active green walls to filter air pollution through laboratory, indoor and outdoor studies. Firstly, laboratory-based experiments revealed that the single pass removal efficiency (SPRE) of different volatile organic compounds (VOCs) by active green walls is influenced by the VOC's chemical properties, with average SPREs ranging from 19.76-96.34%. Modelling revealed that highly polar, small molecular weight molecules were removed with greatest efficiency. Secondly, pilot-scale trials assessed an active green wall's pollutant removal within a classroom, with average total VOC and PM concentrations reduced by ~28% and ~42.6% respectively, over 30 min trial periods, compared to levels with no green wall but having a HVAC-filtration system in operation. Thirdly, botanical biofiltration of NO_2 was assessed at ambient and elevated concentrations within a closed-loop flow reactor, while the concentrations of NO and O_3 were simultaneously monitored. Biofilter treatments using two plant species (*Spathiphyllum wallisii* and *Syngonium podophyllum*) exhibited exponential decay for the biofiltration of all three pollutants at ambient concentrations. Furthermore, both treatments removed elevated concentrations of NO and NO_2. Subsequently, botanical biofilters were field-assessed for the filtration of traffic associated air pollutants – NO_2, O_3 and $PM_{2.5}$ – from roadside ambient air in Sydney, Australia. Over two six-month research campaigns, all of the tested systems filtered NO_2, O_3 and $PM_{2.5}$ with average SPREs of up to 71.5%, 28.1% and 22.1% respectively. Clean air delivery rates of up to 121 m^3/h, 50 m^3/h and 40 m^3/h per m^2 of active green wall were achieved for the three pollutants respectively, with pollutant removal efficiency positively correlated with their ambient concentrations. An additional trial identified that active green walls filtered elevated air pollutant concentrations associated with the *Black Summer* wildfires, with average SPREs of 63.17%, 38.79% and 24.84% for NO_2, O_3 and $PM_{2.5}$ respectively. These cumulative

findings reveal that active green walls may have the capacity to play an important role in enhancing air quality and reducing air pollution exposure.

Preface: Chapter 1

The following chapter comprises text from two peer-reviewed publications, and represents a literature review to provide background for the subsequent chapters:

> Pettit, T., Irga, P.J. and Torpy, F.R., 2018. Towards practical indoor air phytoremediation: a review. *Chemosphere*, *208*, pp.960-974.
>
> Pettit, T., Irga, P. and Torpy, F., 2020, October. The evolution of botanical biofilters: developing practical phytoremediation of air pollution for the built environment. In *1st International Conference on Climate Resilient Built Environment iCRBE*. World Energy and Environment Technology Ltd-WEENTECH.

Author Contributions (for both manuscripts):

Thomas Pettit: Conceptualization, Literature review, original draft preparation, review and editing. **Peter Irga:** Investigation, review and editing, supervision, project administration. **Fraser Torpy:** Conceptualization, Review and editing, supervision, project administration.

For clarity, as a single reference list has been provided at the end of this thesis.

Chapter 1

1. Towards practical indoor air phytoremediation

1.1 Urban air quality

Urban air quality is becoming an increasingly important issue in both developing and developed countries (Gulia et al. 2015), where air pollution exposure has become the fifth most significant human health risk factor around the globe (Gakidou et al. 2017). A greater proportion of the world's population is becoming urbanised, with 28% of the world's populations projected to live in cities with populations over 1 million people by 2030 (United Nations 2018). As the level of exposure to urban air pollution is becoming increasingly significant, the evidence of negative health effects resulting from air pollution exposure is growing (Bowatte et al. 2017; Brook et al. 2010; Chen et al. 2016; Cohen et al. 2017; Knibbs et al. 2018; Lelieveld et al. 2017; Raaschou-Nielsen et al. 2013; Shah et al. 2015; Zhang et al. 2020).

Although most countries and the European Union have taken strong measures to reduce air pollution emissions, air pollution remains a serious health issue for much of the world (Cincinelli and Katsoyiannis 2019). High traffic densities within urban areas (Yuan et al. 2019), along with a range of other sources (Table 1) are associated with considerable air pollution emissions, leading to increased exposure to ambient air pollution in urban areas. The relationship between air quality, urban form and health are complex and multifaceted (Hankey and Marshall 2017; Mansfield et al. 2015), however the geometries of some urban areas may hinder air pollution dispersion (Craig et al. 2001) and thus increase the air pollutant concentration and amplify exposure of some urban inhabitants. The major criteria air pollutants across urban environments that are associated with detrimental health effects include particulate matter (PM), nitrogen oxides (NO_x) and ozone (O_3) (see Table 1) (Cohen et al. 2004).

Table 1. Primary emission sources of urban air pollutants.

Pollutant	Primary emission source	Study area	Reference
PM_{10}	Secondary inorganic aerosols (28%), marine emissions/shipping activities (19%), biomass burning (13%), mineral dust (13%), primary biogenic emissions (9%), fresh sea salts (8%), primary traffic emissions (6%), heavy oil combustion (4%).	Lens, France	Waked et al. (2014)
$PM_{2.5}$ (elemental/black carbon)	On-road heavy diesel vehicles (33-74%), on-road gasoline vehicles (6-38%), residential wood combustion (4-33%), agricultural burning (6-13%)	USA	Chow et al. (2011)
$PM_{2.5}$ (organic carbon)	On-road gasoline vehicles (24-75%), residential wood combustion (22-68%), on-road heavy diesel vehicles (20-47%), agricultural burning (35-40%)	USA	Chow et al. (2011)
$PM_{2.5}$	Secondary sulfates (29%), traffic emissions (25%), secondary nitrates (19%), coal combustion (11%), biomass combustion (12%), soil dust (4%)	Beijing, China	Zíková et al. (2016)
PM_1	Vehicle exhaust (38%), secondary aerosols (22%), incinerator/biomass burning (16%)	Hong Kong	Cheng et al. (2011)
VOCs	Consumer VCPs[1] (38±9%), Industrial VCPs (15±5%), upstream emissions[2] (14±4%), gasoline fuel (13±6%), gasoline exhaust (19±7%)	Los Angeles, USA	McDonald et al. (2018)
NO_x	Road transport (39%), energy production and distribution (17%), commercial, institutional and households (14%), energy use in industry (11%), non-road transport (9%), agriculture (6%)	European Union	European Environment Agency (2018)

[1]Volatile chemical products - including pesticides, coatings, printing inks, adhesives, cleaning agents, and personal care products.
[2]Upstream emissions are those that occur upstream of end users (i.e., oil and natural gas extraction, oil refineries, and chemical manufacturing facilities.)

1.2 Urban Air Pollutants

1.2.1 Particulate matter

PM is of particular concern in many urban centres where it is commonly emitted from combustion activities and formed from gas-to-particle conversion in the atmosphere (secondary aerosols) (Chow et al. 2011; Waked et al. 2014]. As particle size dictates the extent to which PM can penetrate the respiratory system (Xing et al., 2016), PM is categorised as either fine particles ($PM_{2.5}$), which refers to particles with an aerodynamic diameter of less than 2.5 μm, or coarse particles (PM_{10}), which have an aerodynamic diameter less than 10 μm. Smaller size fractions are sometimes also recorded in the literature. Coarse particles are often referred to as PM_{10} and include all particles with an aerodynamic diameter up to 10 μm. Fine particles, with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$), are able to penetrate deeper into the lung's gaseous exchange region and thus have greater potential to enter the circulatory system, and have greater health effects (Xing et al., 2016). This effect is amplified by the larger specific surface area of smaller particles, which promotes the transfer of toxic compounds. Nonetheless, coarse particles are also an important health concern, for example, black carbon generated from incomplete combustion processes, such as diesel exhaust, has been linked to more significant health effects when particles are of greater size (Janssen et al., 2011). There is also a growing body of evidence regarding the negative health effects of ultra-fine particles (Oberdörster and Utell, 2002; Bräuner et al., 2007; Stölzel et al., 2007; Weichenthal et al., 2016), which have an aerodynamic diameter less than 0.1 μm. In comparison to larger particles, ultra-fine particles do not contribute significantly to the airborne PM mass concentration, yet they represent the largest size fraction in terms of particle numbers (Slezakova et al., 2015). This may partly result from vehicle emissions regulations in which mass output of particles is regulated, therefore allowing a considerable number of low mass, ultra-fine particles to be emitted (Oberdörster and Utell, 2002). In comparison

to larger particles, the significant health effects from ultra-fine particles have been hypothesized to result from their (i) increased reactivity, (ii) larger specific surface area, (iii) higher deposition rate in the pulmonary region and (vi) increased likelihood to penetrate epithelial tissues thus reaching interstitial sites (Stölzel et al., 2007).

Both short term exposure (days to weeks) and prolonged exposure (years) have been linked to serious effects on health (Cohen et al. 2004). Exposure to high concentrations of ambient PM is associated with increased morbidity and mortality due to cardiovascular, respiratory and venous thromboembolic disease (Bari et al., 2014). Wang et al. (2016) found a 3% increase in all natural-cause mortality for the whole population with each 2 $\mu g/m^3$ increase in annual $PM_{2.5}$ exposure, suggesting relatively minor increases in PM concentration are linked with significant health impacts (Wang et al., 2016). Crouse et al. (2002) found long-term exposure to relatively low concentrations of $PM_{2.5}$ (average concentration = 8.7 $\mu g/m^3$) was associated with increased mortality from cardiovascular disease.

Adverse health effects resulting from PM exposure are becoming increasingly recognised (Wyzga and Rohr, 2015; Feng et al., 2016; Maji et al., 2017), as is the recognition that problematic PM levels occur in some indoor environments (Morawska et al., 2001; Morawska et al., 2003; He et al., 2004; Fromme et al., 2007; Branco et al., 2014; Challoner and Gill, 2014; Tunno et al., 2015; Stabile et al., 2017). PM concentrations are often high in urban environments, where traffic emissions, in particular emissions from diesel vehicles, contribute significantly to the ambient PM concentration (Rohr and Wyzga, 2012). The ambient outdoor PM can have ramifications for indoor environments, as particles can transfer indoors through building ventilation, including mechanical ventilation systems (HVAC) and natural ventilation (windows and doors). Some activities within the indoor environment, such as cooking (Buonanno et al., 2009), smoking and use of office printers (He et al., 2007), and cleaning can contribute to high indoor PM concentrations either through emissions or re-suspending previously precipitated particles (Long et al., 2000; Wheeler et al., 2011). It has been estimated that indoor generated PM contributes to 10–30% of the total burden of disease from PM exposure (Morawska et al., 2013).

1.2.2 Nitrogen dioxide

Nitrogen dioxide (NO_2) is a gaseous urban air pollutant that is largely associated with combustion processes, and particularly traffic-related emissions (Beevers et al. 2012; Wang et al. 2019). Although NO_2 can be emitted as a primary pollutant (Carslaw and Beevers 2004, 2005), a considerable proportion of NO_2 is formed through the emissions of nitrogen oxide (NO), which then undergo photochemical processes to transform to NO_2 in the atmosphere. Problematic concentrations of NO_2 still occur across many urban areas despite long standing controls over vehicle emissions (Carslaw et al. 2016). Ambient NO_2 concentrations in large urban areas often exceed the World Health Organisations guideline values of 200 $\mu g/m^3$ (Short term: 1 hour mean) and 40 $\mu g/m^3$ (long term: annual mean) (Hoek et al. 2013). Population and cohort studies suggest that long term exposure to NO_2 at concentrations that are compliant with the World Health Organisation's annual guideline may still induce negative health effects (Chaloulakou et al. 2008; WHO 2005).

NO_2 is a free radical, capable of causing injury and inflammation through depleting tissue antioxidant defences (Jarvis et al. 2010). Kelly and Tetley (1997) demonstrated that exposure to NO_2 (at a concentration of 0.05–1.0 ppm) reduces antioxidant defences, such as lower concentrations of uric acid and ascorbic acid, in human bronchoalveolar lavage fluid (Kelly and Tetley 1997). Further mechanisms of NO_2 damage can be elucidated from animal toxicology studies, however care must be taken interpreting these findings due to the use of highly elevated NO_2 concentrations in experimental studies, and the inherent inter-species variation affecting response (Jarvis et al. 2010). Studies of mice, rats, dogs and monkeys have demonstrated that long term NO_2 exposure results in emphysema-like structural changes, including thickening of alveolar capillary membrane, increased lung collagen and reduced ciliated epithelium (Advisory Group on the Medical Aspects of Air Pollution Episodes 1993; Berglund et al. 1993; US Environmental Protection Agency 1993, Verein Deutscher Ingenieure, 1985). Continuous NO_2 exposure (0.2 ppm concentration) has demonstrated reduced pulmonary function in mice, including reduced in end-expiratory volume, vital capacity and respiratory system compliance (Miller et al. 1987).

NO_2 exposure in humans is associated with a range of respiratory symptoms and decreased pulmonary and lung function (Kattan et al. 2007; World Health Organisation 2006; Smith et al. 2000; Just et al. 2002; Belanger et al. 2006) and increases in NO_2 concentrations are associated with increases in all-cause mortality and hospital admissions (Andersen et al. 2007). Individuals with respiratory diseases, such as asthma and chronic obstructive pulmonary disease (COPD), who experience short-term exposure to high concentrations of NO_2 can exhibit short term responses such as changes in lung function or airway responsiveness (Lövblad et al. 1997). Consequently, increased risk to public health has emerged with the growing evidence of the health effects linked to elevated NO_2 exposure (Henschel et al. 2013).

In addition to problems arising from NO_2 exposure, NO_2 can act as an ozone (O_3) precursor (Khan et al. 2018) and is readily photolysed to nitrogen oxide (NO) (Li and Liu, 2012). The relationship between O_3 and NO_x (oxides of nitrogen, i.e. NO + NO_2) is very important, as NO_x are highly reactive and promote O_3 formation in the presence of sunlight, high temperatures and other atmospheric gases, such as methane and volatile organic compounds (VOCs) (Jacob and Winner 2009; Melkonyan and Kuttler 2012).

1.2.3 Ozone

Although stratospheric ozone is formed naturally in the upper atmosphere (i.e the ozone layer) and provides protection from ultraviolet radiation from the sun, tropospheric ozone is considered as one of the most harmful air pollutants (EEA 2011; Sousa et al. 2013). O_3 can enter the troposphere through stratospheric intrusions, however elevated concentrations of O_3 are associated with anthropogenic activities that emit NO_x, leading to an increase in photochecmial production of O_3 (Alvim-Ferraz et al. 2006). Consequently, emissions from traffic may be related to ozone concentrations in some regions and peak ozone concentrations are associated with summer months where by sunlight radiation is highest (Alvim-Ferraz et al. 2006). Photochemical radiation of ozone is a complex and varied process, involving NOx, VOCs or methane, and sunlight (Atkinson and Arey 2003a).

O_3 is a strong oxidant, capable of damaging biological tissues, primarily those within the lungs (OECD 2008), leading to decreased pulmonary function (i.e. alterations in lung volumes, and increased air way responsiveness and resistance)

(Gryparis e al. 2004). Exposure to O_3 is capable of having both acute and chronic health effects (Kim et al. 2020). Epidemiological evidence across Europe has suggested that an increase of 10 ug/m^3 in the 1-hour ozone concentration in the warm season was associated with a 0.33% increase in the total daily number of deaths, a 0.45% increase in the number of cardiovascular deaths, and a 1.13% in the number of respiratory deaths (Gryparis et al. 2004). Additionally, long-term exposure to O_3 has been associated with a greater decline in lung function and the progression of emphysema (Kim et al. 2020).

1.3 Urban air quality and indoor environments

Whilst people within the urban environment spend the majority of their time indoors (Klepeis et al. 2001), the ambient outdoor air quality within urban areas also influences the indoor environment (Katsoyiannis and Bogdal 2012). In many cases, ambient outdoor pollution levels may make a considerable contribution to the air pollution concentration and profile in proximal indoor environments (Lawson et al. 2011). Several studies have focused on relationships between indoor and outdoor PM (Guo et al. 2010; Jamriska et al. 2000; Viana et al. 2011), and have found that outdoor PM concentrations have a strong influence on indoor air quality, as PM can enter buildings through ventilation and infiltration (Chen and Zhao 2011). Similarly, gaseous pollutants such as VOCs and NO_2 of outdoor origin can also have considerable influence on the air quality of the indoor environment (de Blas et al. 2012; Lawson et al. 2011).

In addition to outdoor-sourced air pollutants, air pollutants of indoor origin may also contribute to the pollution load of indoor environments. Indoor emissions of NO_2 and PM are strongly associated with stove top cooking (Lawson et al. 2011) and a diverse range of VOCs can be emitted from building structural materials and furniture, particularly when these products are new (Kang et al. 2017). Consequently the indoor concentration of VOCs can be considerably higher than that of the proximal outdoor environment (Jafari et al. 2015). Relatively smaller emissions of air pollution into a space of smaller volume (i.e. an indoor room as opposed to the ambient outdoor environment) can result in problematic concentrations of air pollution. There are notable differences in the types and concentrations of pollutants

emitted from and found in indoor environments, and these are closely linked to differences in socio-economic development around the globe (Colbeck and Nasir, 2010). In developed countries, the most prominent and well-researched pollutants include VOCs (Wolkoff, 2013) and PM (Morawska et al., 2013).

1.3.1 Volatile organic compounds

VOCs are of particular concern in indoor air, as almost all human VOC exposure occurs indoors (Arulneyam and Swaminathan, 2004). A diverse range of VOCs can be emitted within the indoor environment from building structural materials and furniture (Zhang et al. 1996), cleaning products and plastics (de Gennaro et al. 2015), particularly when these products are new (Kang et al. 2017). Consequently, the indoor concentration of VOCs can be considerably higher than that of the proximal outdoor environment (Jafari et al. 2015).

Although reduced building ventilation rates may reduce the rate at which outdoor air pollutants are transferred to the indoor environment, it simultaneously reduces the rate at which indoor generated pollutants, such as VOCs, are flushed from the indoor atmosphere. When this is coupled with the increasingly widespread use of new products and the rejuvenation of building interiors, indoor generated pollutants can accumulate to the level whereby occupants are exposed to considerable concentrations for prolonged periods (Katsoyiannis and Bogdal 2012). Due to the heterogeneity amongst buildings and indoor activities, the composition and levels of VOCs are highly variable amongst indoor environments (Cooke, 1991).

Short term exposure to VOCs in the indoor environment has been linked to respiratory symptoms such as the exacerbation asthma symptoms (Fuentes-Leonarte et al., 2009; McGwin Jr et al., 2010). Additionally, ‘sick building syndrome’ has been partly attributed to VOC exposure within the indoor environment (Brinke et al. 1998). Exposure to particular VOCs, such as acetyl aldehyde, has been identified as endocrine disruptors (Kawano et al., 2012), whilst other VOCs have been linked to health issues with the nervous, hepatic and respiratory systems (WHO 2000).

1.4 Technologies for indoor air management

Heating, ventilation and air conditioning (HVAC) systems are commonly used to control indoor air quality, however these systems are energy expensive, require

regular maintenance (Montgomery et al. 2012) and are incapable of capturing gaseous pollutants: HVAC systems reduce indoor VOC concentrations solely by dilution with outdoor air. The introduction of "Energy Efficient Buildings" has resulted in buildings with increased air-tightness and fewer air exchanges with the ambient environment. While this may reduce the rate at which outdoor air pollutants are transferred to the indoor environment, it simultaneously reduces the rate at which indoor generated pollutants, such as VOCs, are flushed from the indoor atmosphere. When this is coupled with the increasingly widespread use of new products and the rejuvenation of building interiors, indoor generated pollutants can accumulate to the level whereby occupants are exposed to considerable concentrations for prolonged periods (Katsoyiannis and Bogdal 2012).

There thus is a clear need for air cleaning technologies that are capable of cleaning a comprehensive range of pollutants effectively and in an energy efficient manner. This work explores the history, efficacy and potential of vegetative systems, known as botanical biofilters, to make functional differences to ambient air quality.

1.5 Bioremediation of VOCs with potted-plants

Building on the phytoremediation capacities of aquatic wetland plants to remove toxic wastes that had accumulated from years of firing rockets, NASA began exploring whether plants could also remove VOCs from the air. Experiments using a sealed chamber with a spiked dose of formaldehyde revealed that potted-plants were capable of reducing the concentration of formaldehyde within the chamber (Wolverton and McDonald 1982; Wolverton et al. 1984). With this demonstration of proof-of-concept, a range of experiments explored the application of potted-plants as an alternative air cleaning technology to existing mechanical system. These experiments were frequently conducted in sealed chambers with spiked VOC doses, with VOC concentration decay monitored over time (Irga et al. 2018). These experiments have tested VOC removal by different plant species, different growth substrates, and different VOCs, amongst other variables (Aydogan and Montoya, 2011; Godish and Guindon, 1989; Orwell et al., 2004; Porter 1994; Torpy et al., 2013; Wolverton and Wolverton, 1993; Wolverton et al., 1984; Wolverton et al., 1985; Wolverton, 1988; Wood et al., 2002; Wood et al., 2006), demonstrating significant removal of high concentrations of VOCs from sealed chambers, with reductions

ranging from 10–90% over 24 hours (Llewellyn and Dixon, 2011). Possibly due to the variances in conditions amongst different experiments such as the use of different plant species, VOCs, pollutant concentrations, chamber sizes and light levels (see Table 2), it is difficult to ascertain which components of the potted-plant system are responsible for VOC removal. Most of our understanding of the mechanisms of VOC removal is derived from experiments that have used aluminum foil or Teflon bags to isolate a particular part of the potted-plant microcosm (Aydogan and Montoya, 2011; Treesubsuntorn and Thiravetyan, 2012; Sriprapat et al., 2014b; Kim et al., 2016), or experiments that have assessed VOC removal under different lighting conditions (Porter, 1994; Kondo et al., 1995; Wood et al., 2002; Orwell et al., 2004; Yoo et al., 2006; Kim et al., 2008; Aydogan and Montoya, 2011; Xu et al., 2011; Treesubsuntorn and Thiravetyan, 2012; Hörmann et al., 2018; Teiri et al., 2018), while several experiments have simply assessed VOC drawdown without testing removal mechanisms (Cornejo et al., 1999; Orwell et al., 2006; Liu et al., 2007; Yang et al., 2009; Kim et al., 2010; Kim et al., 2014; Mosaddegh et al., 2014). A thorough understanding of the removal mechanism is crucial if these systems are to be optimized to enhance the VOC removal rate.

1.6 Removal mechanisms of VOCs

1.6.1 Potting substrate material and substrate microorganism effects

While it was initially assumed that VOC removal was primarily an activity performed by the plant foliage, along with small contributions from the soil, roots and rhizospheric microorganisms (Wolverton et al., 1985; Wolverton 1988), this concept was not explicitly tested. In following experiments, Godish and Guindon (1989) and Wolverton et al., (1989) both independently compared the VOC removal efficiencies between ordinary potted-plants and potted-plants with their foliage removed. Both studies concluded that a significant portion of uptake must occur through the potting substrate. Wolverton et al.'s, (1989) comparison between a potted plant and a pot containing only soil led to the inference that plants must be growing in the soil in order for the potted-plant system to remove VOCs efficiently, and that microorganisms within the rhizosphere contribute to considerable VOC removal.

The contribution of the microbial community has further been demonstrated by experiments that have assessed VOC removal under light and dark conditions and have found no significant differences in the VOC removal under these two conditions (Wood et al., 2002; Orwell et al., 2004; Hörmann et al., 2018), suggesting that stomatal uptake by the plant is negligible for the VOCs that were tested. However, numerous studies have demonstrated that microbial degradation, adsorption or stomatal uptake can also take place on the leaf surface, providing an additional removal mechanism for VOCs (Khaksat et al. 2016a; 2016b; Treesubsuntorn et al. 2013; 2017; Treesubsuntorn and Thiravetyan 2012; 2018). Several studies have found that the VOC removal efficiency of the potted-plant microcosm increases when the system is exposed to repeated doses of a pollutant (Wood et al., 2002; Orwell et al., 2004; Torpy et al., 2013), with these authors suggesting that this response is due to biostimulation of the substrate's microbial community. It is currently generally thought that as indoor air passes over a potted-plant and its substrate, pollutants are drawn into the substrate by diffusion and become a carbon nutrient source for some members of the microbial community (Wood et al., 2006).

While many experiments have assessed the potential for the bioremediation of single VOCs independently, hundreds of VOCs may be present simultaneously in a typical indoor environment (Meciarova and Vilcekova, 2016). Simultaneous biodegradation of multiple VOCs provides the opportunity for substrate interactions to occur. For example, the simultaneous microbial biodegradation of benzene and toluene has been shown to exhibit competitive inhibition, which limits the rate of the simultaneous biodegradation of the two pollutants (Yu et al., 2001). Orwell et al. (2006), however, observed a synergistic effect between the biodegradation of toluene and *m*-xylene. Orwell et al. (2006) suggested that this was a result of toluene supporting a specific microbial population and inducing within that population the activity of the enzyme catechol 1,2 dioxygenase which is used for the biodegradation of both pollutants, however when toluene concentrations become limiting, *m*-xylene was then more effectively biodegraded. Sriprapat and Thiravetyan (2013) have suggested that preferential uptake of particular VOCs over others may indicate apparent selectivity in plant VOC uptake.

Numerous studies have noted the innate ability of plant growth substrates to adsorb VOCs (Godish and Guindon, 1989; Hörmann et al., 2017), and consequently substrates of different compositions have been trialled in experiments for their

capacity to influence VOC removal. Aydogan and Montoya, (2011) noted the substrate's contribution to removal efficiency as their activated carbon substrate treatment demonstrated larger reductions in formaldehyde in comparison to expanded clay and growstone substrates, and concluded that substrates that have high adsorption capacities and provide sufficient microbial sites could lead to increased VOC removal. Further evidence for this claim came from Irga et al. (2013) who found differences in the benzene removal efficiency between potted-plants grown in soil and hydroculture, suggesting that differences in the density and diversity of the substrate's microbial community were responsible for the differences in benzene removal efficiency.

1.6.2 Plant foliage and aerial part effects

Several experiments have compared VOC removal efficiencies under different lighting conditions (Porter, 1994; Kondo et al., 1995; Wood et al., 2002; Orwell et al., 2004; Yoo et al., 2006; Aydogan and Montoya, 2011; Xu et al., 2011; Treesubsuntorn and Thiravetyan, 2012; Hörmann et al., 2018; Teiri et al., 2018). These experiments used light intensity as a surrogate for foliage uptake under the assumption that increased light intensity increases stomatal conductance and plant metabolic activity (Porter, 1994). Of these experiments, there is no clear consensus on whether light intensity influences the removal rate of VOCs, however recent work by Hörmann et al. (2018), has suggested that the possible primary removal mechanisms may be both VOC and plant species dependent. Hörmann et al. (2018) tested toluene and 2-ethylhexanol degradation under light and dark conditions and found no differences in the removal rate of toluene between these treatments, yet found that some of their tested plant species exhibited differences in the removal efficiency of 2-ethylhexanol depending on light or dark conditions. Hörmann et al.'s (2018) findings indicate that stomatal uptake of these VOCs – a process requiring light – may be negligible in this case, and other removal mechanisms are likely to be responsible for the majority of VOC removal. Work that has assessed benzene removal has generally found no difference in benzene removal under different light conditions (Orwell et al., 2004; Wood et al., 2002). Alternatively, experiments that have assessed formaldehyde removal efficiency by potted-plants amongst different light intensities have generally found that increased light intensity is associated with increased removal (Kondo et al.,

1995; Xu et al., 2011; Teiri et al., 2018) however Aydogan and Montoya (2011) found that all of their tested plant species demonstrated quicker formaldehyde removal under dark as opposed to light conditions. The removal of some VOCs, such as formaldehyde, is clearly dependent on many factors, and it is possible that formaldehyde may be predominantly taken up by plant foliage processes. It thus remains difficult to quantify the primary removal mechanism of formaldehyde by potted-plants.

Several studies have isolated aboveground plant parts from the root zone and substrate with the use of physical barriers, and have concluded that leaves are capable of VOC removal (Lin et al., 2017; Tani et al., 2007; Tani and Hewitt, 2009; Treesubsuntorn and Thiravetyan, 2012; Sriprapat and Thiravetyan. 2013; Treesubsuntorn et al., 2013; Sriprapat et al., 2014a; Sriprapat et al., 2014b). While stomatal uptake offers one possible means of VOC removal by the aerial part of the plant, some VOCs are also able to become adsorbed to or diffuse across the cuticle (Baur and Schönherr, 1995; Treesubsuntorn et al., 2013), with some authors suggesting that removal by the cuticle is depenendent on wax quanity and chemical structure (Treesubsuntorn et al., 2013). Although this work has suggested that plant leaves are capable of some VOC removal, these studies have not directly made comparisons between removal by the root zone component and the aerial component of the potted-plant system. Alternatively, Aydogan and Montoya, (2011) tested the formaldehyde removal efficiency of the root zone and aerial parts independently and found that while the aerial parts of plants were capable of VOC removal, removal by the root zone occurred at a substantially faster rate. Kim et al., (2016), used Teflon bags to contain certain plant parts, and suggested that although the root zone is important for toluene and xylene degradation, uptake and transport of the pollutants by the stem tissue is critical for transferring the pollutant to the root zone. Setsungnern et al. (2017) measured removal rates by a potted *Chlorophytum comosum* with its roots covered with aluminium foil and measured benzene degradation within plant cells, and concluded that *C. comosum* was capable of removing 68.77% of an initial 500 ppm concentration of benzene over an eight day period. Setsungnern et al. (2017) found that after plant uptake, benzene was oxidised to phenol within plant tissues by the cytochrome P450 monooxygenase system, before being catalysed to catechol and then cleaved to produce cis, cis muconic acid. In comparison, Orwell et al. (2004) found that a potted-plants microbial community was responsible of

removing ~97% of benzene within 24 h after 3 days of exposure to an initial concentration of 25 ppm that was 'topped up' to the starting concentration every 24 hours.

Hörmann et al. (2017) covered the potted-plant's substrate with foil to assess removal by the plant's aerial parts and compared this to a 'potting soil' treatment, and observed similar VOC removal rates between the treatments. While this method revealed that both soil and the plant's aerial components are independently capable of degradation, it has been suggested that the plants play a key role in promoting substrate microbial VOC degradation both through VOC transport (Kim et al., 2016) and microbial biostimulation through the release of root exudates (Wood et al., 2002; Xu et al., 2010; Wang et al., 2014). Regardless of the primary removal mechanism, it is probable that the entirety of the potted-plant system is needed for quantitatively effective VOC removal, as the root zone and aerial components support each other to maintain mutual health (Wood et al., 2002; Xu et al., 2010; Aydogan and Montoya, 2011, Wang et al., 2014).

At the current state of research, it is difficult to determine the exact removal mechanism for a range of behaviourally different VOCS when applied *in situ*. The trialling of the multiple VOC removal performance of botanical bioremediation systems in real indoor environments, using highly sensitive apparatus so as to quantify the very low level pollutants present, will be required to reveal the true value of these systems.

1.6.3 Effects of biostimulated microbial communities

After establishing that microorganisms within the potted-plant system play a role in VOC removal, some experiments have looked at optimizing the system through biostimulating or bioaugmenting the microbial community for enhanced VOC degradation. Torpy et al. (2013), who compared the removal of benzene between ordinary potted-plants and potted-plants with a stimulated substrate microbial community, found that specifically enhancing the growth of the benzene-degrading components of the bacterial community increased benzene removal. Similarly, Sriprapat and Thiravetyan (2016) identified benzene degrading bacteria in the phyllosphere and found that potted-plants with sterilized leaf surfaces exhibited decreased benzene removal rates, while plants inoculated with the identified

endophytic benzene-degrading bacteria showed an increased benzene removal efficiency in comparison to ordinary potted-plants. De Kempeneer et al., (2004) showed that toluene removal rates could be increased by inoculating the leaf surface with a culture of toluene-degrading bacteria. Notably both of these studies used high concentrations of VOCs, and it remains largely unknown how inoculated phyllospheric microbial communities could be sustained in *in situ* conditions (De Kempeneer et al., 2004). Alternatively, Khaksar et al. (2016a) inoculated two non-native host plant species, *Zamioculcas zamiifolia* and *Euphorbia milii*, with an endophytic species of bacterium (*Bacillus cereus), and found that plant with the endophytic Bacillis cereus inoculation experienced increased resilience to formaldehyde phytotoxicity.* An endophytic *Bacillis cereus* inoculation has also been show to enhance *Clitoria ternatea* seed germination and sapling growth under formaldehyde stress and simultaneously enhance gaseous formaldehyde removal (Khaksar et al. 2016b). These methods of system optimisation need to be thoroughly explored for their potential application in long term *in situ* scenarios, while it is also necessary to accurately uncover these removal methods' comparative efficiency in relation to substrate mediated removal effects.

Table 2. A summary of static chamber experiments that have assessed VOC drawdown.

Author	Pollutant(s)	Starting concentration(s)	Removal rate/efficiency	Experimental light conditions	Suggested removal mechanism/conclusion	Was removal mechanism indirectly tested?
Aydogan and Montoya, 2011	Formaldehyde	~2.038 mg/m^3	81-96% over 24 hours	Cycles of ~28–70 µmol/m^2/s for 12 hours followed by a dark period	Removal by the root zone was faster in comparison to the aerial parts of the plants. Furthermore, there was no discontinuity in removal rate with a transition from light to dark. Concluded that both rhizosphere and aerial parts contribute to removal.	Tested differences in removal rates by comparing the removal rate of the entire plant; rhizosphere + substrate (by surgically removing aerial parts); aerial parts (by sealing the rhizosphere and substrate in a Teflon bag). Tested removal rates under light and dark conditions.
Cornejo et al., 1999	Benzene, pentane, toluene, trichloroethylene	33.176 mg/m^3 for benzene; not stated for other VOCs	0.6-8.5 µg/g/24h	Ambient light and incandescent lamps	Did not identify mechanisms. Only suggested that species morphology and physiology, such as stomatal density and enzymatic activity, may affect pollutant uptake.	No
De Kempeneer et al., 2004	Toluene	339 mg/m^3	7-76 hours to remove 95% of the initial dose	Not stated	Did not identify mechanism, but found that removal efficiency could be increased by bioaugmenting the leaves with an inoculum of toluene-degrading bacteria. Uninoculated plants were also capable of removing toluene	Potting soil was covered by polyethylene to prevent sorption by the roots/substrate, but no comparisons were made comparing uptake between substrate, roots or aerial parts.
Hörmann et al.,	Toluene, 2-	14.6-20.0 mg/m^3	~1-9.5 mg/m^3	180 µmol/m^2/s	The potting soil has a similar removal	Covered the substrate with foil to assess

2017	ethylhexanol		over 48 hours		rate to the aerial plant parts.	removal by aerial parts and compared this to a 'potting soil' treatment.
Hörmann et al., 2018	Toluene, 2-ethylhexanol	14.6-20.0 mg/m^3	1.4 to 5.7 $L/h/m^2$ of leaf area	A light treatment of 180 $\mu mol/m^2/s$ and a dark treatment	Aerial plant parts have no major impact on VOC removal. No significant differences in toluene removal under light and dark conditions, and different physiological differences amongst species did not influence removal rate. 2-ethylhexanol removal varied among lighting conditions in some species.	Compared removal rates under light and dark conditions.
Irga et al., 2013	Benzene	80 mg/m^3	739-1444 $\mu g/m^3/h$ per pot	20 $\mu mol/m^2/s$	Suggested that differences in VOC removal amongst substrate treatments were due to differences in the density and diversity of the substrate's microbial community.	Compared VOC removal efficiencies amongst a potting mix treatment, 'virgin' soil treatment, and a hydroculture treatment.
Kim et al., 2010	Formaldehyde	2.472 mg/m^3	0.13-6.64 $\mu g/m^3/cm^2$ of leaf area	20-60 $\mu mol/m^2/s$	Did not identify mechanisms, yet found differences amongst plant species.	No
Kim et al., 2014	Toluene and xylene	1.236 mg/m^3	~15-170 $\mu g/m^3/m^2$ of leaf area	20 $\mu mol/m^2/s$	VOC removal by plants increased as the root zone volume increased. No relationship between leaf surface area or above ground plant tissue volume and removal efficiency.	Tested the VOC removal efficiency amongst plants in different sizes of pots.

Kim et al., 2016	Toluene and xylene	1.303-1.884 mg/m^3	7.0-13.3 μg/m^3/m^2 leaf area over a 24 h period	20 μmol/m^2/s	The root zone is a significant contributor to VOC removal, but VOC transportation to the root zone via the stem plays an important role.	Teflon bags were used to seal aboveground parts from rhizosphere and substrate.
Lin et al., 2017	Formaldehyde	≥6.25 mg/m^3	~4 ppm over 17.1 hours	16.2 μmol/m^2/s	Suggested VOC removal can occur through foliar pathways.	No: the authors covered the substrate with foil to exclusively test foliar removal.
Mosaddegh et al., 2014	Acetone, acetonitrile, benzene, ethylbenzene, methanol, toluene, xylene	2.62-8.68 mg/m^3	0.24-4.42 mg/m^3/day	Cycles of 12 hours of darkness and 12 hour of light at undescribed levels	Did not identify mechanisms.	No
Orwell et al., 2004	Benzene	79.75 mg/m^3	12–27 ppm/d	~120 μmol/m^2/s	Substrate micro-organisms play a major role in VOC removal; plants may contribute to biostimulation of substrate microbes, assistance in VOC diffusion to substrate, or adsorption onto plant foliage.	Tested removal rates under light and dark conditions. Tested for VOC removal efficiency after plants had been removed from the pots.
Orwell et al., 2006	Toluene, *m*-xylene	0.758-437 mg/m^3	0.68-1014 mg/m^2/day	~120 μmol/m^2/s	Suggested that removal is by substrate microbes.	No
Porter, 1994	Toluene, benzene	0-1200 mg/m^3	5.11-35% in 3 h	35-90 μmol/m^2/s	VOC removal efficiency was light dependent.	Tested removal rates under different light levels

Setsungnern et al., 2017	Benzene	1595 mg/m^3	343.85 ppm over 8 days	50 µmol/m^2/s	VOC removal rate was dependent on red or blue light; benzene uptake affected plant gene expression.	No: the authors covered the substrate with foil to exclusively test foliar removal.
Sriprapat and Thiravetyan, 2013	Benzene, ethylbenzene, toluene, xylene	63.8-81.67 mg/m^3	0.86-0.96 mmol/m^2 of leaf area at 72 h	Natural light-dark cycles	Removal can occur through stomatal uptake and diffusion into the cuticle.	No: the authors covered the substrate with foil to exclusively test foliar removal.
Sriprapat and Thiravetyan, 2016	Benzene	1416 mg/m^3	25.30-34.00 µmol/h/m^2 of leaf area	Fluorescent light with a 16 hour photoperiod at undescribed levels	Non sterilised plants removed benzene at a faster rate. Phyllospheric bacteria play a role in VOC removal.	Phyllospheric benzene degrading bacteria were identified, inoculated and applied as a treatment
Sriprapat et al., 2014b	Toluene, ethylbenzene	70.88-81.67 mg/m^3	10.17 µmol/72 h of toluene; 11.11 µmol of ethylbenzene over 72 h	12 h photoperiod at undescribed levels	VOCS may be taken up by adsorbing onto the cuticle. This is influenced by cuticle composition.	No: the authors covered the substrate with foil to exclusively test foliar removal.
Sriprapat et al., 2014a	Xylene	81.6 mg/m^3	59.14-88.20% at 72 hours; 0.66-0.86 mmol/m^2 of leaf area after 72 hours	Natural light-dark cycles	Removal can occur through stomatal uptake and diffusion into the cuticle.	No: the authors covered the substrate with foil to exclusively test foliar removal.
Su and Liang,	Formaldehyde	30, 60 or 120 mg/L	135 µg/h^1 per	14 hours of	Suggested primarily by shoot	Not clearly tested, although tissue samples

2015		applied as a solution	plant (maximum)	light at 260–350 μmol/m^2/s		were taken from different plant parts
Torpy et al., 2013	Benzene	80 mg/m^3	Biostimulation increased removal rates by ~27%	120 μmol/m^2/s	Suggested that removal is due to substrate microbes.	Biostimulation of microbes increased removal efficiency
Treesubsuntorn and Thiravetyan, 2012	Benzene	63.8 mg/m^3	43-77% in 72 h	Light and dark periods at undescribed levels	Removal can occur through stomatal uptake and diffusion into the cuticle.	Roots covered in aluminium foil; light and dark testing
Treesubsuntorn et al., 2013	Benzene	63.8 mg/m^3	1.10-23.46 μmol/g over 3 d	Undescribed	High quantities of cuticle wax was associated with high benzene removal efficiency.	Did not test removal mechanism; only tested leaf removal- did not test pot effects
Wood et al., 2002	Benzene and *n*-hexane	79.75-353 mg/m^3	367-4032 mg/m^3/day/m^2 of leaf area	Light and dark conditions (light = 120 μmol/m^2/s)	Substrate microbes are the primary 'rapid response' agents of VOC removal.	Compared removal efficiencies between light and dark conditions as well as hydroponic and soil treatments.
Xu et al., 2011	Formaldehyde	1-4 mg/m^3, increasing by 0.5 mg/m^3 every 5 d depending on visible foliar injury	14-95% / 3 d; 0-2.2 mg/h	12 h cycles of darkness and light with light at 80, 160, 240 μmol/m^2/s	Both soil and leaves	Tested removal rates amongst different light levels.

Yang et al., 2009	Benzene, octane, α-pinene, toluene, trichloroethylene	31.9-55.7 mg/m^3	0.34-1.03 μg/m^3/3 h; 0.38-1.21 μg/m^3/6 h	~5.45 μmol/m^2/s	Did not identify mechanisms	No
Yoo et al., 2006	Benzene, toluene and a mixture of both	3.204-3.779 mg/m^3	18.8-220.2 ng/m^3/cm^2 of leaf area/h	100 μmol/m^2/s before experiment; unknown during VOC exposure	Day time results were higher in some cases, however removal mechanism not exclusively tested.	Compared removal rates between day and night time.
Zhou et al., 2011	Formaldehyde	15 mg/m^3	2.21-4.60 mg/m^3 over 7 d	Undescribed	Did not identify mechanisms	Used a plantless control treatment consisting of a pot containing only soil.

1.7 Limitations of static chamber experiments

The vast majority of the knowledge regarding the efficacy of potted-plants to remove VOCs comes from static chamber trials, in which a high concentration of a pollutant is spiked into a small sealed chamber containing potted-plants, with VOC concentrations within the chamber headspace monitored over time (Llewellyn and Dixon, 2011). Given the nature of these trials, generalizing their results to realistic indoor air concentrations in larger rooms has been subject to controversy (Llewellyn and Dixon, 2011; Aini Jasmin et al., 2012). Furthermore, there has been uncertainty regarding how the substrate's active microbial populations will be sustained if exposed to fluctuating concentrations of the VOCs that they catabolize, a situation that is likely in real-world situations (Guieysse et al., 2008). These issues have led to work that has experimented with airflow systems that attempt to expose the microbial population to a constant pollutant flux (Wang and Zhang, 2011). This development has made botanical air cleaning more feasible process for the indoor environment (Wang and Zhang, 2011).

1.8 Active botanical biofiltration with functional green walls

Although experiments with potted-plants have produced promising results for air quality maintenance, the *in situ* performance of potted-plants is constrained by the rate at which pollutants diffuse from their source to the potted-plant to be processed. Additionally, the relatively low concentrations of VOCs normally found indoors when compared to the VOC concentrations used in static chamber experiments may reduce the rate of microbial degradation (Llewellyn and Dixon, 2011). To overcome these rate limiting steps, the use of mechanical airflow generated by devices such as fans, in conjunction with planted systems, has been developed. This development aimed to increase the volume of polluted air that is exposed to the plant's growth substrate, whereby bacteria living in the plant root zone could degrade the VOCs and/or the VOCs may adsorb to specialised materials within these substrates. These systems normally take the form of active green walls (Darlington et al., 2001; Irga et al., 2017a; Irga et al., 2017b; Pettit et al., 2017), which, relative to potted-plants, considerably increases the plant density and increase the ease with which the plant growth substrate could be exposed to a polluted air stream (Soreanu, 2016). Such systems may be able to promote the recirculation of air within a building, and

potentially reduce HVAC costs (and the corresponding energy expenditure), by reducing the load on the HVAC required to remove the room's air pollutants. (Darlington et al. 2001; Chen et al., 2005). The use of active airflow in conjunction with increased plant density allows these systems to simultaneously treat indoor generated gaseous air pollutants as well as filtering PM, a function inherent in the industry standard HVAC PM filters.

1.8.1 VOC removal by functional green walls

The use of active airflow allows active green wall pollutant removal rates to be reported as single pass removal efficiencies (SPREs) and clean air delivery rates (CADRs); metrics used for assessing the performance of conventional air handling systems. The SPRE refers to the proportion of a dose of target pollutant that is removed with each pass through the filtration matrix. The CADR is the SPRE multiplied by the volumetric flow rate through the filtration matrix. The CADR is generally the most valuable air cleaning metric used to compare air cleaning performance amongst different systems, as it describes the volume of 'cleaned' or pollutant-free air produced by the system per unit time (Zhang et al. 2011). Importantly, both of these metrics are target pollutant specific where 'cleaned air' describes the elimination of a single specified target pollutant, an important consideration as the chemical properties of each VOC influences its biofiltration rate differentially (Pettit et al. 2019a). The influence of airflow through active green walls has been addressed in numerous experiments assessing the rate of airflow through the green wall and its influence on SPRE and CADR for several VOCs (Darlington et al. 2001; Darlington and Dixon 1999; Llewellyn and Dixon 2000b; Wang and Zhang 2011; Llewellyn et al. 2002). The botanical biofiltration of several VOCs, including toluene, formaldehyde (Wang and Zhang 2011), ethylbenzene, xylene (Darlington et al. 2001), acetone (Darlington and Dixon 1999), methyl ethyl ketone and benzene (Llewellyn and Dixon 2000b; Llewellyn et al. 2002) at different airflow rates demonstrated that although smaller volumetric airflow rates are associated with an increase in the SPRE, the CADR generally increases with larger volumetric flow rates until a threshold is reached. Although this trend has been consistently observed across all VOC studies, the optimum airflow rate through the active green wall is likely VOC dependent. For example, Llewellyn and Dixon (2000b) found that the removal of

methyl ethyl ketone by their active green wall was most effective at the maximum tested airflow rate of 0.4 m s^{-1}, however the removal of toluene was most effective at a smaller airflow rate of 0.1 m s^{-1}. These discrepancies in optimal flow rate may relate to how readily each VOC can absorb into the aqueous phase of the filtration matrix, with VOCs that are more water-soluble being more suited to greater flow rates. Further experimentation is needed to understand optimal flow rates and the factors that are likely to influence this.

These factors notwithstanding, active green walls have considerably improved the capacity of planted systems to remove VOCs from the indoor environment. Guieysse et al. (2008) modelled a CADR of 0.075 m^3 h^{-1} from Wolverton et al.'s (1989) experiment in which a plant within a sealed chamber reduced the concentration of benzene from 765 to 78 μg m^{-3} over a 24 h period. Despite this considerable benzene reduction within the sealed chamber, when the potted-plant's benzene CADR is calculated, it is unlikely to make significant changes to the air quality of a full-sized room (Guieysse et al. 2008). Comparatively, Darlington et al.'s (2001) experiment assessing the removal of toluene, xylene and ethyl benzene by their active green wall exhibited CADRs of ~720 m^3 h^{-1}, however this was dependent on airflow rate and temperature (Guieysse et al. 2008). Although such large differences are in part due to different sizes of the botanical system (amongst other factors), their sizes are reflective of their likely *in situ* operational designs.

1.8.2 PM removal by functional green walls

The plant growing medium in an active botanical system has many of the properties of a filter. Unlike potted-plant systems, where PM removal is limited to deposition on plant foliage, active systems pull air through the plant growth substrate, which can filter out a portion of the PM from the air stream (Irga et al., 2017b). Irga et al. (2017b) and Lee et al. (2015) revealed the potential for active green walls to effectively filter and reduce PM. While the use of highly adsorbent substrates has the potential to improve removal efficiency for VOCs, it is largely unknown how biofilter substrate design affects PM removal. Pettit et al. (2017) revealed that the PM SPRE of active botanical biofilters could be enhanced through appropriate plant species selection, as the different root structures characteristic of each plant species alters the substrate pressure drop properties differentially to influence PM removal efficiency. It

is thus likely that the alteration of other substrate properties that influence pressure drop, along with many other physio-chemical characteristics, could affect the PM removal performance of botanical biofilter systems.

1.8.3 CO_2 removal by functional green walls

Although it is likely that an impractical number of potted-plants will be needed to offset all CO_2 occupant emissions from most built environment applications (Irga et al., 2013), green walls provide a greater density of plants for a given area of floor space, and thus may provide greater value in this regard. Su and Lin (2015) showed that a 5.72 m^2 indoor plant wall could reduce the CO_2 concentration of a 38.88 m^3 room from 2000 to 800 ppm within an hour. Notably, however, each plant's substrate was covered with aluminium foil to eliminate the effect of substrate respiration, which would not be possible for longer-term plant health, and thus largely negates the practical value of this study. Similarly, Torpy et al. (2017) showed that a 1 m^2 active green wall was capable of significant room CO_2 reductions, but only with the provision of considerable supplementary lighting (250 μmol m^{-2} s^{-1}, whilst indoor light levels typically range between 5–12 μmol m^{-2} s^{-1}; Torpy et al., 2017). While, Torpy et al. (2014) found CO_2 removal could be improved through suitable plant species selection, the most efficient CO_2 sequestering plants identified (*Howea fosteriana* and *Dypsis lutescens*) are not suitable for use in current green wall designs. It is not known whether suitable green wall species can be identified that have the ability to reduce CO_2 concentrations efficiently.

1.8.4 Other functions

Active green walls have further benefits related to human comfort, for example, in warm climates, temperature reductions of 4–6°C have been observed in proximity to an indoor wall (Fernández-Cañero et al., 2012), showing potential for reduced reliance upon air conditioning leading to possible energy savings. Similarly, Wang and Zhang (2011) predicted that an active botanical biofilter integrated into a HVAC system could reduce energy usage by 25%, while still maintaining equivalent indoor air quality.

Active green walls can remove a range of air pollutants and provide other benefits relating to comfort. Their current removal efficiencies show that their implementation in full-scale rooms has the potential to provide significant benefits for indoor air quality. There is still, however, a need for realistic, *in situ* tests of these systems, along with an integrated approach to optimise these systems for both improvements in indoor air quality and energy reduction.

1.9 System design

There is range of active botanical biofilters available, each with its own design and claims for air quality remediation. The range of system designs available offers the potential to enhance the technology by selecting the best traits from each system. While all active systems use plants and increased airflow to promote aesthetic appeal and air quality remediation, systems differ with regards to substrate, size, alignment of plants, modularity, as well as water and air supply.

1.9.1 Substrate

Substrate depth and composition are important metrics of biofilter design, as they are key determinants of the plant growing conditions, required watering regimes, pressure drop, microbial composition and pollutant filtration capacity. While some commercially available systems such as the *AgroSci Aerogation*^{TM} green wall system (AgroSci, 2018) make claims about effects on air quality and using an 'engineered soil structure', there is often little information disclosing what substrate is in use.

There is an abundance of research related to the differential capacity of a range of substrates to filter VOCs in non-botanical biofilters, yet it is unknown how plants tolerate such substrates, and furthermore, how these substrates filter out PM. It is, however, known that substrate choice will influence botanical biofilter performance. Darlington et al. (2001) found substantial removal rates of VOCs in a hydroponic system, while Wang and Zhang (2011) found high removal rates of VOCs utilising a substrate consisting of a 50:50 mix (by volume) of activated carbon to shale pebbles. It is thus likely that research that compares the relative performance of different substrates will identify characteristics that will lead to performance development of botanical air filtration systems.

1.9.2 Air supply

A number of different airflow orientations exist amongst different commercially available systems, which may have implications for their air cleaning abilities. Only a limited number of these systems have had experimental results published in the literature. Torpy et al. (2018) experimented with the NAVAA ONE system (Naturvention Pty, Jyväskylä, Finland; Figure 1), in which contaminated air is drawn through the planted face of the green wall before flowing vertically upwards through the substrate, thus passing the polluted air stream over a great length of the system's substrate. The treated air then returns to the ambient air via the top surface of the system.

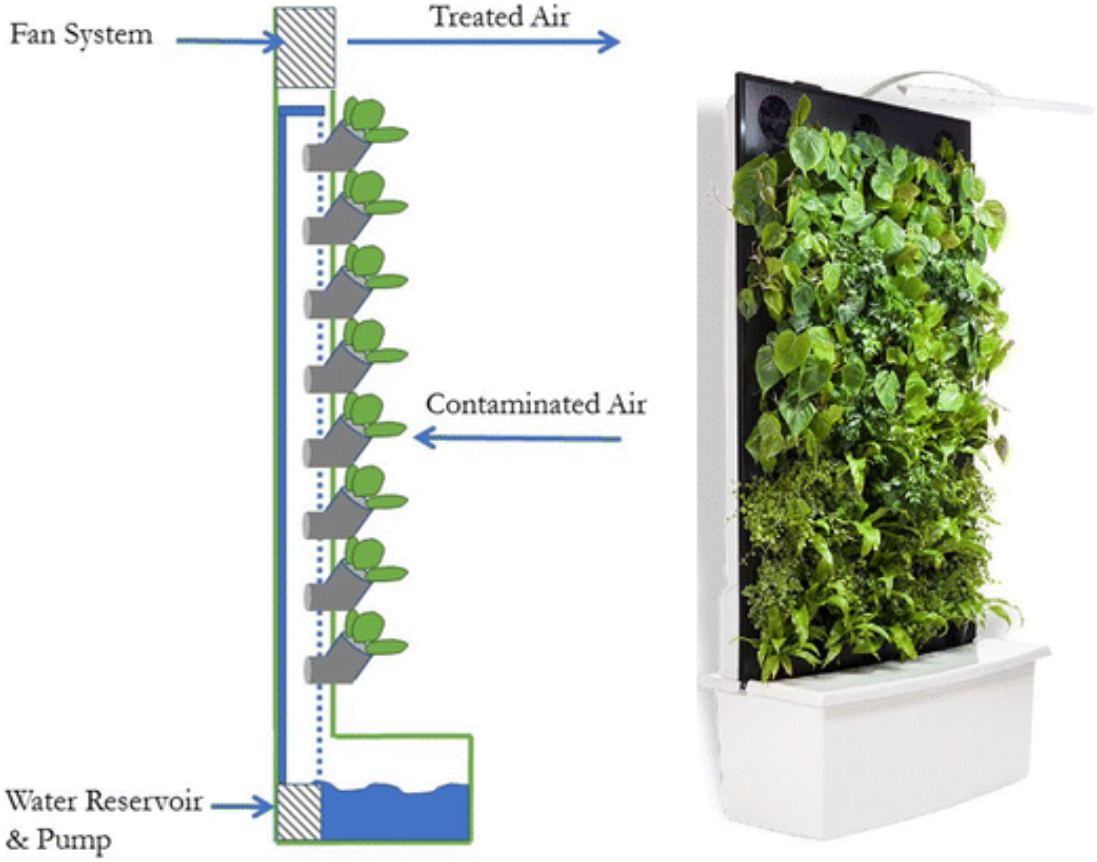

Figure 1. An active botanical biofilter system in which contaminated air is drawn through the planted face and migrates upwards through the substrate before returning to ambient air. Image from Torpy et al., (2018).

Alternatively, other studies have tested systems in which airflow is directed horizontally along the width of the substrate, passing through a duct on the rear side, flowing through the substrate and out through the planted side to ambient air. This

application is generally associated with modular systems such as the *Junglefy Breathing Wall* (Junglefy, 2016; Figure 2) and the *AgroSci Aerogation Green Wall* (AgroSci, 2018), which allow designs to be highly customised. Wang and Zhang (2011) and Treesubsuntorn et al. (2017) tested botanical biofilters (Figure 3) in which contaminated air was pulled through the planted surface of a horizontally aligned plant bed before flowing downwards through the substrate and returning to ambient air or an HVAC system. Due to a reduced path length of airflow, these systems likely experience less resistance to airflow and this may enable them to process larger volumes of air, accompanied with a shorter filtration path length, which may reduce filtration efficiency.

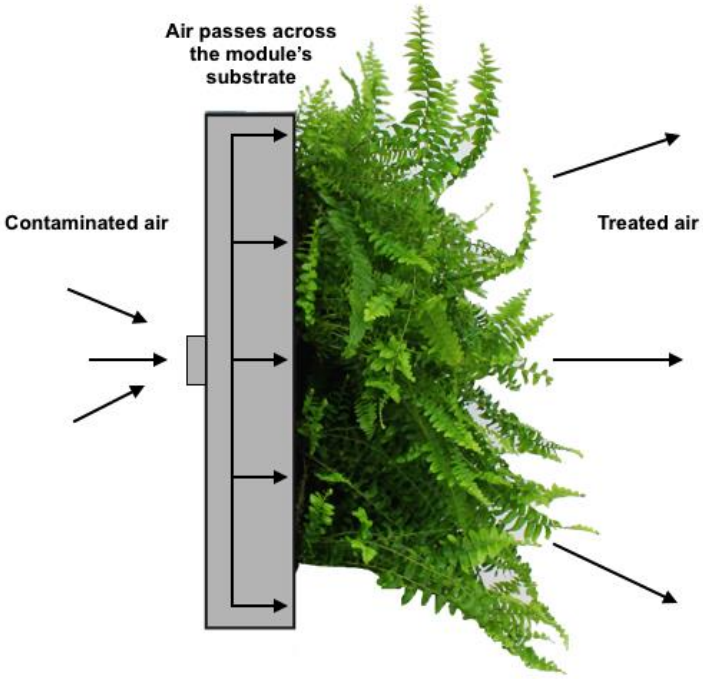

Figure 2. An example of airflow passing through the width of the substrate in an active green wall.

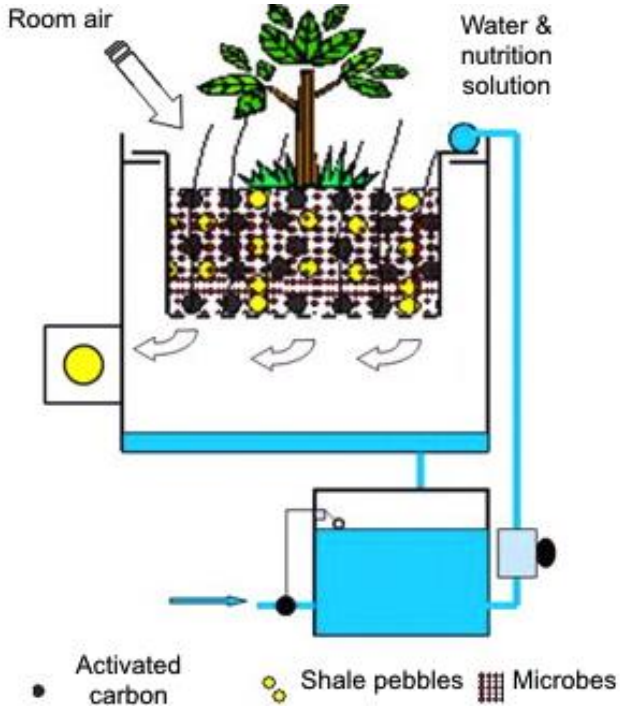

Figure 3. A botanical air filter system in which airflow flows through a horizontal planted surface and downwards through the substrate depth. Image adapted from Wang and Zhang (2011).

A promising innovation is the integration of botanical biofiltration with HVAC systems (Wang and Zhang, 2011), in which HVAC systems distribute clean air while providing an air filtering role, while the air cleaning ability of the botanical biofilter can reduce the load of the HVAC system, as well as removing VOCs and possibly CO_2.

Volumetric airflow rate is another characteristic that has not been compared amongst systems, and this also likely has ramifications for air pollutant filtration. Darlington et al. (2001) found the highest biofilter VOC removal occurred at the lowest tested airflow rate, as this increased the contact time between the polluted air and the substrate. Reduced airflow rates however compromise a system's capacity to process high volumes of air. Although Wang and Zhang (2011) found the lowest single pass removal efficiencies of VOCs at their highest airflow rate, this airflow rate achieved the highest clean air delivery rate (CADR), and thus may be most beneficial when applied *in situ*, depending on energy use.

1.9.3 Water supply

Water is essential for plant life in botanical biofilters, and watering design and regime may be utilised to influence pollutant removal. Some systems, such as that used by Darlington et al. (2001), incorporate biotrickling water regimes that provide a constant trickle of water that runs down the substrate where it is captured at the bottom and recirculated (Figure 4). Biotricklers allow higher surface volumetric loading rates, and through the provision of constant water, ensure that the water source does not reach the pollutants' saturation point (Guieysse et al., 2008). Another innovation is the use of a combined irrigation and air supply system such as that used by AgroSci, which uses a wick to provide a constant water supply while air is delivered through a central channel within the wick (Figure 5).

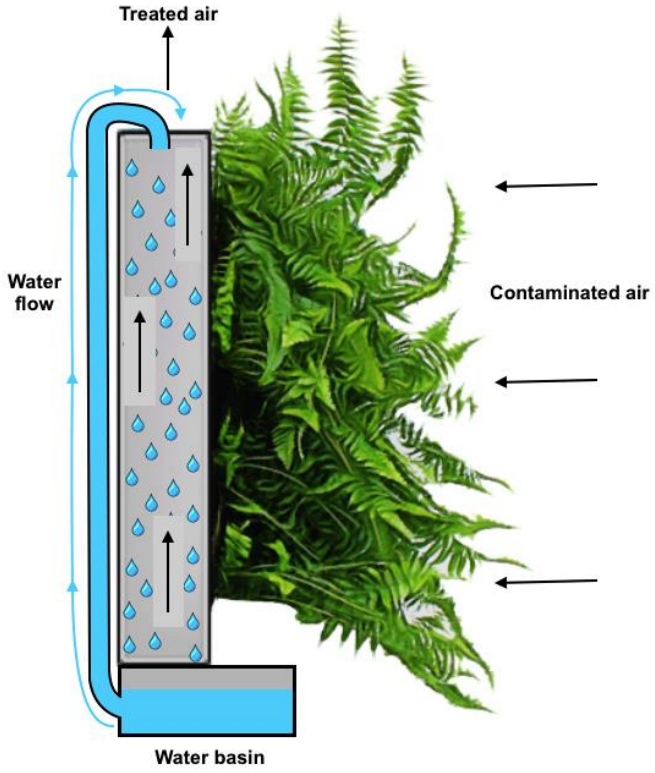

Figure 4. A botanical biotrickler. Within the substrate, contaminated air flows upwards, while a constant supply of water drips downwards where it is caught in a basin.

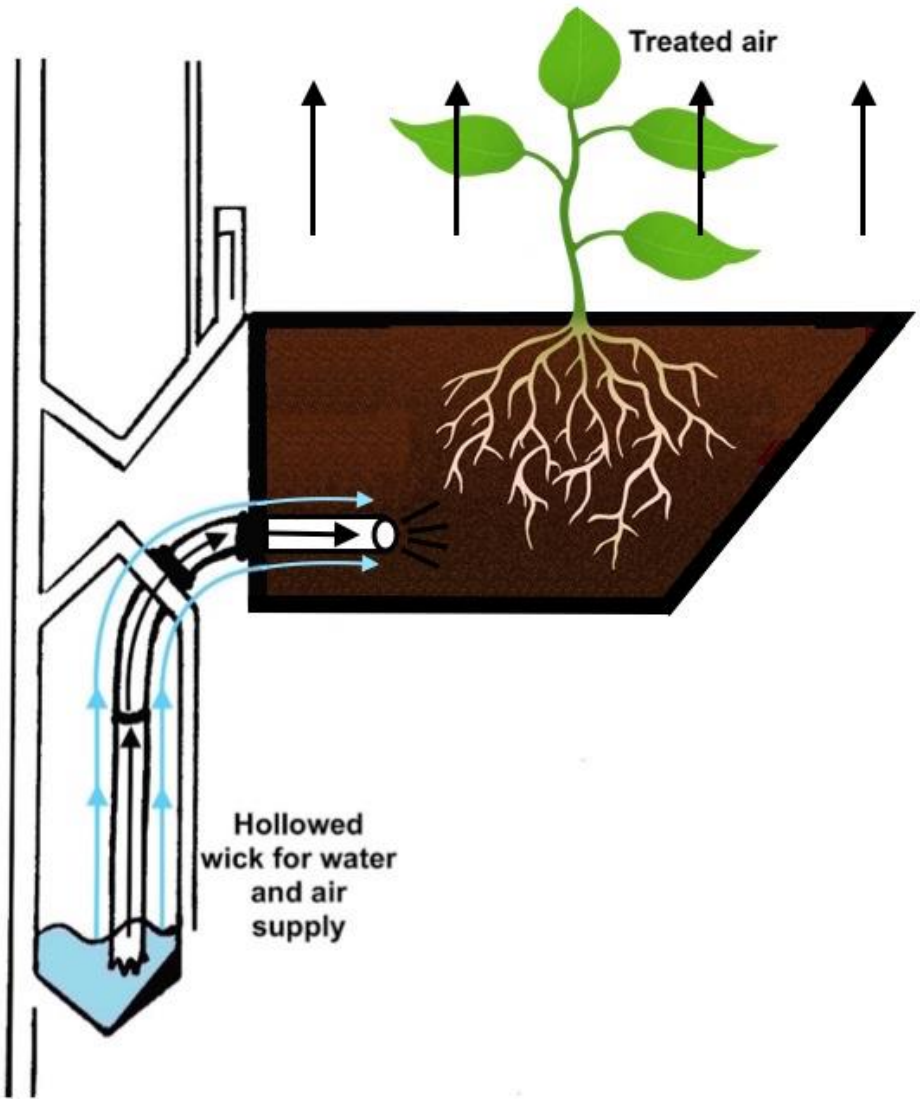

Figure 5. The *AgroSci Aerogation* system that uses a hollowed wick to supply water as needed from a reservoir, while air is supplied through a central channel within the wick.

There may be, however, considerable potential to optimize these systems for air quality improvement: to date there has been little developmental work, with commercial development based almost solely around plant health. Thus potential improvements may relate to airflow rate, position of airflow source and direction of airflow, along with substrate composition and depth, lighting, irrigation regimes, plant selection and management of the microbial population.

1.10 Botanical biofiltration challenges and limitations

One of the most challenging issues associated with the use of biological air filtration relates to the levels of maintenance required for the persistence of healthy plants and their associated microbial populations. The absorption of pollutants into the substrate and plant tissues may differentially compromise the health of different plant species, and thus in conjunction with species-specific lighting requirements, plant selection may become a crucial aspect for the development of biofiltration technologies (Soreanu et al., 2013). There is limited evidence of plant tolerance to long term air pollution exposure, particularly PM, however limited evidence suggests that relatively short-term (5 weeks) exposure to high concentrations of PM is unlikely to severely affect plant health (Paull et al. 2018). Furthermore, vertically aligned plants may require specialised irrigation regimes due to substrate drainage and increased drying due to airflow across the substrate. While some studies have suggested that certain species are more efficient at phytoremediating certain pollutants than others (Kim et al., 2010; Torpy et al., 2014; Pettit et al., 2017), it is likely that all plant species and their innate microflora have some pollutant removal capabilities, and thus in some cases the capacity of the species to thrive in active botanical biofilter conditions may be a more important consideration than pollutant removal capacity.

The presence of large numbers of plants and aerated, moist substrates clearly presents the potential to increase building relative humidity (Guieysse et al., 2008). Wang and Zhang (2011) noted an increase of up to 18% in their room-sized experimental chamber containing an active botanical biofilter. Increased relative humidity may promote mould formation and deterioration of building materials, and therefore should be kept below 65% (Soreanu et al., 2013), which may be achieved through a balance between appropriate irrigation, air flow rates and substrate selection, as these are all factors likely to influence effluent air humidity. Once again, further research in this area will be required before biofiltration can be effectively used in particular types of buildings and locations.

It has been proposed that indoor plants could act as a significant source of fungal inocula (Staib et al., 1978; Botzenhart et al., 1984; Summerbell et al., 1989; Hedayati et al., 2004; Engelhart et al., 2009), and it is a logical inference that active airflow may promote the emission of fungal spores and bacteria from botanical

biofilters into ambient air. However to date, no work has found evidence to support this hypothesis and conversely, Irga et al. (2017a) compared airborne bioparticle densities is offices with active biofilters to those without and concluded that active biofilters are unlikely to make hazardous contributions to indoor fungi. Similarly, experiments conducted by Darlington et al. (2000) and Mallany et al. (2002) both found that botanical biofilters did not increase the concentration of culturable fungal bioaerosols. While bacterial emissions have not been thoroughly studied in active botanical biofiltration, Zilli et al. (2005) found that the bacterial aerosols in the effluent air from laboratory scale biofilters were only slightly denser than those found in the ambient air. The evidence combined thus far suggests that properly maintained active botanical biofilters are unlikely to emit aerosolized fungi or bacteria in concentrations or community compositions that differ from the ambient indoor air.

1.11 Active botanical biofilter experimental design

Although there is significant literature examining the capacity of a range of passive and active botanical biofilters to remediate different air pollutants, the vast majority of these experiments have been conducted on a laboratory scale, generally using small (<1 m^3) sealed chambers and often with unrealistically high concentrations of pollutants. There is therefore difficulty extrapolating these results to a building scale due to the comparatively low pollutant concentration and potentially reduced diffusion effects found in larger rooms. Due to the wide range of pollutants generally found in buildings, in conjunction with room-specific factors such as moisture, temperature, size, ambient airflows etc., experiments that comprehensively assess the capacity of biofilters to enhance indoor air quality with reproducible testing conditions, controls and independent replication, are difficult to achieve (Guieysse et al., 2008). Furthermore, many studies have focused on assessing the short term or single pass pollutant removal efficiency (e.g. Darlington et al., 2001; Lee et al., 2015; Irga et al., 2017b; Pettit et al., 2017), thus there is a paucity of research relating to the CADR of these systems; although the CADR achieved by Wang and Zhang (2011) provides a promising insight into their potential. Similarly, the short-term experimental approach has largely left long-term effects on plant health unknown.

With numerous active botanical biofilter designs in existence, the use of inconsistent experimental approaches makes it difficult to compare systems. The use

of differently sized walls, different VOCs, different doses of pollutants, and different time frames confounds valid comparisons. There is a clear need to standardise experimental procedures to some degree to allow comparisons across studies so different system aspects can be accurately evaluated for the technology to progress.

1.12 Opportunities

In addition to the body of research that has looked at potted-plants and green walls to clean contaminated air in the indoor environment, there is a large body of research looking at the capacity of urban forestry to provide enhanced air quality in the ambient urban environment. Although active green wall research has been limited to laboratory studies and the indoor air quality investigations, traditional urban forestry such as street trees, hedges and shrubs have been thoroughly studied for their capacity to remove urban air pollutants (Abhijith et al. 2017). Nowak et al. (2006) suggested that urban trees and shrubs remove 711, 000 metric tons (US$ 3.8 billion value) of air pollution (O_3, PM_{10}, NO_2, SO_2, CO) across the United States of America each year, whereby pollutants are removed through foliar processes such as stomatal uptake and wet and dry deposition. Several studies however, have noted that in some cases, particularly in street canyons, there is potential for urban tree canopies to limit the diffusion of air pollution from sources such as traffic, and thus, increase the concentration of air pollution at ground level (Gromke et al 2008; Jeanjean et al. 2017; Salmond et al. 2013; Vos et al. 2013). Alternatively, passive green walls may be used in both street canyons and open road settings to provide improvements to air quality, primarily through hindering the dispersion of pollutants from reaching relevant exposure zones (Abhijith et al. 2017). Nonetheless, current technologies that attempt to mitigate air pollution exposure in urban contexts, including roadside vegetation barriers and solid barriers (Tong et al. 2016; Gallagher et al. 2015), primarily work through altering pollutant dispersion rather than reducing the pollutant load from the ambient air through filtration and bioremediation.

The use of airflow in active green walls promotes substrate removal processes, bioremediation and filtration as additional removal mechanisms; thus removing air pollution from the ambient air rather than simply shifting pollutant dispersion. Consequently, fusing botanical biofiltration technology with urban forestry to create outdoor active green walls, is a promising means to considerably

improve urban air quality. Additionally, the small ground and canopy footprint of green walls allows such technologies to be installed in spatially constrained urban areas (Abhijith et al. 2017). Due to the extensive range of environments in which this technology can be applied and the vast range of benefits provided by green walls, including urban stormwater management, temperature reductions, acoustic attenuation and enhanced scenic landscape (Manso and Castro-Gomes 2015; Horoshenkov et al. 2011; Attal et al. 2017); the assessment of active green walls for air quality enhancement is critical for sustainable urban design and is of international scope. It is clear that assessments of technologies that can promote sustainability and improve public health outcomes through reducing the concentration of traffic related pollutants in urban areas are of great value.

The potential large-scale implementation of active green walls through incorporation into urban infrastructure allows them to treat complex mixtures of air pollution *in situ,* regardless of the pollutant source. While traffic emissions are well recognised as a problematic source of air pollution in urban areas, the 2019-2020 *Black Summer* wildfires across Australia led to an increasing concern of the resulting air quality associated with wildfire emissions. The *Black Summer* wildfires occurred on an unprecedented scale, burning 18 million hectares of land (Filkov et al. 2020), causing 429 smoke-related human deaths (Johnston et al. 2020), and exposing a considerable proportion of the Australian population to harmful air pollution levels (Di Virgilio et al. 2021). With wildfires expected to increase in both frequency and severity (Di Virgilio et al. 2019; Dowdy et al. 2019), any technology that can reduce exposure to smoke emissions will clearly be beneficial and it would be valuable to test existing technologies that are capable of treating a comprehensive range of pollutants, such as active green walls, for their capacity to additionally treat wildfire emissions during such events.

1.13 Gaps in Knowledge

Since first recognising the potential of potted-plants to enhance indoor air quality over three decades ago (Wolverton et al., 1984; Wolverton et al., 1985), there has been a progressive increase in research that has measured the air treatment capabilities of the potted-plant, as well extending this capacity in the form of active botanical biofilters. While this work has produced promising findings, and the industry is expected to grow significantly, there is still a need for further research that accurately assesses the air cleaning capacity of these systems, before this technology will become widely adopted and implemented in the indoor environment.

The current work will thus be the first to trial active, botanical biofiltration in areas with genuine air pollution exposure concern, along with the providing the first realistic estimate of the capabilities of this technology to improve indoor and urban environments. To discover the genuine potential of these systems for air quality remediation, reproducible laboratory and field experimentation is required to identify whether these systems can be effectively designed and employed. Only with this knowledge can these systems be developed to provide genuine value to our cities, and promoted as a valuable addition to modern urban spaces. This project will assist in the development of the air cleaning capacity of botanical biofilters, and will investigate the function of the system *in situ,* in close collaboration with major external partners who will play a key role in the large-scale deployment of the system.

Specifically, the project objectives are to:

1. Assess an active green wall system's capacity to filter a range of common volatile organic compounds (VOCs) and investigate which chemical properties are associated with differences in their removal efficiencies.

2. Systematically compare, under realistic *in situ* conditions, the capacity of active and passive biofilter technologies to quantitatively remove suspended PM (particulate matter) and VOCs through two pilot-scale field studies.

3. Test the capacity of active green walls to remove NO_2 and O_3 with comparisons made across two different plant species commonly used green walls.

4. Determine the potential of active green walls to reduce the concentrations of NO_2, $PM_{2.5}$ and O_3 in two different roadside environments.

5. Investigate the potential of active green walls to NO_2, $PM_{2.5}$ and O_3, associated with wildfire emissions.

Preface: Chapter 2

In comparison to passive potted-plants, it is likely that the increased pollutant removal performance of active botanical biofilters is through an enhanced combination of substrate adsorption and microbial degradation resulting from the use of active airflow, rather than passive uptake of potted-plant systems (Wang et al., 2014). Similarly to potted-plants however, the plants in active biofilters may support and stimulate the rhizospheric microbial community to allow efficient pollutant removal (Xu et al., 2010). As botanical biofilters require nearly water saturated substrates, biodegradation or adsorption of VOCs is a step-wise process, where a VOC must transfer into the aqueous phase before diffusion to a microbial cell where it is degraded, or to an adsorbent site within the substrate (Darlington et al., 2001; Karanfil and Dastgheib, 2004). It is therefore likely that the removal of VOCs will be influenced by VOC chemical properties in addition to substrate properties. Despite the potential for substrates to influence removal rates, it is still unclear how removal efficiency varies depending on the specific VOC being tested.

Investigating the removal rate of different VOCs through the current literature remains difficult as the immense variance in the experimental VOC concentrations prevents accurate comparisons across studies (see Pettit et al. 2018a). While the rate of microbial VOC degradation is known to follow first order kinetics (Wang, 2011) and is thus independent of the VOC dose, it is unknown if the pollutant-substrate adsorption processes of active green wall systems are also dose-independent, and thus whether this also influences removal efficiency. This knowledge is also essential to determine whether the large VOC doses typically used in *in vitro* studies are representative of *in situ* air cleaning potential.

This experiment assesses an active green wall system's capacity to filter a range of common VOCs and investigates which chemical properties influence removal efficiencies.

The work presented in this chapter has been published in the Journal *Atmospheric Environment*:

Pettit, T., Bettes, M., Chapman, A.R., Hoch, L.M., James, N.D., Irga, P.J., and Torpy, F.R., 2019. The botanical biofiltration of VOCs with active airflow: is removal efficiency related to chemical properties? *Atmospheric Environment*, *214*, p.116839. This chapter is written verbatim to this article.

Author Contributions:

Thomas Pettit: Conceptualization, methodology, analysis, investigation, resources, data curation, original draft preparation, review and editing. **Miranda Bettes**: Data collection. **Ailis Chapman**: Data collection. **Lilian Hoch**: Data collection. **Nicholas James**: Data collection. **Peter Irga:** Investigation, resources, review and editing, supervision, project administration. **Fraser Torpy:** Conceptualization, methodology, review and editing, supervision, project administration.

Chapter 2

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

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2.1 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.

2.2 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., 2000a).

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.

2.3 Methods

2.3.1 Active green wall description and trial VOCs

A modular active botanical biofilter ('The Breathing Wall', Junglefy Pty Ltd; Banksmeadow, NSW, Australia; Figure 6) 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., 2017a). 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.

2.3.2 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 3). 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 3. 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%

2.3.3 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 6). 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 Appendix 1). 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.

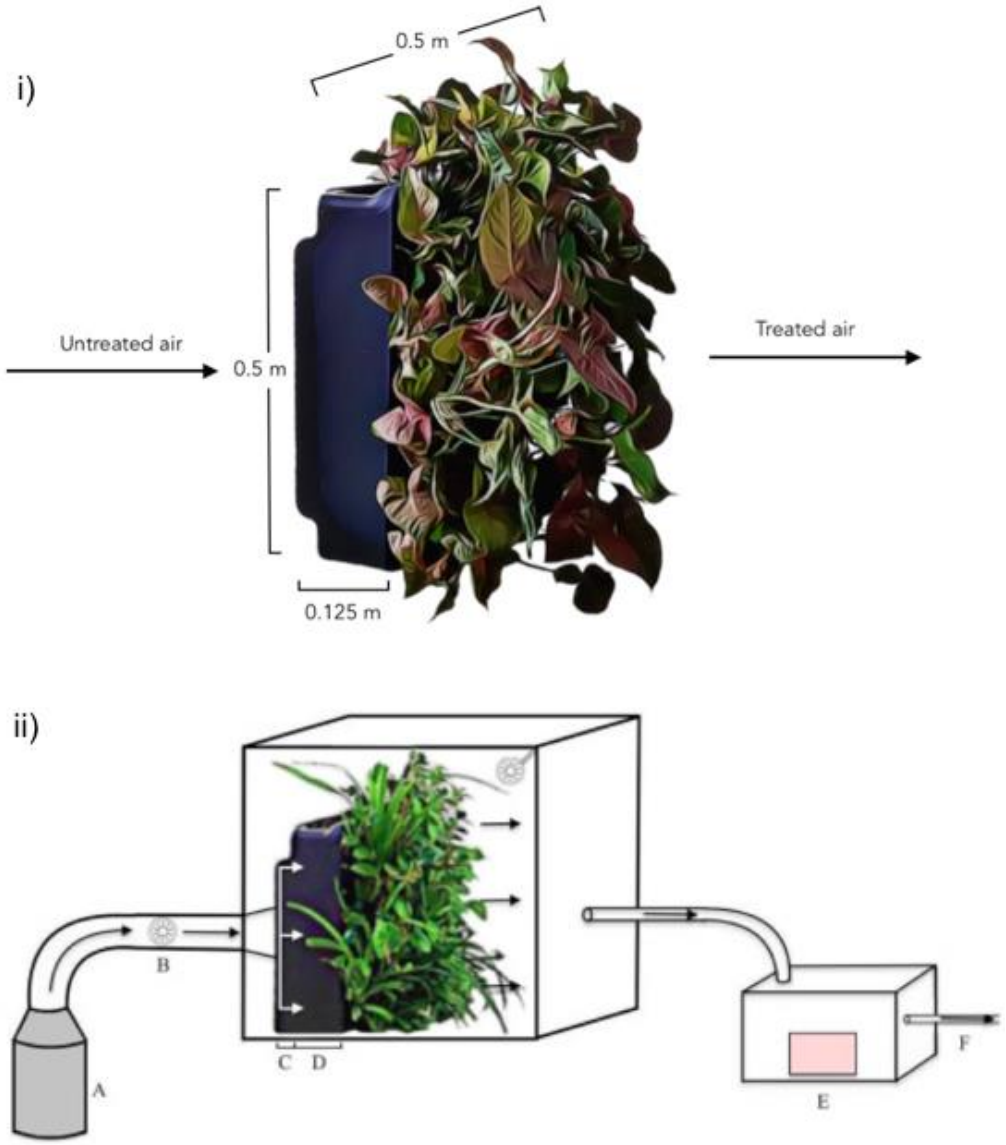

Figure 6. i) The active green wall module used in this study; ii) Single pass flow-through chamber: A = VOC injection port; B = axial impeller; C = plenum within green wall module; D = coconut husk growth media; E = photoionization detector; F = vacuum exhaust. Figure adapted from Pettit et al. (2017).

2.3.4 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, 1.275×10^{-5} moles of each gaseous VOC were tested, as per (Pettit et al., 2018b).

Each VOC was trialed 10 times with an independent active green wall module in the chamber for each trial 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.

2.3.5 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.

2.4 Results and Discussion

2.4.1 VOC removal rates

The SPREs of different VOCs by the active green wall are shown in Figure 7. 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 4). 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.

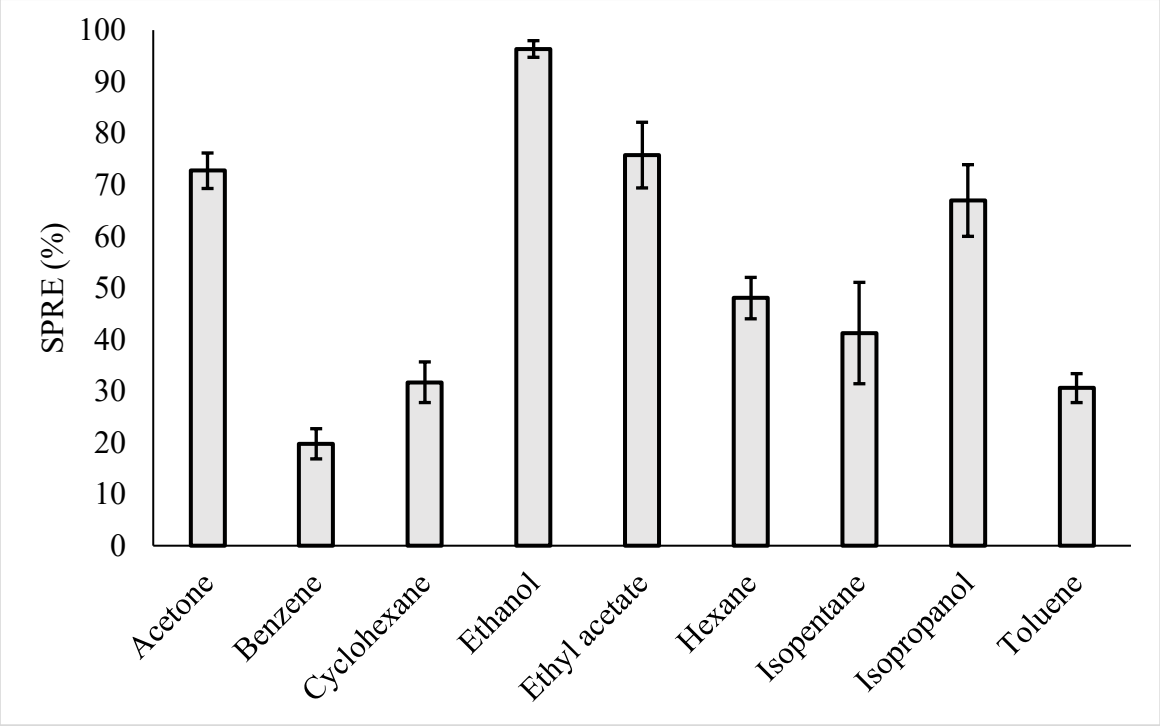

Figure 7. Average SPREs of an active green wall across different VOCs. Error bars represent standard error of the mean (*n*=10).

Table 4. 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*

2.4.2 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 5). 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 5. Regression coefficients of VOC SPRE predictive model. *B* = unstandardized beta*; SE* of *B* = the unstandardized error of the unstandardized beta; β = the standardised beta.

	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.

2.4.3 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., 2017a) 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.

2.5 Acknowledgements

T. Pettit is supported by an Australian Government Research Training Program Scholarship.

P.J. Irga is supported by the UTS Chancellor's Postdoctoral Research Fellowship scheme, facilitated through The Centre for Technology in Water and Wastewater.
Declarations of competing interests: none

Preface: Chapter 3

The plant growing medium in an active botanical system has many of the properties of a filter. Unlike potted-plant systems, where PM removal is limited to deposition on plant foliage, active systems pull air through the plant growth substrate, which can filter out a proportion of the PM from the air stream through various, undescribed physio-chemical mechanisms (Irga et al., 2017b).

As these systems can clean a comprehensive range of pollutants, including PM and VOCs, it is feasible that they may be implemented in indoor environments to reduce pollutant concentrations in the ambient air. Several studies have measured the SPRE or clean air delivery rate (CADR) of active green walls based on certain pollutants (Darlington et al. 2001; Irga et al. 2017b; Torpy et al. 2018) with results suggesting that these systems have the potential to make functional reductions in ambient PM and VOC concentrations. However, there is a clear need for research that quantifies the *in situ* PM and VOC removal capacity of such systems to provide proof-of-concept. Furthermore, before this technology can be universally applied as an air cleaning solution, it needs to be tested against existing technologies that are used to clean ambient air in highly polluted environments, where users are likely to benefit the most from such technologies.

This experiment represents two pilot-scale field studies to systematically compare, under realistic *in situ* conditions, the quantitative capacity of phytoremediation technologies to remove generated doses of PM and VOCs.

The work presented in this chapter has been published in the Journal *Air Quality, Atmosphere and Health*:

Pettit, T., Irga, P.J. and Torpy, F.R., 2019. The *in situ* pilot-scale phytoremediation of airborne VOCs and particulate matter with an active green wall. *Air Quality, Atmosphere & Health*, *12*(1), pp.33-44.

This chapter is written verbatim to this article.

Author Contributions:

Thomas Pettit: Conceptualization, methodology, analysis, investigation, resources, data curation, original draft preparation, review and editing. **Peter Irga:** Investigation, resources, review and editing, supervision, project administration. **Fraser Torpy:** Conceptualization, methodology, review and editing, supervision, project administration.

Chapter 3
3. The *in situ* pilot-scale phytoremediation of airborne VOCs and particulate matter with an active green wall

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3.1 Abstract

Atmospheric pollutant phytoremediation technologies, such as potted-plants and green walls, have been thoroughly tested in lab-scale experiments for their potential to remove air pollutants. The functional value of these technologies, however, is yet to be adequately assessed *in situ,* in 'high value' environments, where pollutant removal will provide the greatest occupant health benefits. Air pollution in countries such as China is a significant public health issue, and efficient air pollution control technologies are needed. This work used pilot-scale trials to test the capacity of potted-plants, a passive green wall and an active green wall (AGW) to remove particulate matter (PM) and total volatile organic compounds (TVOCs) from a room in a suburban residential house in Sydney, Australia, followed by an assessment of the AGW's potential to remove these pollutants from a classroom in Beijing. In the residential room; compared to potted-plants and the passive green wall, the AGW maintained TVOCs at significantly lower concentrations throughout the experimental period (average TVOC concentration 72.5% lower than the control), with a similar trend observed for PM. In the classroom, the AGW reduced the average TVOC concentration by ~28% over a 20 min testing period compared to levels with no green wall and a filtered HVAC system in operation. The average ambient PM concentration in the classroom with the HVAC system operating was 101.18 $\mu g/m^3$, which was reduced by 42.6% by the AGW. With further empirical validation, AGWs may be implemented to efficiently clean indoor air through functional reductions in PM and TVOC concentrations.

Keywords: active green wall; botanical biofilter; living wall; indoor air quality; potted plant; green infrastructure.

3.2 Introduction

The indoor air quality of urban non-occupational environments, such as residences, schools, child-care facilities and nursing homes, is becoming an important public health issue, as populations susceptible to health effects from air pollutant exposure, such as children and the elderly, spend a considerable amount of time within these settings (Al-Hemoud et al. 2018). Urban areas are often associated with poor air quality (Gulia et al. 2015; Han et al. 2014), as the activities in these areas promote the generation of airborne pollutants, primarily particulate matter (PM) (Guo et al. 2010; Jamriska et al. 2000), which can penetrate and contaminate the urban indoor environment (Perez et al. 2016). Additionally, a range of common household and office materials and products, such as building materials, furnishings, plastics and solvents can emit volatile organic compounds (VOCs) (Aini Jasmin et al. 2012; Dela Cruz et al. 2014a); thus allowing the potential for these pollutants to accumulate within the indoor environment (Weschler 2009). For many VOCs, such as benzene and poly-aromatic hydrocarbons, the World Health Organisation recommends no safe level of exposure (World Health Organization 2010). High concentrations of VOCs are most commonly treated by flushing them from the indoor environment with outdoor air from which a proportion of the PM is filtered as it enters the building. This approach is problematic in urban areas with highly polluted outdoor air, as filter efficiency is highly variable, especially for small particles (Ren et al. 2017).

While poor air quality remains a global issue (World Health Organization 2014), cities within China have experienced unprecedented urban growth in terms of scale and speed. This has led to a corresponding decline in air quality across many of China's cities (Liu et al. 2018), where indoor air pollution mitigation strategies have focused on PM reduction primarily through ventilation filtration technology integrated within heating, ventilation and air conditioning (HVAC) systems (Liu and Liu 2005). Despite the considerable energy that this technology requires (Liu et al. 2017), the success of this approach has been limited (Ren et al. 2017). Additionally, in situations with limited ventilation rates, VOC concentrations are often problematic, as VOC concentration has been

shown to negatively correlate with building ventilation (Cheng et al. 2016a). Thus, the prevalence of high concentrations of VOCs is becoming an important public health issue in China (Clean Air Alliance of China 2017).

Within China, schools represent a quantitatively important indoor environment, with >90 million students across more than 250,000 primary schools (Hou et al. 2015). Children are highly susceptible to the adverse health effects from air pollutant exposure due to their relatively higher ventilation rates and immature immune systems (Buka et al. 2006). In addition to direct health effects, poor indoor air quality affects student learning performance (Bakó-Biró et al. 2012). Mechanical ventilation systems are not commonly used in public primary schools in China and consequently ambient outdoor particles and other outdoor air pollutants are introduced into the indoor environment as 'fresh air' is brought in through natural ventilation to flush out indoor generated VOCs (Peng et al. 2017). It is thus clear that comprehensive indoor air cleaning technologies that can reduce the high concentrations of ambient particles and VOCs in an energy efficient manner will have high public health and environmental value.

As a possible solution to mitigate poor indoor air quality, a large body of research has tested the capacity of potted-plants to clean VOCs from the indoor environment (Aydogan and Montoya 2011; Dela Cruz et al. 2014a; Dela Cruz et al. 2014b; Hörmann et al. 2017; Hörmann et al. 2018; Irga et al. 2013; Orwell et al. 2004; Sriprapat et al. 2014b; Sriprapat and Thiravetyan 2013; Teiri et al. 2018; Treesubsuntorn et al. 2013; Treesubsuntorn and Thiravetyan 2012; Wood et al. 2002). The use of plants for indoor air remediation offers an economical and sustainable departure from conventional techniques such as adsorption filters, photocatalytic oxidation purifiers, and ozone generators, that are often expensive, remove a constrained range of VOCs, and can produce harmful by-products (Irga et al. 2018). However, the existing experiments on potted-plant VOC removal have most commonly been limited to laboratory-scale chambers, and despite the high VOC removal rates documented in these studies, it has been proposed that their removal rates *in situ* may be of lower practical value (Irga et al. 2013; Llewellyn and Dixon 2011), as the pollutant removal rate is dependent upon the rate at which polluted air can diffuse to the active components of the potted-plant microcosm.

Active botanical biofiltration involves the application of active airflow, through mechanisms such as low power fans, to draw polluted air towards the plant's foliage and substrate. When applied in a green wall format, it is likely that the VOC removal rates of these systems will be significantly higher than those of potted-plants due to the increased rate

at which pollutants can be delivered to the system and the increased planting density per unit of floor area possible with these systems (Torpy et al. 2015). Several studies have tested the single pass removal efficiencies (SPREs) of these systems to remove PM (Irga et al. 2017b; Pettit et al. 2017) and a range of VOCs (Darlington et al. 2001), with results that suggest that active green walls have a high air cleaning potential. There is, however, a lack of empirical, *in situ* assessments of air pollutant removal for active green walls, a necessary requirement before this technology can be confidently recommended for functional use (Pettit et al. 2018a). Furthermore, before this technology can be universally applied as an air cleaning solution, it needs to be tested against existing technologies that are used to clean the air of ambient pollutants.

The current work represents two pilot-scale field studies to systematically compare, under realistic *in situ* conditions, the capacity of major phytoremediation technologies to quantitatively remove generated doses of PM and VOCs. As different biofilter designs, such as green walls and potted-plants, generally use different plant species, plant species typical of each biofilter design were chosen to ensure that the biofilters were representative of their real world application, thus allowing accurate comparisons of the *in situ* air cleaning abilities of different biofilters. The work therefore assesses whether botanical biofiltration designs may be a viable means to realistically clean indoor air. To provide practical outcomes, each biofilter design is representative of its real world application, with plant species typical of each biofilter design used in that application.

3.3 Methods

3.3.1 Field study 1: assessment of different forms of phytoremediation technologies

Phytoremediation technologies and room description

This experiment was conducted in a room within a residential building located in a suburban area of Sydney, Australia. The room had a floor area of 8.75 m^2 and a total volume of 22.70 m^3 (Figure 8). There was no HVAC or mechanical ventilation serving this room, and the door and windows were closed to create a sealed environment, representative of the conditions that would be normal in hot or cold seasons in this region. Nonetheless, a control treatment (described later) was used to eliminate any effects associated with the distribution and concentration of pollutants within the test space that might otherwise confound comparisons as per the conservation of mass model (Dockery and Spengler 1981). Experiments were conducted when the room's ambient temperature was between 20 and 24 °C. A ceiling fan in

the room operated at a low setting for all trials to promote the distribution and homogenization of pollutants in the room, and to provide turbulence within the experimental space, as would be experienced in an occupied room. Indoor light levels were provided by an indoor compact fluorescent lamp and were consistent at the midpoint of the green wall surface of 9 μmol m^{-2} s^{-1}

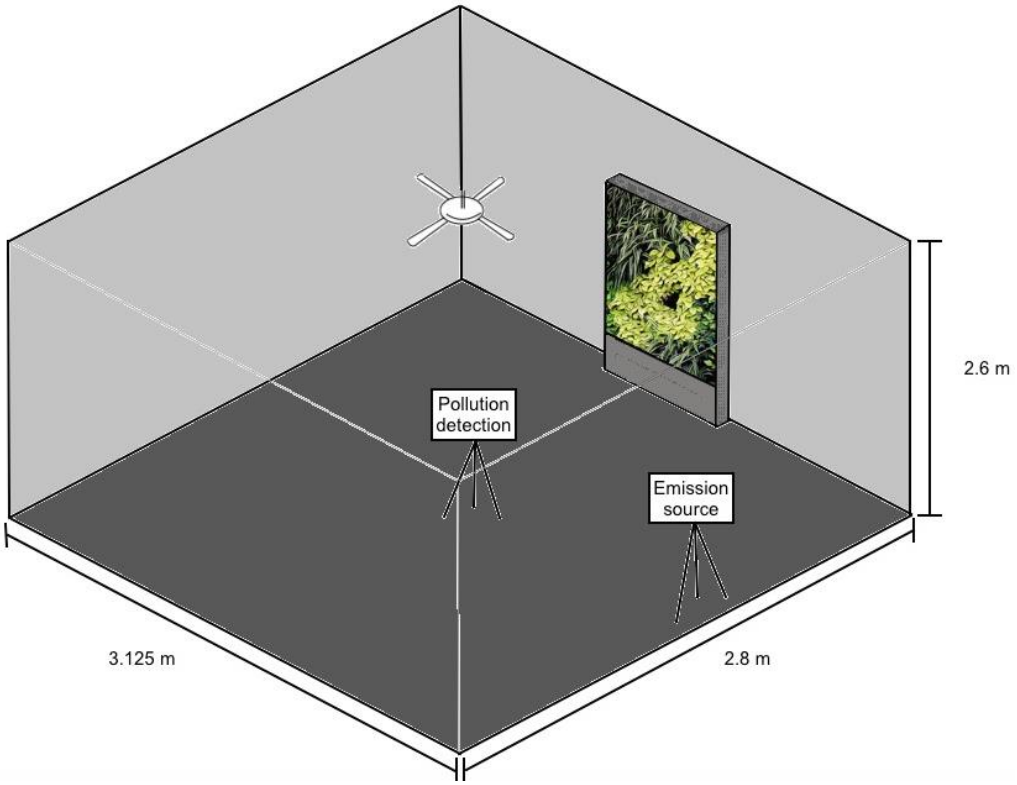

Figure 8. Diagram of the suburban residential test room. The biofilter was located in the centre against the long wall. Emission source was located in the centre against the short wall. Pollution detectors were located in the centre of the room. A ceiling fan was in the centre of the ceiling.

Three different types of botanical biofilters were tested in this room for their capacity to filter VOCs and PM.

Potted-plants: For each experimental replicate, three potted-plants (250 mm internal diameter, with the substrate comprised of commercial potting-mix) were placed in the room, representing a commonly-used planting density for a room of this size. Plant species used in the potted-plant treatment are species that are commonly grown in indoor environments; thus the plant species used in each trial consisted of one *Ficus lyrata* (fiddle leaf fig), one *Schefflera arboricola* (dwarf umbrella), and one *Philodendron tatei* ('Rojo Congo').

Passive green wall: The system tested was as previously described (Torpy et al. 2017). This system consisted of a 1.5 m2 vertical green wall made up of six 0.25 m2 modules (Junglefy Pty Ltd; Sydney, Australia), with each module having 16 holes from which plants can grow; thus the passive green wall contained 96 plants grown in a vertical alignment. The plant growth substrate in this system was comprised of coir fibre. The plant species used were *Chamaedorea elegans* (6 plants), *Epipremnum aureum* (34 plants), *Ficus lyrata* (4 plants), *Neomarica gracillis* (5 plants), *Peperomia obtusifolia* (10 plants), *Spathiphyllum wallisii* (20 plants) and *Syngonium podophyllum* (18 plants), representing 6%, 34%, 4%, 5%, 10%, 21%, and 19% of the total plants respectively. Different plant species amongst the different treatments was seen as an inherent trait within each biofilter design and was thus left out of analyses, allowing direct comparisons of different biofilters representative of their real world application. Furthermore, the gravitropic effects on the growth and health of green wall species (Burritt 2013), do not allow potted-plant species to be used interchangeably with green wall species. As with the potted-plant treatment, this system had no active airflow, and was thus dependent upon diffusion for pollutant transfer, with assistance provided by the ceiling fan.

Active green wall: The system used (The Junglefy Breathing Wall, Figure 9) was as described in Pettit et al. (2017). To allow direct comparison with the passive wall, the active green wall was also a 1.5 m2 vertical system made up of six 0.25 m2 modules. The modules were attached to a plywood box forming an external plenum (depth = 100 mm; volume = 0.18 m3). Two 240 V AC fans (DETA, 200 mm dia., 28 W), each with an open air volumetric flow rate of 320 m3·h-1, drew ambient air into the external plenum which was then forced through 75 mm ports on the rear face of each module. Within each module, the air was distributed evenly within an internal plenum (20 mm depth), where it then flowed through the plant growth substrate and foliage before returning to the ambient air. Both green wall designs used a substrate consisting of coconut husk, with a water holding capacity of 41.03 ± 1.26 % and an air filled porosity of 53.27 ± 0.98 % (Pettit et al. 2018b). This substrate has been used in other active green wall experiments, and is favourable as it does not contribute to airborne aeromycota (Irga et al. 2017a). The active green wall was comprised of similar plant species to the passive green wall. In both the passive and active green wall treatments, the location of each planted module within the frame structure was randomised amongst replicates to eliminate any bias associated with the orientation of the plant species within the wall.

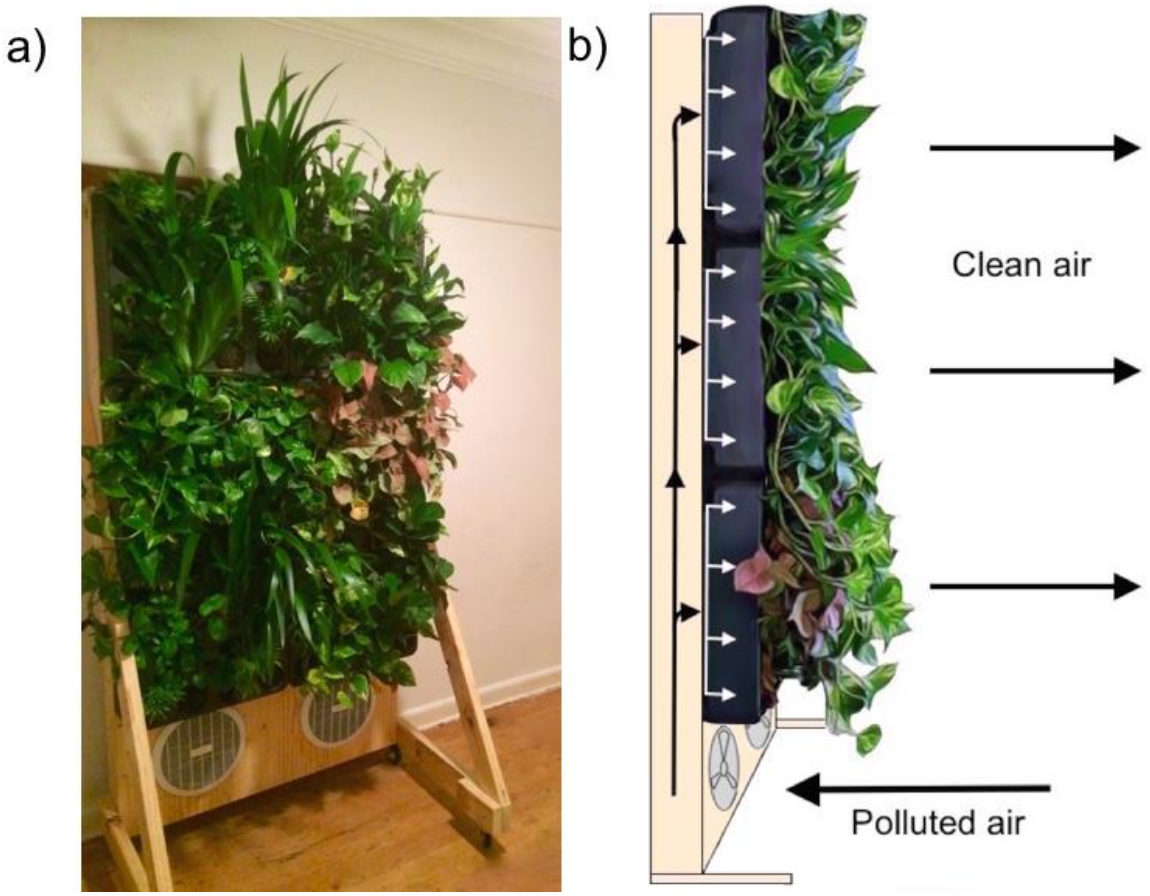

Figure 9. a) The active green wall within the tested residential room. b) Diagram of the active green wall system used in this study. Ambient air is taken in through the fans and pushed upwards through the external plenum. The air passes through an inlet into each green wall module where an internal plenum within the modules further distributes the air before it passes through the substrate and foliage.

Procedural control: As the active green wall treatment utilised mechanically-activated airflow, a procedural control was used to assess whether the influence of air movement facilitated by the use of the device affected the concentration of pollutants detected by the sensors. The procedural control consisted of the external plenum with the two fans operating, but with no green wall modules attached to it; thus mimicking the airflow pathway of the active green wall but without passing the air through any biofiltration matrix.

3.3.2 Pollution generation and sampling procedure

Treatments detailed in *Section 3.3.1* were tested for their capacity to phytoremediate a generated dose of VOCs and PM.

The ambient concentration of TVOCS was negligible ranging from 0-25 ppb Thus, to avoid the release of toxic VOCs in the residential house, lavender oil was used as a surrogate VOC. While lavender oil is usually not regarded as toxic, Chiu et al. (2009) observed that at high ambient temperatures (40 °C), it can emit a range of harmful VOCs such as toluene and *o*-xylene, while Su et al. (2007) report that linalool, D-limonene and terpinene-4-ol are emitted from lavender oil.

VOCs were generated by pipetting 100 μL of lavender oil (Thursday Plantation; Queensland, Australia) onto a 113.1 cm^2 sheet of 536:2012 80 gsm paper. The saturated paper was then suspended 10 cm in front of an axial impeller (FANTECH TEF-100 fan 16W) that was housed on a stand located at one end of the room, keeping the fan and paper 90 cm off the ground. This produced a TVOC concentration gradient in the room that rose from 0 ppb to an average maximum concentration of 120 ppb, representing a maximum concentration similar to the Australian National Health & Medical Research Council's recommended TVOC limit of ~125 ppb (Haag 2005).

A photoionization detector (PID; ppbRAE 3000, RAE Systems, San Jose, CA, USA; detection resolution of 1 ppbv of VOC concentrations ranging from 1 ppbv to 10,000 ppbv), located in the centre of the room on a 90 cm high stand, was used to measure the concentration of TVOCs over the length of each 2200 second (36.66 minute) trial. Pilot data indicated that this was the time required to remediate the entire room of the generated VOC dose or for VOC concentration to asymptote, thus the trial period was applied to all experiments thereafter.

An independent series of trials were performed to assess the capacity of the three phytoremediation technologies to filter suspended PM. In these trials, PM was generated by burning a widely-available incense stick (Meditation incense; S.D. Lovely Incense, Nepal; composition: red sandalwood 20%, sandalwood 15%, spoonpati 10%, Rhododendron 10%, medicinal plants 25%, natural glue 20%). Burning incense is a known particle emission source (Chang et al. 2007; Jetter et al. 2002; Ji et al. 2010; Lung and Hu 2003; See et al. 2007) and has been used previously for indoor plant PM remediation experiments (Panyametheekul et al. 2018). For each trial, a single incense stick was burned for approximately 5 minutes until the room's TSP concentration reached 400 $\mu g \cdot m^{-3}$; at this point, the incense was extinguished and the room's concentration of total suspended particles (TSP) was measured for the following 1900 seconds (31.66 minutes). Although PM concentrations at this level are not usually encountered in indoor environments (however see Huang et al. 2017; Shi et al. 2008; Tian et al. 2009), a high PM dose was selected as the

starting concentration to assess how effectively this system can filter PM at levels that have been recorded in Beijing's urban areas on poor air quality days (e.g. TSP = ~400 $\mu g \cdot m^{-3}$ (US Environmental Protection Agency 2016)); an essential function if these systems are to be a room's primary air cleaning device.

A DustTrak II 8532 nephelometer (TSI Incorporated, Shoreview, Minnesota, USA; detection limit: 0.01 mg/m^3; resolution 0.01 mg/ m^3) was used to log the concentration of TSP in each trial. The locations of the PM generation and PM sensor in the room were the same positions as for the VOC generator and sensor respectively.

PM and VOC treatments were replicated eight times each for the potted-plant, passive green wall and active green wall treatments, and also the procedural control along with an empty room trial.

Experimental replication was achieved with time-for-space substitution, with a period of ventilation between samples, thus eliminating carry over effects generated from previous tests. All experimental air samples were taken with the door closed and sealed.

3.3.3 Data analysis

For each VOC trial, the VOC concentration was plotted as a function of time, and the corresponding area under the curve (AUC) was used as a response variable for a single factor ANOVA (IBM SPSS Statistics Ver 21) to test the mean differences amongst treatments. As the PM trials used an initial 'spiked' generation of particles as opposed to a continuous emission of pollutants, the area under the decay curve of TSP as a function of time was used as a response variable in a single factor ANOVA. Pairwise differences were identified using Tukey's HSD test where required. The clean air delivery rate (CADR) was calculated by using the static room test decay curves by taking the log loss function of particle concentration corrected for the rate of natural decay, and factoring in the test room size.

3.3.4 Field study 2: Active green wall and HVAC system trials

Room description

Before active botanical biofiltration can be applied universally as an air cleaning system, it is important to assess the pollutant remediation effects of these systems in high ambient pollution environments, and to compare these to current technologies such as HVAC systems.

Trials were conducted in a secondary school classroom located in Chaoyang District Beijing, China. The room's ventilation was served by a compartmentalised HVAC system that had 3 influent and 3 effluent ducts providing 2.5 air exchanges per hour. This system included a filter with a MERV H13 rating that filtered out a proportion of the outdoor ambient particles before they enter the indoor environment. As is commonplace in most buildings, this HVAC system removes VOCs from the room's atmosphere solely by flushing with filtered outdoor air. The room had a floor area of 40.07 m^2 and a volume of 120.2 m^3. A pedestal fan was placed in the corner of the room to ensure that air pollutants were distributed homogenously throughout the room. Whilst a fan would not normally be used in the room, occupant movement would lead to significant air mixing; thus the fan does not represent abnormal circumstances. Experimental replication was again achieved with time-for-space substitution, as described in *Section 3.3.2*.

3.3.5 Ambient air pollutant sampling

Ambient samples of suspended PM and TVOCs were taken across eight 30-minute trials in the room prior to active green wall installation. In these samples, the HVAC system was operating, thus this data reflects the concentration of pollutants in the room's normally operational state.

The mass concentration of total suspended particles (TSP) was recorded with a laser nephelometer (DustTrak II 8532), while a second 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 / ft3 at 5% coincidence loss) was used to calculate the size distribution and average concentration for a range of independent particle size fractions. The concentration of TVOCs was recorded with a PID (ppbRAE 3000).

3.3.6 Active botanical biofilter air pollutant sampling

The active green wall was constructed from 36, 0.25 m2 modules, creating a wall with a surface area of 9 m2 (Figure 10). These modules, which were of the same type as used in the residential room trial, contained mixed plant species, including *Epipremnum aureum*, *Nephrolepis exaltata*, *Peperomia obtusifolia*, *Schefflera arboricola* and *Spathiphyllum wallisii*. The approximate percentages of each species growing in the green wall were 40 %, 3 %, 10 %, 5 %, 42 % respectively. The modules were attached to a plywood box that was

separated into 3 180 mm deep plenums, with each plenum containing 12 modules. Three 12 V DC fans, each with an open air volumetric flow rate of 185 m3·h-1, drew ambient air from ~40 cm above ground level into each plenum, which was then forced into the rear face of the modules, flowed through the plant growth substrate and foliage before returning to the ambient air. The volumetric flow rate through the green wall was 283.53 m3·h-1, representing 2.36 air changes per hour for the test room.

Once the active botanical biofilter was installed in the room, the room's HVAC system was turned off and the ducting sealed with plastic sheets to ensure no air exchange between the room and the HVAC ducting. Each trial that tested the active green wall (n=3) was conducted for 20 minutes, which was the time taken for the TSP concentration in the biofilter treatment to approach an asymptote. The concentration of TVOCs and the size distribution and concentration of particles were recorded as previously outlined. All samples were taken from a distance of ~2 m away from the active botanical biofilter and ~1 m above the ground.

Figure 10. The active green wall used to filter ambient PM and VOCs installed in a classroom in Beijing, China.

3.3.7 Data analysis

Two separate t-tests were used to compare the mean concentrations of TSP and TVOC between the ambient HVAC system and active green wall treatments. Data was analysed using IBM SPSS Statistics Ver 21.

3.4 Results

3.4.1 Field study 1: Sydney Australia suburban residential

A one-factor ANOVA revealed significant differences in the concentration of TVOCs amongst treatments (Figure 11; d.f. = 4 and 36, $F = 89.198$, $p = 0.000$). Subsequent Tukey's HSD *post hoc* tests found that the active green wall treatment was significantly different to all of the other treatments ($p = 0.000$ for all comparisons), while no other significant differences were found amongst any of the other treatments. The active green wall led to considerably lower concentrations of TVOCs throughout the experimental period (Figure 11), in which the active green wall produced an average time-weighted TVOC concentration 72.5% lower than the TVOC concentration present in the empty room.

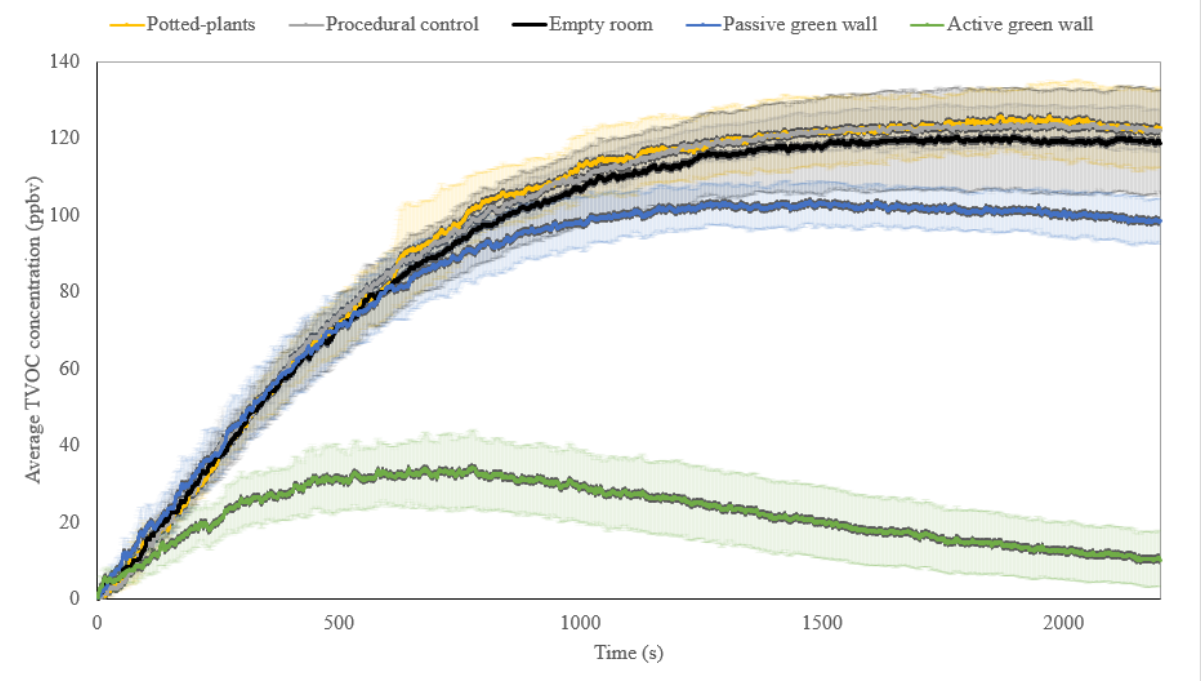

Figure 11. The average concentration of TVOCs for each treatment. Error bars represent the standard error of the mean (*n*=8).

There were significant differences amongst treatments in the AUC of TSP concentration as a function of time (Figure 12; ANOVA: d.f. = 4 and 36, F = 34.970, p = 0.000). Tukey's HSD *post hoc* tests indicated that AUC of TSP in the active green wall treatment was significantly lower than all other treatments ($p < 0.000$ for all comparisons), while the passive wall had a significantly lower AUC than then empty room (p = 0.000) and the potted-plant treatment (p = 0.004). The total decay rate constant for the active green wall treatment was 4.53 x 10^{-4} s^{-1} and the CADR calculated from the decay curves was 21.98 m^3/h.

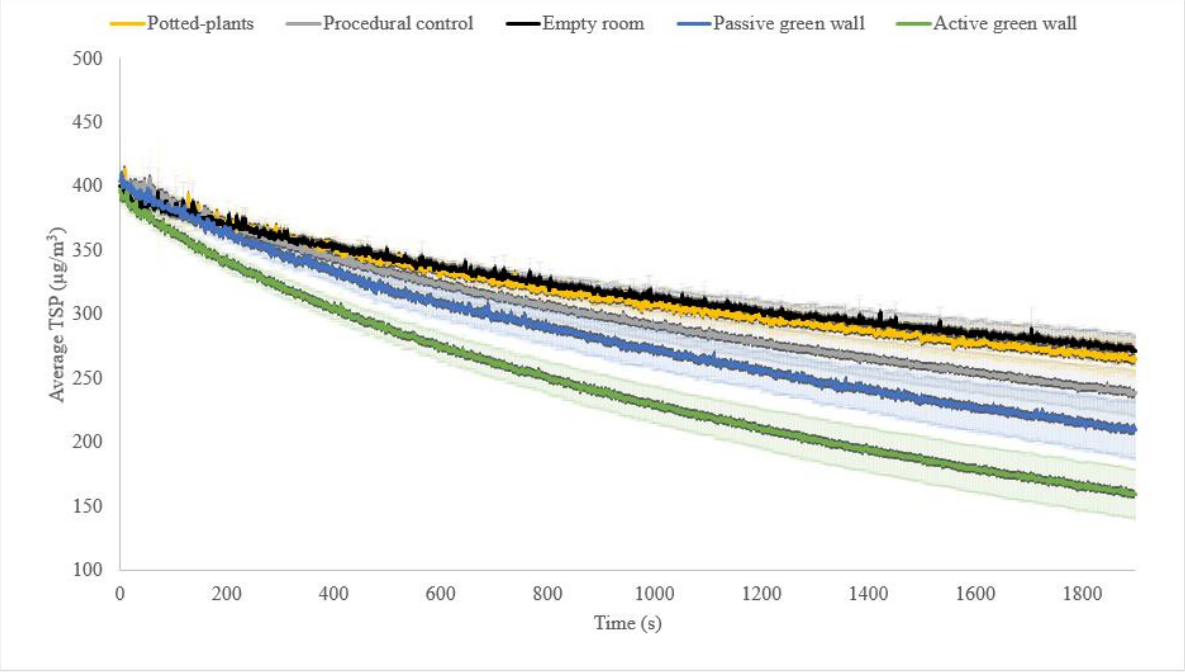

Figure 12. The average concentration of TSP over the trial time. Error bars represent 95% confidence intervals.

3.4.2 Field study 2: Beijing, China urban classroom trial

Prior to the installation of the active green wall, the average concentration of TVOCs within the room with the HVAC system operating was 300 ± 3.04 ppbv, and this concentration was relatively stable throughout the sampling period. Following the installation of the active green wall, the average concentration of TVOCs was reduced to 217 ± 2.00 ppbv over the 20 min trial period, representing a reduction of ~28%. The average concentration of TVOCs was significantly lower in the active green wall treatment compared to the HVAC ambient air treatment (t = 3.311, d.f. = 7, p = 0.011).

The average ambient concentration of particles (as TSP) in the room with the HVAC operating was 101.18 ± 0.29 $\mu g \cdot m^{-3}$. The mass concentration of particles was distributed relatively evenly over a range of different particle size fractions (Figure 13). Once the active green wall was installed, the mass concentration of all particle sizes was reduced, with relatively rapid removal (Figure 14). The mass concentration of TSP in the room was reduced by 42.6% by the active green wall relative to the building HVAC system over 20 minutes. A t-test revealed that the difference in the TSP concentration between the HVAC ambient air treatment and the active green wall treatment was statistically significant ($t = 2.679$, d.f. = 7, $p = 0.037$).

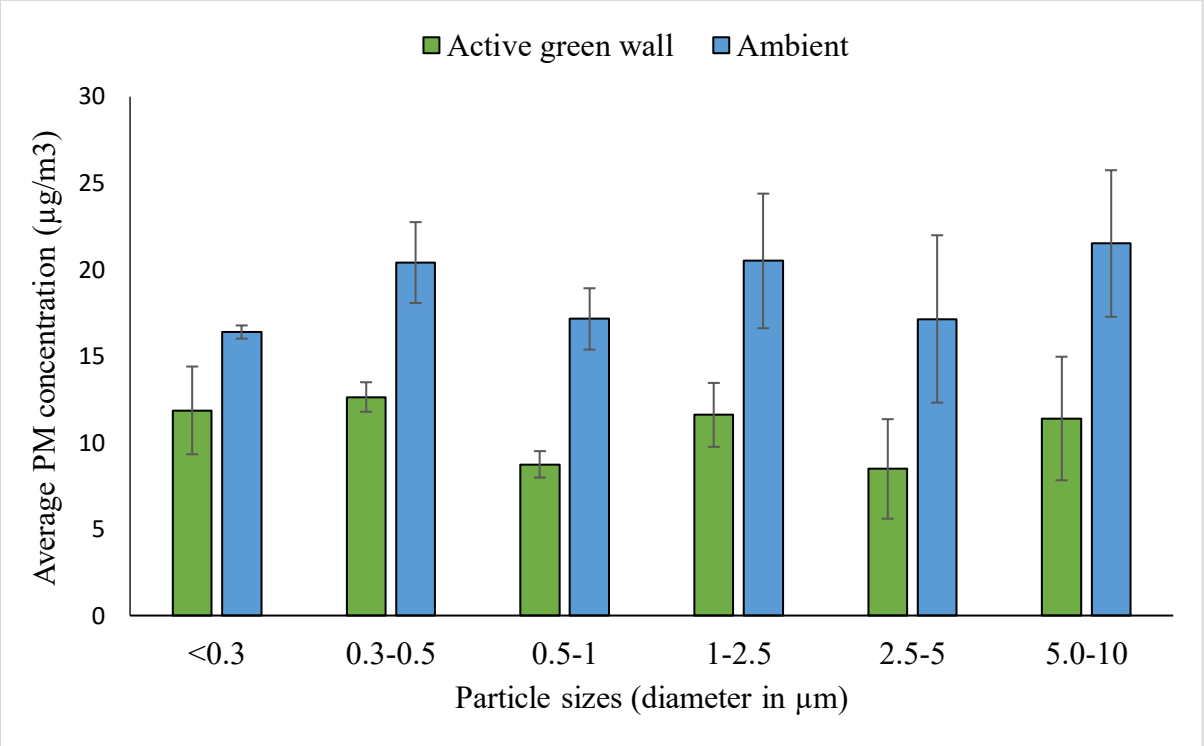

Figure 13. The average particle size fraction concentrations for ambient HVAC and botanical biofilter treatments. Error bars represent standard error of the mean (control: n= 8; active green wall: n=3).

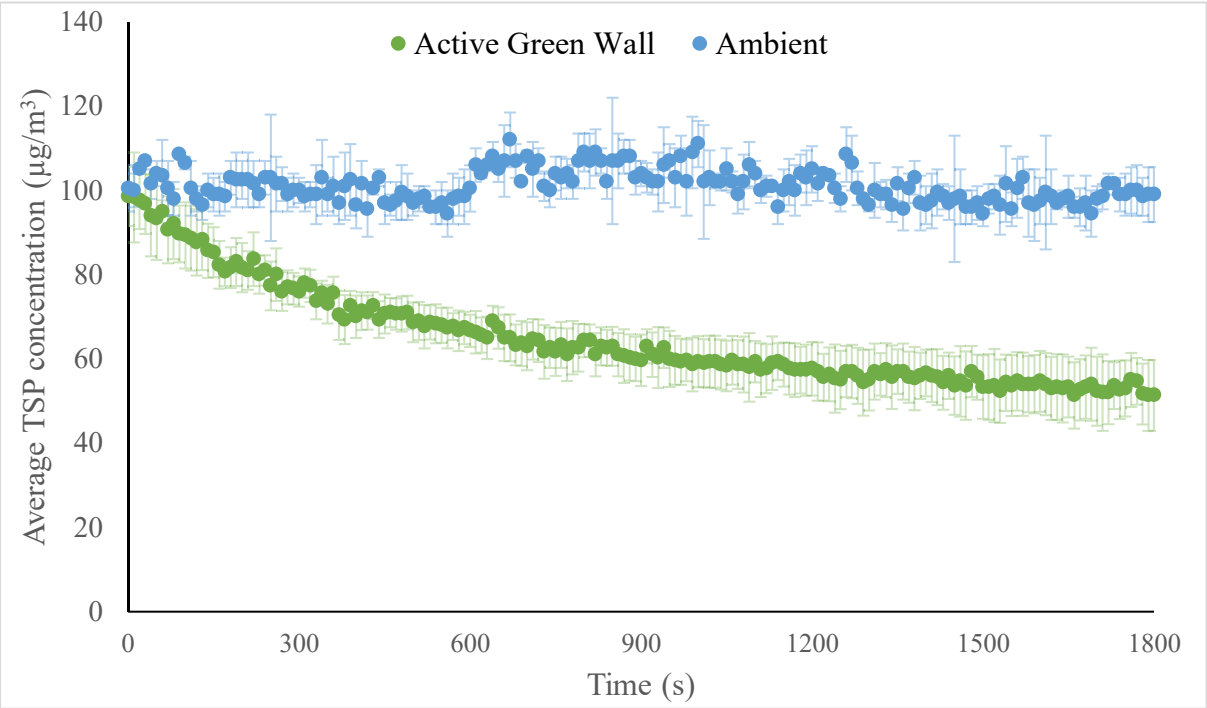

Figure 14. The average concentration of ambient total suspended particles over a 20-minute sampling period with and without an active green wall biofilter present. Error bars represent 95% confidence intervals (control: *n*= 8; active green wall: *n*=3).

3.5 Discussion

The current study represents the first work conducted to compare the *in situ* VOC and PM removal capabilities of the major phytoremediation technologies to add further evidence to support the use of these systems as plausible solutions for managing indoor air quality. Several previous studies have assessed the capacity of potted-plants (or parts of potted-plants) to adsorb and degrade VOCs (Aydogan and Montoya 2011; Hörmann et al. 2018; Irga et al. 2013; Kim et al. 2016; Sriprapat et al. 2014b; Sriprapat and Thiravetyan 2013; Sriprapat and Thiravetyan 2016; Treesubsuntorn et al. 2013; Treesubsuntorn and Thiravetyan 2012), while a lesser number of studies have measured the effects that potted-plants have had on ambient concentrations of VOCs in realistically sized rooms (Wood et al. 2006), and only a very limited number of studies have demonstrated VOC removal by active or passive green walls *in situ* (Darlington et al. 2001). The current work has shown that in a small airtight room with elevated VOC concentrations, a reasonable density of potted-plants or a reasonably sized passive green wall do not provide substantial reductions in the concentrations of VOCs

within a relatively short time period (i.e. ~37 minutes in this experiment). Alternatively, the active green wall effectively reduced the concentration of VOCs to levels that are unlikely to have health effects. Towards the end of the trial period, the active green wall began to remove VOCs at a faster rate than they were emitted, so that the concentration of VOCs had almost returned to their starting concentration. This comparison suggests that active green walls can provide practical reductions in VOC concentrations, while other forms of phytoremediation system may not provide equally rapid reductions. While previous *in situ* studies have suggested that potted-plants can reduce in-room VOC concentrations over longer time periods (e.g. 24 h (Wood et al. 2006)), this performance did not extend to the short duration study presented here. Although some laboratory scale experiments have shown that plant tissues are capable of removing VOCs from chambers over several hours (Liang et al. 2018; Parseh et al. 2018; Su et al. 2019), the relatively short trial time in this experiment suggests that VOCs were most likely removed through adsorption processes as opposed to microbial degradation.

Orwell et al. (2004) found that the substrate microbial community's VOC removal efficiency improves with repeated exposure to multiple doses, and it is possible that considerably lengthening the experimental trial period, or testing the VOC removal of repeated VOC doses, may have provided improved removal rates. Alternatively, Inouye et al. (2003) has shown that lavender oil may inhibit the growth of microorganisms, and thus the use of lavender-derived VOCs may have differentially affected the removal rates observed if longer trials were performed. In any case, the demonstration of fast-response VOC removal by the active green wall is indicative of considerable practical value, as the system has the capacity to remove VOCs as they are emitted, maintaining low room VOC concentrations without the need for a lengthy adaptation period where VOCs in an indoor space would still be at high levels.

The accumulation of particles on the plant foliage of passive green walls (Perini et al. 2017; Weerakkody et al. 2017; Weerakkody et al. 2018a; Weerakkody et al. 2018b) and potted-plants (Gawrońska and Bakera 2015) has been noted as a promising potential means for the removal of atmospheric PM. Although it is clear that plant foliage can provide PM deposition sites, it has previously been difficult to determine if this quality corresponds with functional reductions in ambient indoor PM concentrations. The current results comparing TSP removal efficacy across different phytoremediation treatments suggest that passive green walls can reduce the PM concentration of the surrounding air. Furthermore, the active green wall provided significantly lower concentrations of TSP than all other treatments, which is

unsurprising as this treatment uses active airflow to treat a greater quantity of polluted air, thus having both the capacity to capture PM on the plant's foliage and to filter PM through the substrate matrix. Importantly, this study only made these comparisons under a relatively high initial PM concentration in a relatively small room, and the removal capacity of such systems may be different under different conditions. Given these findings, it is thus essential that subsequent experiments measure ambient air pollution reductions associated with botanical biofilters to gauge their potential to functionally enhance air quality, rather than to only measure variables that may be associated with providing cleaner air such as particle accumulation.

As both passive and active green walls had effects on the ambient PM concentration in this study, it is likely that a proportion of the PM is filtered by the plant's foliage in both wall designs. In this case it is critical to consider the planting design within the wall and how vegetation 'topography' may influence PM removal (Weerakkody et al. 2019). Topographic heterogeneity in the vegetation form in passive green walls has been shown to accumulate greater amounts of traffic-derived PM in outdoor environments than green walls comprised of plants with more consistent topography (Weerakkody et al. 2019). It is unknown how interspecies variation in plant structure and planting design may have influenced PM filtration in this study as these aspects have not been tested for active biofilters, and this remains an important consideration in further studies conducted in indoor environments. In addition to plant topography, leaf traits associated with interspecies variation are an important consideration for both the removal of PM (Weerakkody et al. 2018a; 2018b) and VOCs (Irga et al. 2019)

In the second field study located in China, the active green wall outperformed the tested HVAC system in terms of both VOC and PM mitigation. The MERV H13 filter used in the HVAC treatment has particle size removal efficiencies of >90 % for particles with diameters of 1-10 µm (ASHRAE 2007), and is typically applied in "superior commercial buildings, smoke removal systems and hospitals" (ASHRAE 2007). These metrics notwithstanding, the active green wall system outperformed the HVAC treatment by significant margins for all particle size fractions. The high filtration performance of the active green wall indicates a high air cleaning capacity, and suggests that it may have considerable practical potential. Importantly, these two technologies filter ambient particles with different airflow pathways. HVAC systems most frequently filter particles from outdoor air as the airstream enters the building, while the active green walls (in the form used here) filtered recycling ambient air from within the building. While this characteristic of the active green

wall negates the requirement to temperature modulate outdoor air to the desired indoor temperature as is necessary for the HVAC, the overall performance of the system relies on being able to draw air from all regions of the indoor space in which it is situated. Thus, further studies will be needed to understand the airflow dynamics of active green walls in differently sized and shaped rooms, and how this interacts with biofilter dimensions with fan mass airflow rates.

The concentration of VOCs was significantly reduced in the active green wall treatment when compared to the HVAC system treatment. This is a differentiating function of active botanical biofilters, as HVAC systems simply reduce high concentrations of indoor-generated VOCs by flushing with outdoor air. The observed capacity to mitigate high *in situ* concentrations of both PM and VOCs lends support to Darlington et al.'s (2001) proposal that air pollutants can be treated by recirculating and treating the air within a building, thus partially eliminating the energy intensive process of flushing the building with temperature modulated, filtered outdoor air to control problematic concentrations of PM and VOCs. Increasing concentrations of CO_2 resulting from occupant respiration, however, remain difficult for green wall technology to treat with practical removal rates (Torpy et al. 2017), as CO_2 removal is dependent on plant photosynthetic activity; a process largely governed by photon flux density in the wavelength ranges used by plants for photosynthesis, which are typically low in indoor environments (Safe Work Australia 2011). As such, further development is needed before botanical systems can be effectively implemented to offset high CO_2 concentrations in addition to the demonstrated effects on PM and VOCs. Furthermore, while current research suggests that active biofilters do not emit bioaerosols in harmful concentrations (Irga et al. 2017a; Mallany et al. 2002; Zilli et al. 2005), further testing is needed to ensure that these findings remain valid across different indoor environments.

A number of previous studies have assessed the VOC single pass removal efficiencies (SPRE) and calculated clean air delivery rates for phytoremediation technologies. Torpy et al. (2018) tested a botanical biofilter that had the same planted surface area as the active green wall used in the residential experiment in the current study. They found that their active botanical biofilter could remove ~57% of methyl ethyl ketone (MEK) from a constant stream of contaminated air, thus providing a clean air delivery rate (CADR) of 28.4 $m^3 \cdot h^{-1}$. Wang and Zhang (2011) assessed the SPRE of their 'dynamic botanical air filtration' system and recorded SPREs of 50.1–91.7% and 73.2–98.7% for toluene and formaldehyde respectively, depending on soil moisture levels and airflow rate providing CADRs ranging from 232.4–

759.7 $m^3 \cdot h^{-1}$ (Wang and Zhang 2011). Comparisons across systems suffer from low validity, however, due to the use of different VOCs, different room sizes and layouts, inconsistent plant species and substrates, and different remediation metrics. Despite the impressive VOC removal rates demonstrated by active botanical biofilters, the influence of system operation on *in situ* PM concentrations is a novel finding that supports the value of active green walls as a technology capable of remediating high concentrations of a range of behaviourally diverse air pollutants.

It is likely that positive health impacts would be associated with the reductions in VOCs and PM observed for the active green wall treatments in both room trials. VOC exposure has been shown to have dose-response relationships for upper and lower respiratory symptoms (Pappas et al. 2000), and research suggests that chronic exposure to relatively small concentrations of certain VOCs is associated with detrimental health effects (Khanchi et al. 2015; Qu et al. 2002). Thus, even small reductions in VOCs are likely to have quantitatively positive health outcomes. Similarly, significant health impacts have been associated with exposure to relatively minor increases in PM (in particular fine particles) concentrations: Wang et al. (2016) found that whole population all natural-cause mortality increased by 3% with each 2 $\mu g \cdot m^{-3}$ increase in $PM_{2.5}$ exposure. There is strong evidence to suggest that a 10 $\mu g \cdot m^{-3}$ incremental increase in the concentration of $PM_{2.5}$ is associated with a detectable increase in total population mortality, specifically that related to cardiovascular disease and respiratory disease risk (Li et al. 2017). The active green wall used in the schoolroom thus potentially produced an indoor environment that could lead to quantifiably improved health outcomes. Before such epidemiological claims can be made, however, this technology needs to be widely implemented over various temporal and spatial scales, with air quality monitoring and health outcome assessment programs.

The schoolroom setting represents an ideal environment for active botanical biofiltration to be implemented, as children are particularly vulnerable to adverse health effects related to air pollution exposure (Buka et al. 2006), notwithstanding the well-documented biophilic satisfaction and increased school performance associated with indoor greening (Daly et al. 2010).

3.6 Conclusion

Potted-plants, passive green walls and active green walls were tested for their capacity to reduce in room concentrations of VOCs and PM, with active green walls providing

significant reductions in VOC and PM concentrations, while passive walls showed a lesser reduction in PM concentration. Active green walls reduced the concentration of PM and VOCs from a classroom to provide greater air quality than that provided by the classroom's current HVAC system. Although these pilot-scale results indicate that active green wall systems are capable of improving indoor air quality, further empirical validation, incorporating long-term studies in varied indoor environments are needed to ensure active botanical biofiltration can be implemented to efficiently and reliably clean indoor air.

3.7 Acknowledgements

The authors would like to acknowledge Junglefy Pty for providing the green wall modules. The authors would additionally like to thank Junglefy, Ornatec International Consultancy and Beijing Florascape for their effort and assistance that allowed these trials to occur. This research is supported by The UTS Centre for Technology in Water and Wastewater (CTWW). T Pettit is supported by an Australian Government Research Training Program Scholarship.

Preface: Chapter 4

With active green walls demonstrating indoor air cleaning potential (Chapter 3), it is possible that these systems may also be capable of filtering air pollution in outdoor or semi-outdoor environments such as car parks or traffic tunnels. Urban environments not only experience high rates of air pollution emission; the urban geometry of street canyons, characterised by dense, tall buildings along both sides of many roads, limits the dispersion of pollutants into the atmospheric boundary layer, and thus promotes the accumulation of a range of harmful air pollutants (Mazzeo et al. 2010). While conventional urban forestry, such as street trees, has been found to be generally associated with reduced air pollution, spatial constraints and rapid urbanisation are resulting in reductions in the extent and quality of conventional urban greening. Simultaneously, in many cities around the world, there has been a significant uptake of green roofs and green walls to fill this growing gap (Irga et al. 2017c). It is thus possible that active botanical biofilters may be used outdoors to contribute to both urban green space and enhanced ambient outdoor air quality in areas where reductions in personal exposure to air pollution will be beneficial.

Similarly to interior greening, urban trees have the capacity to remove air pollutants from the ambient air through stomatal uptake and / or deposition of pollutants onto the plant foliage or stem (Grote et al. 2016). Urban trees may also alter wind flows and act as a barrier that prevents air pollution from entering specific areas within an urban context (Salmond et al. 2013; Al-Dabbous and Kumar 2014; Janhäll 2015; Tong et al. 2016), however studies have also noted that this effect may prevent air pollutants dispersing from street canyons, therefore increasing the concentrations of pollutants within street canyons (Buccolieri et al. 2009; Abhijith and Gokhale 2015). Despite the benefits associated with urban forestry, densely populated urban areas present several challenges to street tree greening, such as a lack of growing space, poor soil quality and conflicts with human activities, structures and paving (Jim et al. 2018). These effects often lead to poor plant health and massive die-offs (Dmuchowski et al. 2011).

Resilient urban forestry strategies that overcome the spatial constraints imposed by urban areas may provide several benefits to the residents. Increasing the implementation of green walls in urban areas may be an effective method to address this concern. In several

cities around the globe there has been a significant interest in the use of green roof and green wall projects to contribute to urban green space, with several governments implementing policies or incentives to encourage increased greening in these forms (Irga et al. 2017c). The enhanced pollutant removal effects of active green walls may provide a means by which the services provided by existing forms of green wall may be substantially enhanced. The geometry, orientation (Rao et al. 2014) and mechanical airflow of active green walls suggest that they may be an especially effective form of urban forestry implemented to phytoremediate air pollutants in high pollutant environments where natural dispersal of pollution is limited, such as car parks and traffic tunnels.

Before active botanical biofilters can be installed in these semi-outdoor environments, their capacity to reduce the concentration of nitrogen dioxide (NO_2) needs to be assessed. While indoor phytoremediation has primarily focused on the removal of VOCs, NO_2 is becoming an increasingly important air pollutant in urban areas where it is largely associated with traffic related emissions (Beevers et al. 2012). High concentrations of NO_2 remain problematic across many European urban areas despite the implementation of vehicle emissions controls for several decades (Carslaw et al. 2016). Recent research has demonstrated that passive forms of green infrastructure are able to alter the dispersion of particles and NO_2 from roadways, leading to a reduction in the concentrations of these pollutants on the non-road facing side of the green infrastructure barrier (Pearce et al. 2021). While these results are very promising, it remains unclear whether active systems are capable of filtering out NO_2. Additionally, it is important to understand what effects any NO_2 filtration processes may have on the ambient air quality, as it there is potential for NO_2 to react with the filtration matrix, other pollutants in the atmosphere and VOCs, which may be emitted from the plant (Atkinson 2000).

This chapter tests the capacity of active green walls to remove NO_2, with comparisons made across two different plant species commonly grown in active green walls.

The work presented in this chapter has been published in the journal *Atmosphere*:
Pettit, T., Irga, P.J., Surawski, N.C. and Torpy, F.R., 2019. An Assessment of the Suitability of Active Green Walls for NO_2 Reduction in Green Buildings Using a Closed-Loop Flow Reactor. *Atmosphere*, *10*(12), p.801.
This chapter is written verbatim to this article.

Author Contributions:

Thomas Pettit: Conceptualization, methodology, analysis, investigation, resources, data curation, original draft preparation, review and editing. **Peter Irga:** Investigation, resources, review and editing, supervision, project administration. **Nic Surawski:** Software, resources, data curation, review and editing, project administration. **Fraser Torpy:** Conceptualization, methodology, review and editing, supervision, project administration.

Chapter 4

4. An assessment of the suitability of active green walls for NO_2 reduction in green buildings using a closed-loop flow reactor

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4.1 Abstract

Nitrogen dioxide (NO_2) is a common urban air pollutant that is associated with several adverse human health effects from both short and long term exposure. Additionally, NO_2 is highly reactive and can influence the mixing ratios of nitrogen oxide (NO) and ozone (O_3). Active green walls can filter numerous air pollutants whilst using little energy, and are thus a candidate for inclusion in green buildings, however the remediation of NO_2 by active green walls remains untested. This work assessed the capacity of replicate active green walls to filter NO_2 at both ambient and elevated concentrations within a closed-loop flow reactor, while the concentrations of NO and O_3 were simultaneously monitored. Comparisons of each pollutant's decay rate were made for green walls containing two plant species (*Spathiphyllum wallisii* and *Syngonium podophyllum*) and two lighting conditions (indoor and ultraviolet). Both plant species biofilter treatments exhibited exponential decay for the biofiltration of all three pollutants at ambient concentrations. Furthermore, both treatments removed elevated concentrations of NO and NO_2, (average NO_2 clean air delivery rate of 661.32 and 550.8 $m^3 \cdot h^{-1} \cdot m^{-3}$ of biofilter substrate for the respective plant species), although plant species and lighting conditions influenced the degree of NO_x removal. Elevated concentrations of NO_x compromised the removal efficiency of O_3. Whilst the current work provided evidence that effective filtration of NO_x is possible with green wall technology, long term experiments

under *in situ* conditions are needed to establish practical removal rates and plant health effects from prolonged exposure to air pollution.

Keywords: green building; sustainability; indoor air quality; green wall; living wall; living façade; botanical biofilter; ozone; nitrogen dioxide; potted plant.

4.2 Introduction

Nitrogen dioxide (NO_2) is a common urban air pollutant that is largely associated with combustion processes, and particularly traffic-related emissions (Beevers et al. 2012; Wang et al. 2019). High concentrations of NO_2 remain problematic across many urban centres despite the implementation of vehicle emissions controls over several decades (Carslaw et al. 2016). Frequently, in large urban centres, ambient outdoor NO_2 concentrations, and thus human exposure, exceed the World Health Organisations guideline values of 200 $\mu g/m^3$ (Short term: 1 hour mean) and 40 $\mu g/m^3$ (long term: annual mean) (Hoek et al. 2013). Indoor NO_2 exposure is associated with a range of respiratory symptoms and decreased pulmonary and lung function (Kattan et al. 2017; World Health Organisation 2006; Smith et al. 2000; Just et al. 2002; Belanger et al. 2006) and increases in NO_2 concentrations are associated with increases in all-cause mortality and hospital admissions (Andersen et al. 2007). Consequently, increased risk to public health has emerged with the growing evidence of the health effects linked to elevated NO_2 exposure (Henschel et al. 2013). As is the case with most emissions, roadside emissions may make a considerable contribution to the NO_2 concentration of nearby indoor environments (Lawson et al. 2011).

In addition to problems arising from NO_2 exposure, NO_2 can act as an ozone (O_3) precursor (Khan et al. 2018) and is readily photolysed to nitrogen dioxide (NO) (Li and Liu et al. 2012). The relationship between O_3 and NO_x (oxides of nitrogen, i.e. NO + NO_2) is very important, as NO_x are highly reactive and promote O_3 formation in the presence of sunlight, high temperatures and other atmospheric gases, such as methane and volatile organic compounds (VOCs) (Jacob and Winner 2009; Melkonyan et al. 2012).

Current indoor environmental quality management systems for buildings are reliant on heating, ventilation and air-conditioning systems (HVAC) to manage indoor air quality and climate. These functions are based around ventilation with fresh air; however this air must be temperature modulated, using very large quantities of energy (Leavey et al. 2015). Further, some green building certification schemes promote increased mechanical ventilation

as the preferred or only method to maintain indoor air quality (Green Building Council Australia 2009). While ventilation is effective in many circumstances, simply increasing ventilation rates may not provide improved indoor air quality for all areas, in particular those with high outdoor pollution or episodic and uncontrolled release of gaseous air pollutants. Common ventilation systems do not filter gaseous pollutants, such as NO_2, and thus, the use of mechanical ventilation may increase the rate at which outdoor generated pollutants infiltrate into the indoor environment (Challoner and Gill 2014). We propose, it would therefore be beneficial if green building schemes included foci on reducing human–air pollution exposure, such as rewarding actions that result in source control and energy efficient means of air pollution reduction. It is thus paramount to advance technologies capable of controlling NO_2 concentrations both near the emission source (i.e. roadsides) and in areas relevant to urban peoples' breathing zones (i.e. the indoor environment).

Although plants can phytoremediate NO_2, their ability to filter NO_2 is primarily limited to studies that have assessed the potential of urban forestry to provide enhanced air quality (Abhijith et al. 2017). NO_2 can be removed through both dry deposition to the leaf surface and direct dissolution into a water film present on the plant surface (Grote et al. 2016). It has been estimated that urban trees can remove considerable volumes of NO_2 from the ambient air: Nowak et al. (2006) estimate that urban trees in the coterminous United States are capable of removing ~ 97, 800 t of NO_2 per year at a value of USD $660 million. Despite these benefits, it has been suggested that in some cases, plants may compromise the air quality as their emission of biogenic VOCs interacts with urban NOx to produce Ozone (Rao et al. 2014). Nonetheless, fusing the removal mechanisms of the plant foliage with biofiltration technology to create active green walls (botanical biofilters) has proven an efficient means for the removal of other gaseous pollutants, primarily different species of VOCs (Pettit et al. 2018a), however it is unknown whether botanical biofilters are capable of filtering NO_x, and what implications this may have for the ambient O_3 concentration.

Active green wall technology has been proposed as an effective and innovative approach for indoor gaseous pollutant control (Torpy et al. 2015). Active green walls are a green technology that can simultaneously treat a large number of air pollutants at a relatively low cost. This technology builds upon the vast literature purporting the air phytoremediation potential of potted plants (Dela Cruz et al. 2014a; Irga et al. 2019; Pettit et al. 2018a; Weyens et al. 2015). Whilst pollutant reduction by potted plants has been well described, for *in situ* use such systems will be severely limited in their efficacy (Llewellyn and Dixon 2011). Several recent studies have reported that green wall systems, in particular active green walls,

have a high capacity to phytoremediate several air pollutants, including particulate matter (PM) (Irga et al. 2017b; Pettit et al. 2017) and VOCs (Torpy et al. 2018; Pettit et al. 2019a). Regarding green wall VOC removal, biodegradation of VOCs by the rhizospheric bacteria along with substrate adsorption are considered as the primary sinks for VOC removal (Pettit et al. 2018b), however, plant-associated effects also play a role in VOC removal (Irga et al. 2019). In the current experiment, all treatments contained both plants and substrate as discriminating between substrate and plant effects are of no interest in practical applications of this technology. Green walls have practical advantages over potted plants for practical pollutant removal due to their increased plant density, vertical alignment and the efficiency with which polluted air can be passed through the substrate and roots through the use of mechanically-assisted ventilation, which is a defining characteristic of active systems. Furthermore, their design allows them to have potential applications in both unique high-pollution applications such as traffic tunnels and carparks, as well as in green buildings to achieve an energy efficient equivalent to ventilation and thermal comfort (Tudiwer and Korjenic 2017). This has led to the possibility of maintaining indoor air quality through the biofiltration of air recirculating through the active green wall within a building rather than through the traditional approach of ventilation through HVAC systems (Darlington et al. 2001).

Previous research testing the pollutant removal capabilities of this technology has been limited to VOCs (Darlington et al. 1999; 2001; Llewellyn et al. 2000b; Pettit et al. 2019a), CO_2 (Torpy et al. 2017) and PM (Irga et al. 2017b; Pettit et al. 2017) and thus the use of active green wall technology for the remediation of other criteria air pollutants, including NO_2, remains untested. In addition to these previously tested functions, a potential reduction of the ambient NO_x concentration through botanical biofiltration is an important consideration that could further improve air quality and reduce occupant exposure to these pollutants. Plant species-dependent differences in NO_2 removal have been linked to stomatal uptake in trees (Chaparro-Suarez et al. 2011), however, if active botanical biofiltration systems primarily remove NO_2 through substrate-pollutant adsorption and dissolution into the aqueous phase, it is possible that differences in NO_2 removal amongst different plant species will be less variable. Additionally, it is possible that the potential reactions between NO_2 and VOCs, including biogenic VOCs associated with the biofilter itself, may have implications for the concentrations of associated pollutants such as NO and O_3 (Sillman and He 2002). Despite potential reductions in the NO_2 concentration through phytoremediation, any

production of NO or O_3 is clearly problematic if botanical systems are placed in environments with high concentrations NO_2.

This work provides the first assessment of the botanical biofiltration of NO_x with O_3 concentrations simultaneously monitored. Specifically, this work assessed the capacity of active green walls to remove both ambient and elevated concentrations of NO_2, with comparisons made between two plant species (*Spathiphyllum wallisii* and *Syngonium podophyllum*) that are commonly grown in active green walls. Additionally, the associated gases, NO and O_3, were simultaneously monitored to ensure that potential reductions of one hazardous chemical did not lead to the production of an alternative hazardous gas.

4.3 Methods

4.3.1 Biofilter design and plant selection

Replicate biofilters were housed in open-ended poly vinyl chloride (PVC) pipe (88 mm internal diameter, 120 mm in length). Each PVC pipe contained a coconut husk-based growth substrate packed to a depth of 85 mm, to represent a realistic active green wall substrate depth that would be sufficient to support plant growth, as has been tested in previous research (Pettit et al. 2018b; 2019). Coconut husk is a favourable substrate for use as a growth substrate in botanical biofilters, as it has not been associated with bioaerosol emissions (Irga et al. 2017a), and has a demonstrated capacity to filter VOCs (Pettit et al. 2019a) and PM (Irga et al. 2017b). The substrate was retained within the pipe by loose weave high-density polyethylene (HDPE) cloth at each end of the pipe. A single plant was planted into each biofilter; the plant roots were supported by the substrate while the aerial phytomass grew through a small incision cut through the HDPE cloth (Figure 15). To provide nutrients to the plants, the growth substrate was fertilised with a general purpose fertiliser (Green Jacket 12–14 month controlled release fertiliser [N-P-K:18-2.5-10; N as nitrate = 8.3%; N as ammonium = 9.8%; N as urea = 0%; P = 2.5%; K as soluble potash = 10%; S = 4%) at an application rate of 4 $kg \cdot m^{-3}$ as per the manufacturer's recommendations (Australian Growing Solutions; Tyabb, Vic, Australia]).

Biofilters containing two different plant species were tested for their capacity to filter NO_2. These species were *Spathiphyllum wallisii* (peace lily) and *Syngonium podophyllum* (arrowhead vine). These species are both common indoor houseplants and green wall species, and both have been tested for their capacity to phytoremediate a range of VOCs (Hörmann 2017; 2018; Irga et al. 2013; Pettit et al. 2019a; Sriprapat and Thiravetyan 2016; Torpy et al.

2013). All tested plants were grown in their biofilters in a glasshouse (Sydney, Australia) for ~8 weeks prior to testing. During this period plants were stored vertically, placed on saucers, and watered to field capacity once weekly. The average solar exposure over this period was 12.4 $MJ \cdot m^{-2}$ per day and the average daily photoperiod (bright sun exposure) was 7.65 h (Bureau of Meteorology 2019).

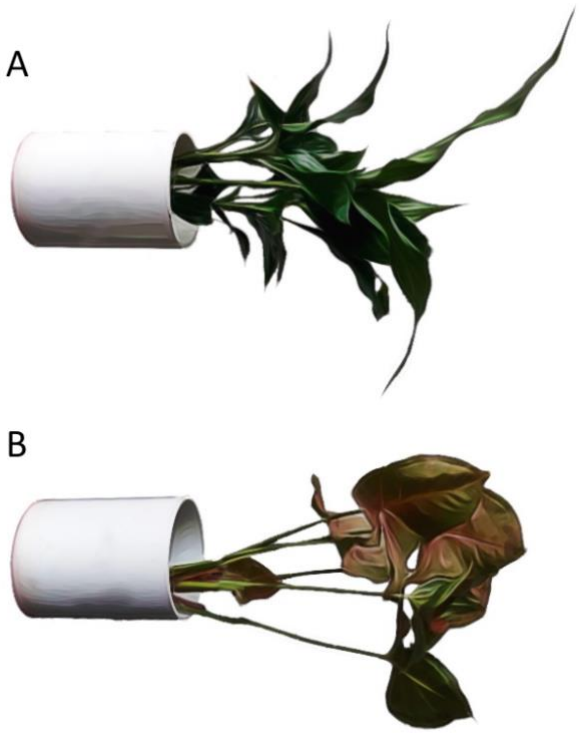

Figure 15. The replicate biofilters used in this experiment. A: a replicate biofilter with *Spathiphyllum wallisii*; B: a replicate biofilter with *Syngonium podophyllum*.

4.3.2 Closed-loop flow reactor

For testing, botanical biofilters were placed individually into a closed-loop flow reactor (Figure 16). In this system, air circulated through the loop and passed through the biofilter once for each completed circuit. The closed-loop flow reactor, composed of polyvinyl chloride (PVC) ducting, glass tubing and clear polycarbonate tubing, had a 100 mm internal diameter and was 2.80 m in length with several sensors embedded throughout. Total reactor internal volume was 0.9 m^3. Two axial impellers (FANTECH TEF-100 fan 16W) were ducted in series into the flow reactor to provide active airflow. The fans were connected to a potentiometer to enable modifications to fan power, ensuring each trial was conducted at the same airflow rate. Airflow generated by the fans passed through the biofilter substrate and then the foliage, after which the airstream was exposed to several sensors before return to the

axial impellers and thus recirculated through the flow reactor. Pressure drop across the botanical biofilters within the closed loop flow reactor was measured with a Sensirion digital sensor (SDP610 125 Pa) and the average pressure drop was 83.2 and 84.3 Pa for *S. wallisii* and *S. podophyllum* respectively. An anemometer (Digitech Thermo-anemometer QM1646) was embedded on the downstream side of the biofilter to measure the air velocity flowing through the biofilter, from which the volumetric airflow rate could be determined. Instruments for measuring the concentrations of NO, NO_2 (Ecotech EC9841 nitrogen oxides analyser) and O_3 (Ecotech Serinus 10 ozone analyser) were ducted into the biofilter's leeward side within the flow reactor with Teflon tubing.

The downstream end of the biofilter from which the plant's foliage emerged was connected to a clear polycarbonate pipe so that the photosynthetic plant parts were exposed to light. The level of photosynthetically active radiation (PAR) within the section of the flow reactor where the plant foliage was exposed was measured with a LI-250A Light Meter with an LI 190 Quantum Sensor (LI-COR Biosciences; Lincoln, NE, USA) and had an average photosynthetic flux density of 9.95 $\mu mol \cdot m^{-2} \cdot s^{-1}$. Finally, a septum located between the axial impellers and biofilter allowed the addition of reagents to the flow reactor to facilitate pollutant generation (see below; section 4.3.4). All experiments were conducted in a laboratory at 22°C.

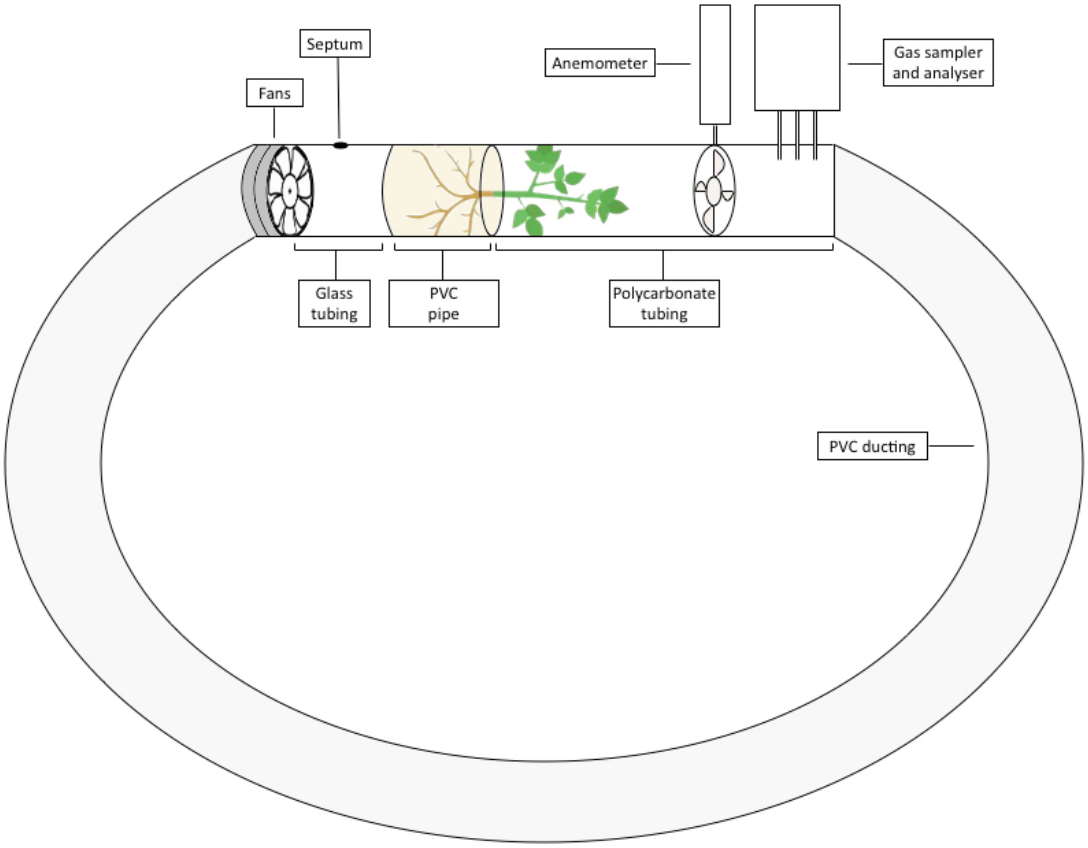

Figure 16. The closed loop flow reactor used in this experiment.

Pollutant generation and experimental trials

4.3.3 Biofiltration of ambient NO_2

Biofilters were firstly trialled for their capacity to remove ambient concentrations of NO, NO_2 and O_3. Six biofilters containing *S. wallisii* and six biofilters containing *S. podophyllum* were used for this experiment. Additionally, 10 trials were conducted without any biofilter in the flow reactor to represent a procedural control to account for any effects resulting from loss by diffusion, chemical reactions, and adsorption to the flow reactor surfaces. Species and control treatments were conducted in a randomised order. Trials were run for 40 minutes, which was sufficient time for the concentration of NO_2 to reach an asymptote across both biofilter treatments. The average ambient concentrations of pollutants detected within the flow reactor for the procedural control were 46.39 ± 0.006 ppbv for NO, 70.08 ± 0.017 ppbv for NO_2, and 0.486 ± 0.004 ppbv for O_3; Figure 17.

4.3.4 Biofiltration of elevated NO_2 concentrations

As the concentrations of the trial pollutants within the ambient laboratory atmosphere were unlikely to be representative of pollutant concentrations in urban areas exposed to high traffic density, an additional series of experiments were conducted where biofilters were assessed for their capacity to remove elevated concentrations of NO_2. For this experiment, pollutants were generated by placing a 1.00 cm^2 x 0.06 mm thick pure copper sheet into the flow reactor between the fans and the biofilter, and beneath the septum. Once the flow reactor was sealed, 1.50 µL of nitric acid (70% AR Grade; UNIVAR Australia PTY Ltd) was injected through the septum onto the copper sheet, thus generating gaseous NO_2 by the reaction (Yoo et al. 2015):

$$Cu(s) + 4HNO_3(aq) \rightarrow Cu(NO_3)_2(aq) + 2NO_2(g) + 2H_2O\ (l)$$

This produced an average peak NO_2 concentration of 6.656 ± 0.607 ppm at the NO_2 sensor within the flow reactor, which was similar to the values achieved in other studies assessing non-biological methods for the filtration of NO_2 (Yoo et al. 2015). Additionally, peak NO concentrations of 1.124 ± 0.088 ppm and 7.280 ± 0.064 ppb for O_3 were generated.

For this experiment, six biofilters containing *S. wallisii* and six biofilters containing *S. podophyllum* were tested. Additionally, 10 trials were conducted without any biofilter in the flow reactor as a procedural control to account for any effects resulting from diffusion, reaction, or adsorption to the flow reactor surfaces, as per experiment 1. All trials were conducted in a randomised order. Trials were run for 20 minutes, which was sufficient time for the concentration of NO_2 to reach an asymptote across both biofilter treatments.

4.3.5 Removal of elevated NO_2 concentrations with UV exposure

As exposure to UV can initiate chemical reactions, it is critical to test biofiltration under UV exposure to determine how botanical biofilters might perform under conditions where UV exposure is significant, such as outdoors. NO_2 is susceptible to photolysis (Bohn et al. 2005), i.e.

$$NO_2 + hv\ (\lambda \leq 420\ nm) \rightarrow O(^3P) + NO$$

Additionally, O_3 can also be photolysed (Atkinson 2000), i.e.

$$O_3 + hv\ (\lambda \leq 335\ nm) \rightarrow O(^1D) + O_2$$

Thus disassociation through photolysis, followed by a series of chemical reactions (often involving VOCs) (Atkinson 2000), results in the potential for O_3 and NO_2 to influence the concentrations of each other. To explore the effects of UV exposure on the concentrations of NO_x and O_3, a series of experiments were conducted with the flow reactor exposed to UV light. These experiments were conducted using an identical method to that used for the second experiment, however the closed-loop flow reactor was placed in a biosafety cabinet (Gelaire BH-EN Class II biological safety cabinet) where the system was exposed to artificially generated UV light (germicidal UV peaking at 254 nm at an intensity of 400 $mW \cdot m^{-2}$) according to Australian Standard AS1807.23, which corresponds to the peak absorption cross section for O_3 (σ = 113.05 x 10^{19} cm^2 at 295 K and λ = 253.65) (Malicet et al. 1995). Four independent replicates of this trial were run.

4.3.6 Statistical analysis

Concentrations of all pollutants within each trial were normalised by their peak concentrations. Exponential decay curves of pollutant concentration as a function of time were calculated (Microsoft Excel 2016) for each pollutant in each trial. The exponential decay describes the process of reducing the gases concentration by a consistent percentage rate over a period of time. The resulting exponential decay rates were used as response variables for subsequent statistical analyses.

Firstly, three separate independent–samples *t*-tests (IBM SPSS Statistics Ver 25) were used to test for differences in the decay rates for the removal of ambient concentrations of NO, NO_2 and O_3 between the two plant species (Experiment 1). Statistical comparisons of the exponential decay rates between these treatments and the procedural control treatment were not conducted in this experiment, since all pollutant concentrations in the procedural control did not change in an exponential manner throughout the experimental period (Figure 17). A series of general linear model regressions indicated that the concentration of NO did not significantly vary throughout the experimental time period for the procedural control (R^2 = 0.000, F = 0.000, p = 1.000; average gradient = 1 x 10^{-6}), nor did NO_2 (R^2 = 0.000, F = 0.000,

p = 1.000; average gradient = 7 x 10^{-8}) or O_3 (R^2 = 0.018, F = 0.238, p = 1.000; average gradient = 1 x 10^{-7}).

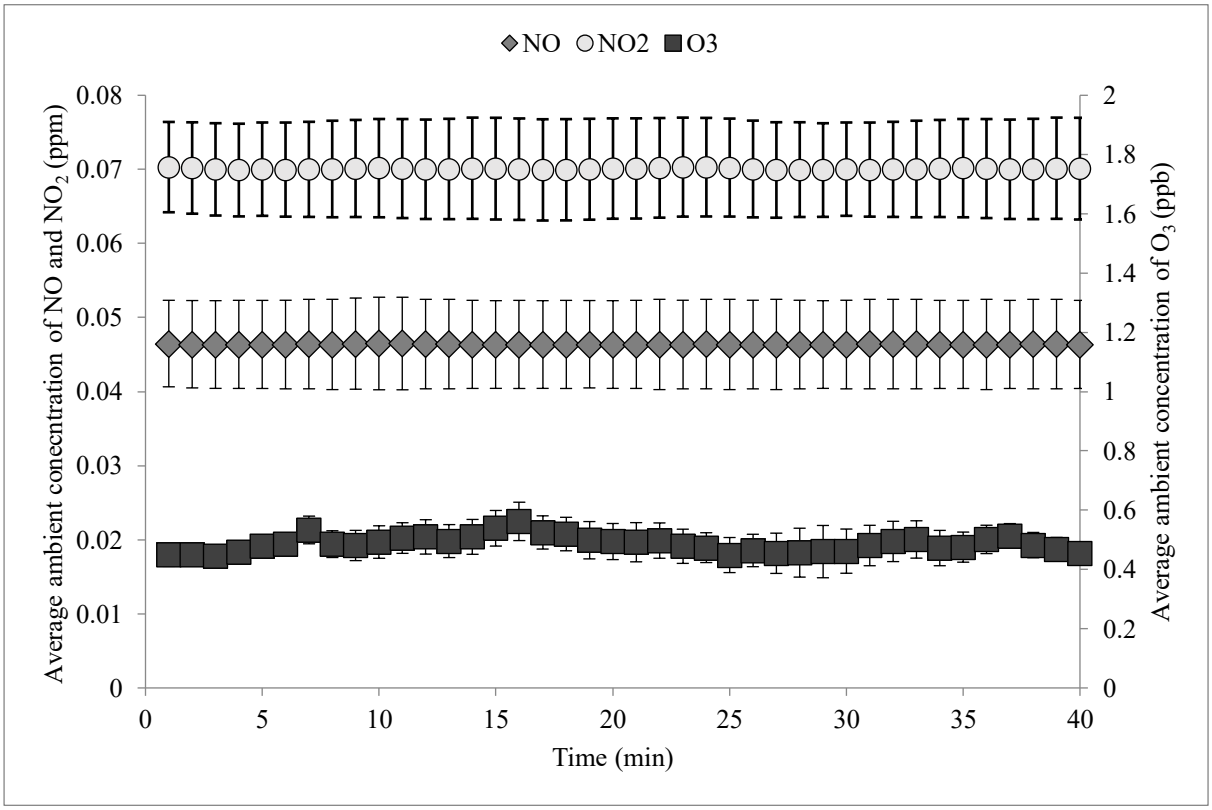

Figure 17. The ambient pollution concentration profiles within the flow reactor procedural control treatments (data are means, n = 14, errors bars represent the SEM).

Finally, three independent two factor ANOVAs were used to compare the exponential decay rates of the elevated concentrations of NO, NO_2 and O_3 amongst light source (UV supplemented light or indoor light) and biofilter (*S. wallisii*, *S. podophyllum*, procedural control) treatments for Experiments two and three.

For each experiment, the single pass removal efficiency (SPRE) of each pollutant was estimated through a rearrangement of Dumont and Héquet's (2017) equation:

$$\mathrm{SPRE} = -\ln\left(\left(\frac{\left(\ln\left(\frac{C}{C_0}\right)T_c\right)}{t}\right)+1\right)$$

Where T_c is the pollutant residence time in the flow reactor's empty chamber space; t = time; C_0 is the initial pollutant concentration; and C is the pollutant concentration at time t.

Dumont and Héquet (2017) examined the removal of VOCs by photocatalytic oxidation in a closed loop reactor, noting that the calculations for SPRE were dependent upon, amongst other factors, a perfectly mixed system. As a spiked source of a reactive pollutant was generated within the closed loop flow reactor in the current work (Experiments two and three) and additionally, pollutant concentrations within the flow reactor were influenced by diffusion, reaction rates, adsorption to the flow reactor surfaces, and possibly photolytic reactions, all SPRE values were corrected by subtracting the average SPRE value obtained from the corresponding procedural control treatment from the SPRE value calculated for each of the independent biofilter treatments. For all SPRE calculations, C_0 was defined as the time when the peak concentration of each pollutant was reached after generation, and C was taken at t = 600 s to avoid increased discrepancies between the observed and calculated values associated with longer time periods, as discussed by Dumont and Héquet (2017). The clean air delivery rate (CADR) of the biofilters for the different pollutants was calculated by multiplying the SPRE by the volumetric flow rate through the biofilter, and standardised per unit of biofilter volume.

4.4 Results

Both plant species biofilter treatments exhibited exponential decay for the biofiltration of all three pollutants at ambient concentrations (Figures 18–20). The average exponential decay rates for biofilters containing *S. wallisii* and *S. podophyllum* were 0.021 and 0.023 respectively for NO_2, 0.012 and 0.031 for NO, and 0.040 and 0.048 for O_3. The exponential decay rates were not significantly different between the plant treatments for any of the tested pollutants (independent samples t-tests: NO_2: T = 0.908, p = 0.385, Figure 18; NO: T = 1.367, p = 0.214, Figure 19; O_3: T = 0.919, p = 0.380, Figure 20).

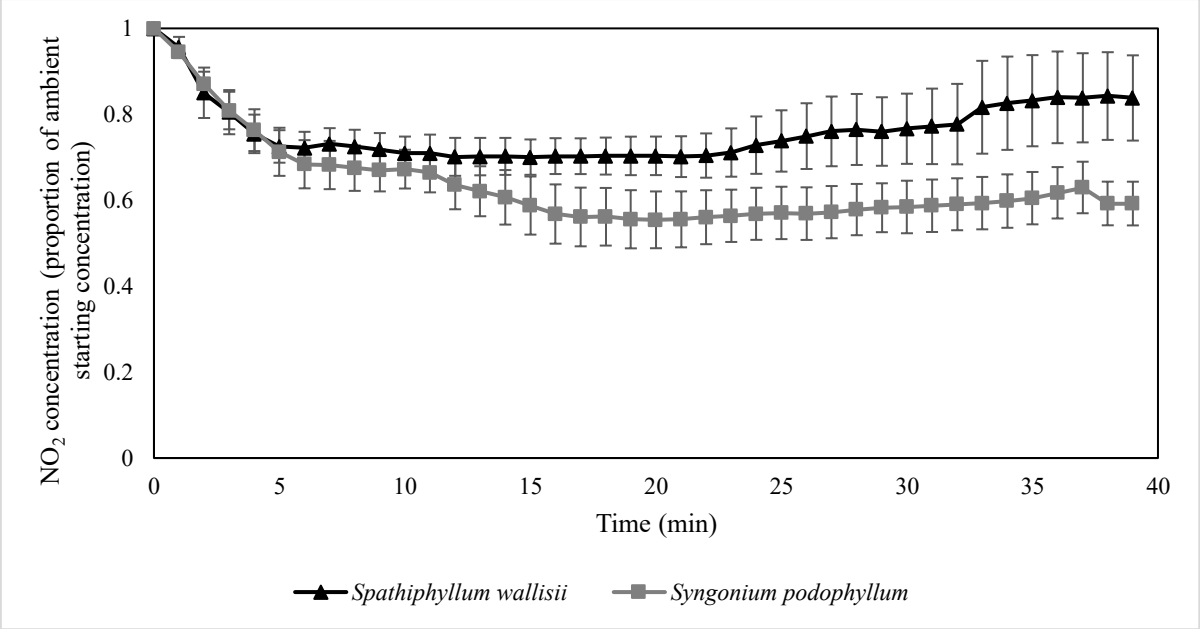

Figure 18. The biofiltration of ambient concentrations of NO_2 by biofilters containing two different plant species. NO_2 concentrations were normalised by the starting ambient concentration of NO_2. n = 4 independent samples per treatment, error bars represent the SEM.

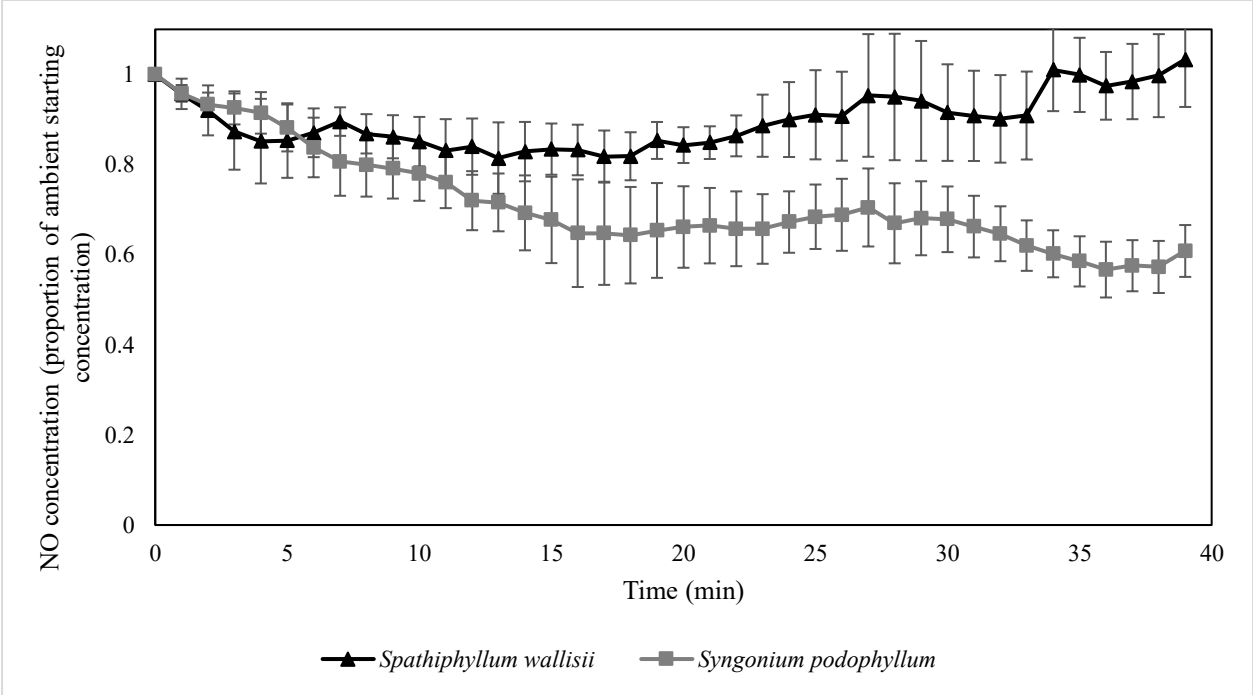

Figure 19. The biofiltration of ambient concentrations of NO by biofilters containing two different plant species. NO concentrations were normalised by the starting ambient concentration of NO. n = 4 independent samples per treatment, error bars represent the SEM.

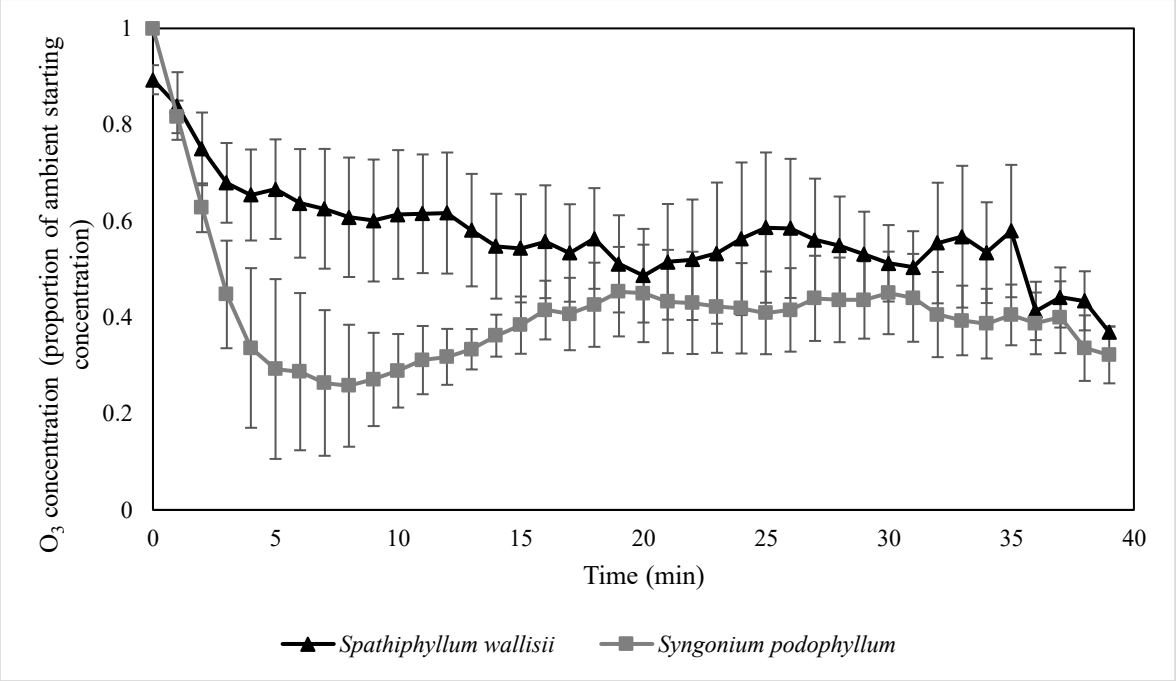

Figure 20.The biofiltration of ambient concentrations of O_3 by biofilters containing two different plant species. O_3 concentrations were normalised by the starting ambient concentration of O_3. n = 4 independent samples per treatment, error bars represent the SEM.

In trials with elevated pollution concentrations, all treatments effectively produced negative decay rates (Figures 21–26). While biofilter treatments with both plant species removed NO and NO_2 at greater exponential rates than their respective control treatments, this was not the case for O_3, where the control treatment had the highest decay rate for O_3 across both light conditions (Figures 23 and 26).

Significant differences were observed for the interaction of the plant species treatment and light type (F = 30.747, p = 0.000) for the NO_2 decay rate. *Post hoc* Tukey HSD tests indicated that the control treatment had a significantly slower NO_2 decay rate constant relative to both the *S. wallisii* and *S. podophyllum* biofilters (p = 0.000 for both comparisons), while the *S. wallisii* and *S. podophyllum* biofilters had significantly different NO_2 decay rates (p = 0.004), with *S. podophyllum* being slightly more effective for NO_2 removal.

There were significant differences in NO exponential decay rates between both light type (F= 15.760, p = 0.000) and biofilter treatments (F=26.939, p = 0.000), however there was no significant interaction between the two factors for NO decay rates (F = 1.214, p = 0.312). Subsequent Tukey HSD *post hoc* tests showed that the control treatment lost NO at a

significantly slower rate than both of the biofilter treatments (p = 0.000 for both comparisons), while the biofilters containing *S. wallisii* and *S. podophyllum* biofilters did not have significantly different NO decay rates (p = 0.104).

A two factor ANOVA comparing O_3 decay rates amongst the groups showed that the O_3 decay rate differed significantly amongst biofilter types (F = 10.406, p = 0.000) with *post hoc* Tukey tests showing the control treatment removed O_3 at a significantly faster rate than the *S. wallisii* and *S. podophyllum* biofilters (p = 0.001 and 0.000 for the respective comparisons).

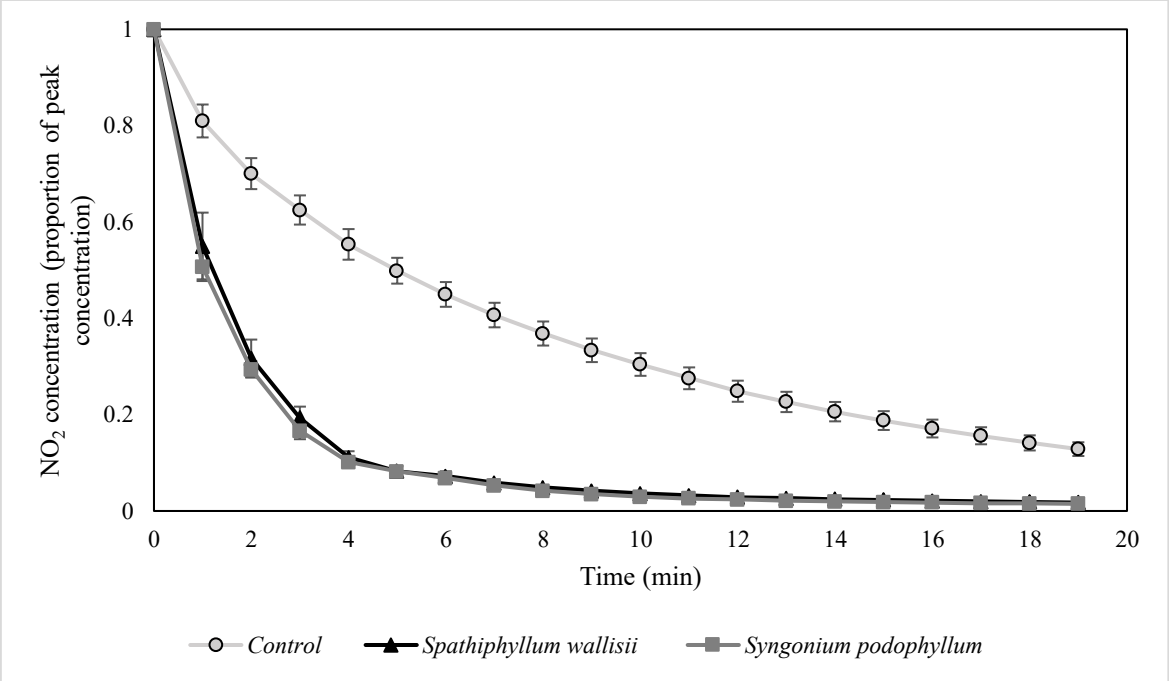

Figure 21. The biofiltration of elevated concentrations of NO_2 by biofilters containing two different plant species at indoor light levels. NO_2 concentrations were normalised by the starting ambient concentration of NO_2. n = 4 independent samples per treatment, error bars represent the SEM.

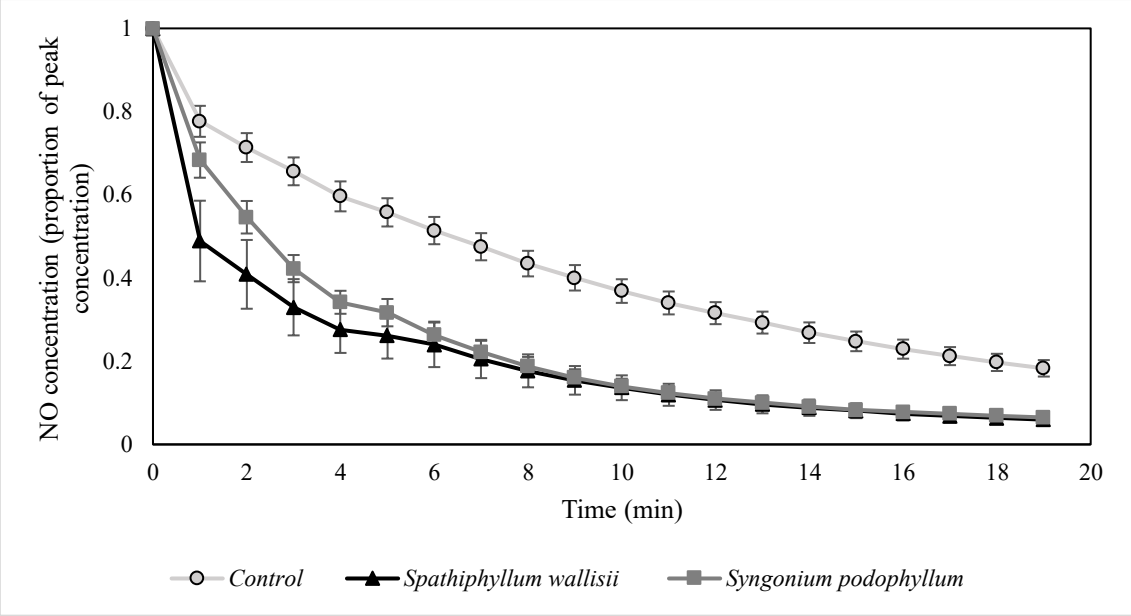

Figure 22. The biofiltration of elevated concentrations of NO by biofilters containing two different plant species at indoor light levels. NO concentrations were normalised by the starting ambient concentration of NO. n = 4 independent samples per treatment, error bars represent the SEM.

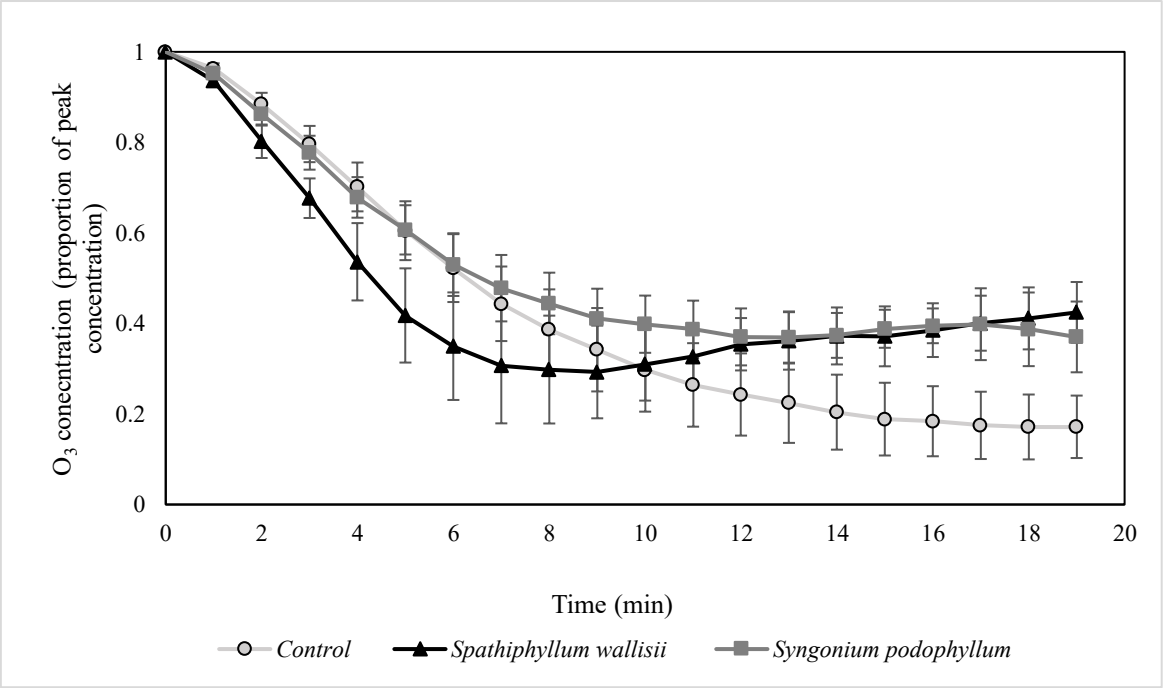

Figure 23. The biofiltration of elevated concentrations of O_3 by biofilters containing two different plant species at indoor light levels. O_3 concentrations were normalised by the starting ambient concentration of O_3. n = 4 independent samples per treatment, error bars represent the SEM.

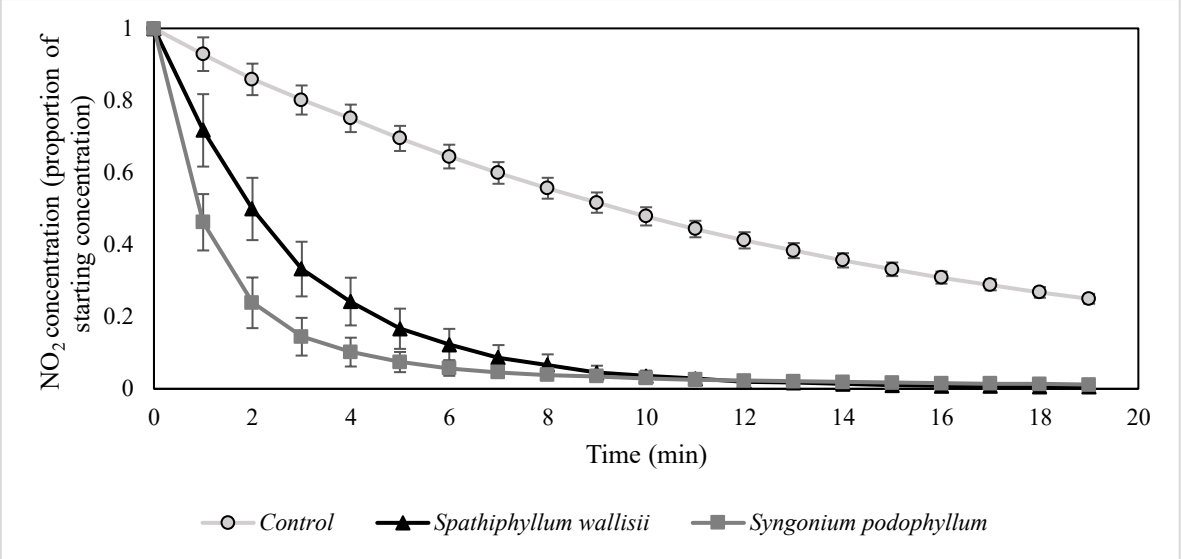

Figure 24. The biofiltration of elevated concentrations of NO_2 by biofilters containing two different plant species under UV light. NO_2 concentrations were normalised by the starting ambient concentration of NO_2. n = 4 independent samples per treatment, error bars represent the SEM.

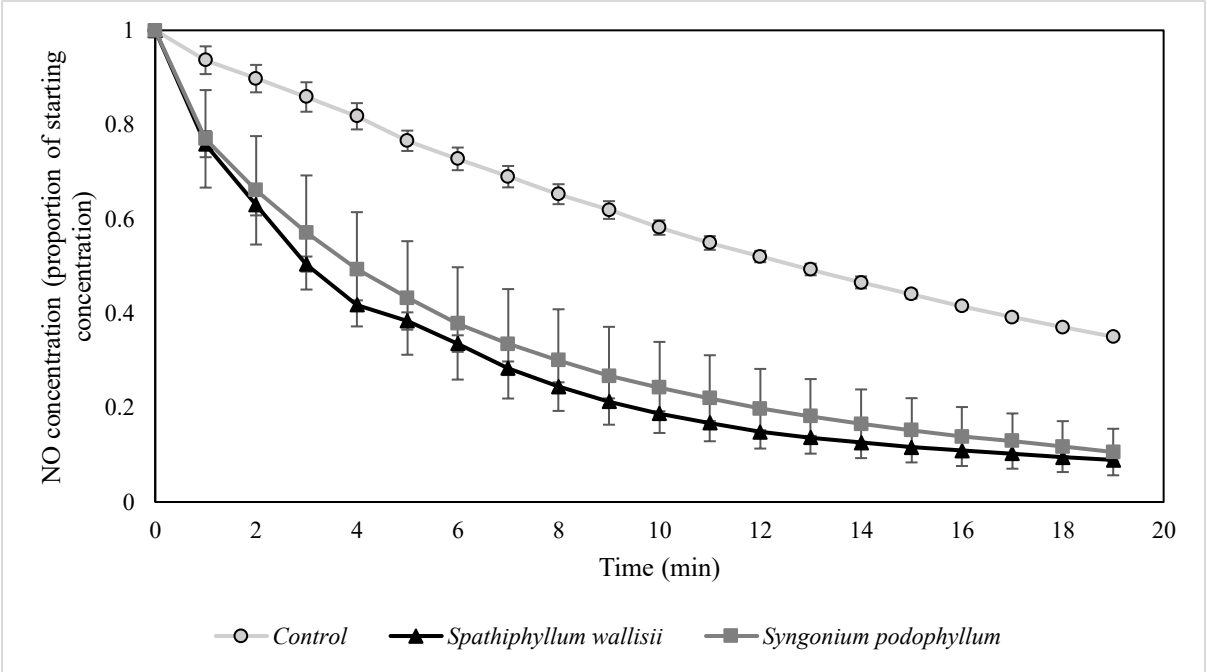

Figure 25. The biofiltration of elevated concentrations of NO by biofilters containing two different plant species under UV light. NO concentrations were normalised by the starting ambient concentration of NO. n = 4 independent samples per treatment, error bars represent the SEM.

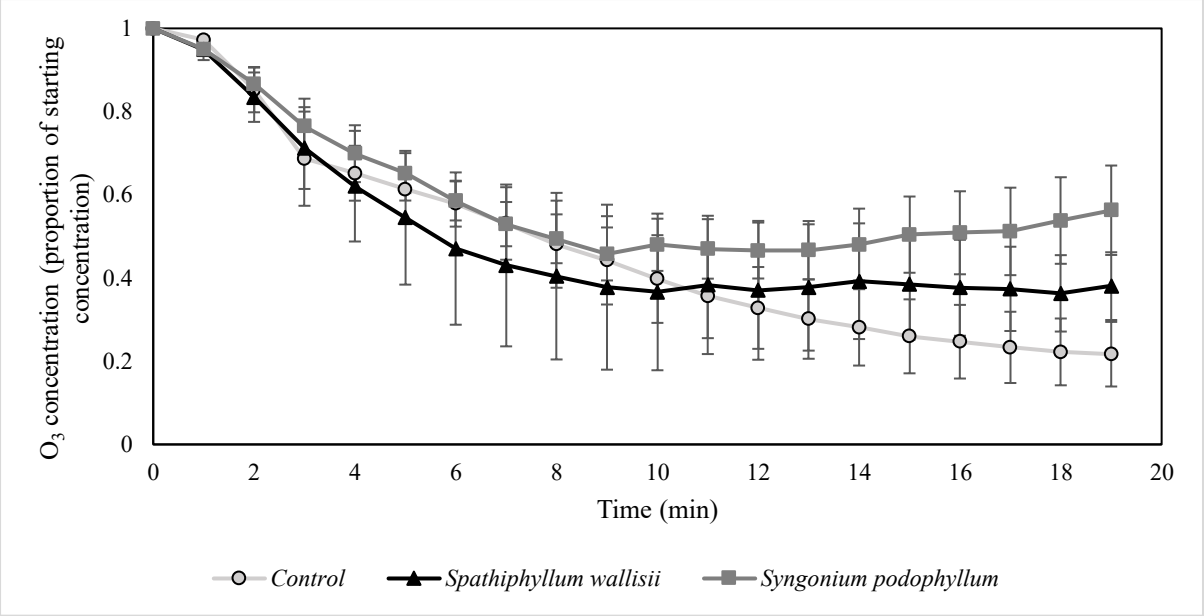

Figure 26. The biofiltration of elevated concentrations of O_3 by biofilters containing two different plant species under UV light. O_3 concentrations were normalised by the starting ambient concentration of O_3. n = 4 independent samples per treatment, error bars represent the SEM.

The estimated CADRs for all treatments are shown in Table 6. The botanical biofilters demonstrated the capacity to produce air with reduced concentrations of all of the pollutants. For NO and NO_2, the capacity to provide clean air appeared to be concentration dependent, with higher CADRs for these pollutants detected in the experiments that used elevated pollutant concentrations. Although highly variable, the CADR for O_3 showed no clear associations with any of the test treatments.

Table 6. Calculated CADRs normalised by biofilter volume ($m^3 \cdot h^{-1} \cdot m^{-3}$ of biofilter substrate). These values represent the amount of air that is cleaned of the corresponding pollutant per hour per m^3 of biofilter substrate.

Pollution treatment	Light type	Biofilter plant species	NO	NO_2	O_3
Ambient	Indoor	*Spathiphyllum wallisii*	33.48 ± 11.52	79.92 ± 9.00	135 ± 52.92
		Syngonium podophyllum	52.2 ± 15.48	87.84 ± 15.84	248.83 ± 29.88
Elevated	Indoor	*Spathiphyllum wallisii*	381.24 ± 90.72	661.32 ± 53.28	95.04 ± 34.92
		Syngonium podophyllum	242.64 ± 21.60	550.8 ± 19.08	23.04 ± 51.84
Elevated	UV	*Spathiphyllum wallisii*	277.76 ± 14.40	741.24 ± 199.80	228.6 ± 169.56
		Syngonium podophyllum	240.48 ± 77.76	676.08 ± 125.64	118.08 ± 137.16

4.5 Discussion

This study is the first to test the botanical biofiltration of NO_2 with active airflow while simultaneously monitoring NO and O_3 concentrations. Although differences in decay rates were observed amongst the different pollutants and experimental factors, all biofilters exhibited removal of NO_x. Importantly, no emissions (i.e. positive decay rate constants) of NO_x were detected in any treatment. Botanical biofilters with two plant species were capable of reducing ambient NO_2 to threshold concentrations specific to each treatment, however the higher NO_2 decay rates were observed under elevated NO_2 concentrations, with the highest decay pattern observed for *S. podophyllum* biofilters when exposed to UV.

Interestingly, the influence of light type lead to differences in the decay rates of both NO and NO_2. Botanical biofilters with both plant species exhibited NO decay rates greater than natural decay, and the presence of botanical biofilters clearly enhanced the rate of NO removal from the flow reactor. NO was removed more rapidly under indoor light conditions, most likely because this light type favourably influenced the photochemical route that generates NO from NO_2 (Atkinson and Carter 1984).

The differences in NO_2 decay rates observed between the two botanical biofilters under UV light may have been influenced by differences in the VOCs generated by the biotic components within the biofilters that were additional to ambient, anthropogenic VOCs. Biogenic VOCs can react with NO to generate NO_2 (Atkinson and Arey 2003b), which can then undergo photolysis. As the mixture of VOC species and quantity of emitted VOCs varies amongst different plant species (Seco et al. 2007), it is possible that differences in biogenic

VOC emissions between the *S. wallisii* and *S. podophyllum* biofilters may have contributed to the interaction between light type and botanical biofilter species influencing the rate of NO_2 decay. Additionally, botanical biofilters are also capable of filtering out a range of VOCs (Pettit et al. 2019a) and the degree to which various VOCs are filtered is dependent on the plant species present within the biofilter (Irga et al. 2019). These traits may have also differentially influenced the VOC concentration profile within the flow reactor and therefore, it is possible that the VOC profile associated with each plant species may have had ramifications for the NO_2 decay rate constants of each of the botanical biofilters. It is thus recommended that future work related to NO_x biofiltration includes profiles of the biogenic VOCs emitted by the filters.

Additionally, during the elevated pollution trials, the O_3 decay rate differed between biofilter treatments across both lighting conditions, with the O_3 concentration declining more rapidly in the empty flow reactor (control) than the flow reactors with biofilters present, and it is possible that VOCs may have also had a role in forming O_3 (Yao et al. 2015). Furthermore, the botanical biofilters were able to reduce the concentration of ambient O_3 when NO and NO_2 concentrations were also low, however O_3 was removed more rapidly by the control treatments than the botanical biofilter treatments under both lighting conditions with elevated NO_2. This may result from biogenic VOCs reacting with NO_x to form O_3 (Atkinson 2000), however, it has alternatively been suggested that biogenic VOCs and NO may react so as to scavenge O_3 (Neirynck et al. 2012). Together with these effects, it is difficult to estimate the extent of this effect *in situ* where larger air volumes (i.e. buildings) would preclude VOCs accumulating to the degree caused by the small reactor volume used here, and the NO_x concentration would generally be considerably lower. Decay of O_3 in the control may have resulted from reactions with NO_x and O_3, forming NO_2 (Atkinson and Carter 1984) leading to the production of other species such as NO_3 and N_2O_5 (Atkinson 2000). Although these experiments used an elevated concentration of NO_x, the concentration of O_3 was not proportionately elevated to the same extent and it is possible that the differential contribution of each contaminant to the overall air pollution load would influence the chemical transformations and thus the capacity to produce clean air.

In conjunction with substrate-mediated effects, NO_x and O_3 may also be removed by the aerial components of the plants, such as through adsorption to leaf surfaces and uptake through the plant's stomata (Weyens et al. 2015). This has been well documented as a pathway for the removal of gaseous pollutants by traditional forms of urban forestry (Abhijith et al. 2017), however the contribution of this pathway to the overall removal process remains

unknown when active airflow is used to pass an airstream through both the plant foliage and growth substrate. Determining the contribution of each pathway and assessing plant traits associated with removal is a valuable area of future research that will assist with performance optimization. The interaction between plant species and light type on NO_2 decay rates may have been influenced by the plants responding differently to the different light sources (i.e. different rates of photosynthesis) so that the rate at which NO_2 was taken up through stomata may have been affected.

It is further possible that the threshold for removal may be limited by saturation effects or alternatively, limited through substrate NO_2 emissions. Broad scale substrate NO_x emissions have been detected across agricultural areas, which are driven by soil fertilisation and precipitation, but which are subsequently suppressed due to canopy effects (Bertram et al. 2005). It is thus plausible that minor NO_x emissions from the growth substrate may occur in botanical biofilters, and the NO_2 concentration equilibrium between removal and emissions may lead to a threshold at which NO_2 concentrations can no longer be reduced.

It is, however, likely that due to the relatively sort trial duration, the majority of the observed NO_2 removal occurred through abiotic mechanisms. Amongst other reactions (see Atkinson 2000 for a discussion on the atmospheric chemistry of NO_x), NO_2 can react with water vapour and also substrate irrigation water (Zheng et al. 2016):

$$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$$

The products of such reactions may be problematic for biofilter plant health, as the accumulation of HNO_3 would acidify the growth substrate, and thus affect plant health along with causing shifts in the microbial community, while the generation of NO is potentially problematic due to its toxicity to bacteria (Stern et al. 2013). Due to the considerable variety of removal pathways and the potential for hazardous by-products, identifying the precise contribution of each removal mechanism is an important area of further research. Furthermore, longer term experiments are required to uncover the effects of NO_2 exposure and removal on the health of the plants, the biofilter's microbial community, and to establish whether pollution saturation effects will occur.

The SPRE estimation method developed by Dumont and Héquet (2017) was based on calculating removal efficiencies for VOCs by photocatalytic oxidisers, and thus the comparatively larger proportion of the flow reactor volume taken up by the biofilters in the current work (~2.5% by volume) may have led to some error in the predicted values.

Nonetheless, the botanical biofilters had a greater capacity to clean the air under elevated pollution concentrations and this is reflected in the considerably larger NO_2 CADRs (550.8-741.24 $m^3 \cdot h^{-1} \cdot m^{-3}$ of biofilter) detected under higher NO_2 loading. CADRs provide the best estimate of the air cleaning potential of botanical biofilters. Although this experiment used scaled-down model biofilters, larger botanical biofilters would by extension be capable of providing a considerable volume of NO_2 cleaned air. Although this is the first work to calculate NO_2 CADRs from botanical biofiltration, Wang and Zhang (2011) calculated CADRs for toluene and formaldehyde through their botanical biofilter, producing estimates that were considerably larger than those found for NO_x in the current work (4309 and 4690 $m^3 \cdot h^{-1} \cdot m^{-3}$ of biofilter bed respectively for formaldehyde and toluene). Interestingly, the CADR values found by Wang and Zhang (2011) varied depending on the airflow rate and substrate moisture level, and these are factors that need to be explored for their effect on NO_2 biofiltration.

This work represents the first work to assess the botanical biofiltration of NO_x. Although higher NO_x single pass removal efficiencies have been recorded for non-botanical biofilters (Barnes et al. 1995; Jiang et al. 2008) comparisons amongst other these studies remain difficult due to variation in biofilter volume and airflow rates: non-botanical biofilters are usually designed to treat a limited number of target pollutants with much lower airflow rates through a substrate of greater depth. Comparatively, botanical biofilters process large volumes of air, treat a variety of air pollutants (i.e. VOCs, PM and NO_x), and generally have a limited substrate depth (i.e. reduce the space occupied and maintain aesthetic appeal). In this regard, it is important that active green walls are considered within the context of their full functionality (i.e. VOC filtration (Pettit et al. 2019a), PM filtration (Irga et al. 2017b; Pettit et al. 2017), CO_2 reduction (Torpy et al. 2017), enhanced humidity and temperature (Tudiwer and Korjenic 2017), biophilic benefits (Gunawardena and Steemers 2018) and not solely as phytoremediators of a limited number of pollutants.

Although the NO_2 concentration in the experiment with spiked pollutant concentrations represents a level that is considerably higher (approximately by two orders of magnitude) than those commonly encountered in urban areas, the comparisons of NO_2 removal between the two different pollution concentrations (ambient and elevated) indicates that removal is a concentration dependent process. Furthermore, the high NO_x concentration used in this experiment was associated with compromised O_3 removal, however it is difficult to ascertain whether the biofiltration of NO_x in concentrations found in urban areas along

with variable environmental conditions (i.e. temperature and humidity) would be associated with O_3 production.

The installation of botanical biofilters into urban design and green buildings is a promising solution to mitigating personal exposure to urban air pollution. Integrating botanical biofilters into HVAC systems using IoT (Internet of things) technology for system monitoring is at the forefront of green technology, and may lead to enhanced management of indoor air quality by allowing real time system optimization (i.e. flow rate alterations) for target pollutants, while simultaneously monitoring and balancing HVAC energy expenditure (Wang and Zhang 2011). Real time monitoring of air quality combined with pollutant mitigation using with botanical biofiltration may reduce reliance on HVAC use and thus reduce the energy intensive step of temperature modulating influent ventilation air as it enters the building. For this development to be successful however, a thorough assessment of the pressure drop across a green wall (see (Abdo et al. 2016; 2018; 2019)) is needed to ensure energy use does not become inflated.

While these results provide insight into the chemical transformations associated with the biofiltration of NO_2, it is important to consider that different concentrations of these gases would likely influence the rate of removal of each of the pollutants. This work was limited to two plant species and thus care should be taken when extrapolating these results to large green walls containing many different plant species, in particular when the green walls contain plant species that may emit considerable volumes of biogenic VOCs. The limited trial time in this experiment was unable to establish saturation points and thus future work should focus on longer trial periods to assess whether the removal efficiency of these gases changes with time.

Long-term experiments also remain crucial for establishing the physiological responses of the plants when exposed to high concentrations of pollutants. Exposure to elevated concentrations of NO_2 have been found to influence some physiological characteristics, such as pH and total chlorophyll content, of trees (Uka et al. 2019), however it is unclear what sort of additive effects actively filtering NO_2 through the growth substrate for prolonged periods of time is likely to have on plant health. While short term acute exposure to NO_2 does not seem to initiate severe effect on active green wall plant health (Paull et al. 2018), systems that are deployed in high NO_2 environments will be exposed to, and filtering, NO_2 for prolonged periods of time. Regardless of whether plant health is compromised, there is potential for NO_2 exposure to alter both plant and microbial physiological processes that are key for efficient pollutant removal. There is potential for

such NO_2 stress-induced effects to contribute to VOC emissions from the plant, and this may not only influence NO_2 removal, but may also lead to O_3 production through VOC-NO_2 reactions. Further research on plant responses to NO_2 exposure is needed here to understand how these systems may tolerate elevated NO_2 concentrations and to understand what effects such exposure may have for pollutant removal.

4.6 Conclusions

Botanical biofilters represent a promising technology for reducing urban air pollutants. The current research highlights that botanical biofilters have potential to be used to reduce ambient indoor concentrations of NO_x and O_3. Under elevated NO_2 concentrations (approximately 100 times that of urban environments), the removal efficiency of NO_x increased, however the removal of O_3 was compromised. Nonetheless, in these conditions the average NO_2 clean air delivery rate was 661.32 and 550.8 $m^3 \cdot h^{-1} \cdot m^{-3}$ of biofilter substrate respectively for *S. wallisii* and *S. podophyllum*. Furthermore, the lighting conditions and selection of plant species affected the degree of NO_x removal. It is possible that differences in plant surface area or surface composition may have influenced the rate of pollutant deposition. In addition to these affects, the VOC emission profile and concentration associated with each plant species may have affected the chemical transformations of NO_x and O_3. Further research is needed to establish how these chemical transformations may play out under pollutant concentrations and conditions representative of urban environments. Long term experiments under *in situ* conditions are needed to establish practical removal rates and plant health effects resulting from prolonged exposure to air pollution.

4.7 Author Contributions

Conceptualization, T.P. and F.R.T; methodology, T.P.; software, N.C.S.; formal analysis, T.P.; investigation, T.P., P.J.I., N.C.S. and F.R.T.; resources, T.P. and N.C.S.; data curation, T.P. and N.C.S.; writing—original draft preparation, T.P.; writing—review and editing, P.J.I., N.C.S. and F.R.T.; supervision, P.J.I., N.C.S. and F.R.T.; project administration, T.P., P.J.I., N.C.S. and F.R.T.

4.8 Funding

This research received no external funding. T. Pettit is supported by an Australian Government Research Training Program Scholarship. P.J. Irga is supported by the UTS Chancellor's Postdoctoral Research Fellowship scheme, facilitated through The Centre for Green Technology.

4.9 Acknowledgements

The authors thank Sue Fenech, Gemma Armstrong and Rachel Keeys for their technical support.

Preface: Chapter 5

The filtration capacities demonstrated in the previous laboratory and indoor studies (Chapters 2-4) has led to the need to implement active green walls in outdoor environments and assess their capacity to filter traffic associated pollutants *in situ*. This chapter assesses the botanical biofiltration of traffic associated air pollutants by 5 active green walls at two sites in Sydney.

The work presented in this chapter has been published in the *Journal of Hazardous Materials*:
Pettit, T., Torpy, F.R., Surawski, N.C., Fleck, R. and Irga, P.J., 2021. Effective reduction of roadside air pollution with botanical biofiltration. *Journal of Hazardous Materials*, p.125566.
This chapter is written verbatim to this article.

Author Contributions:
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Chapter 5

5. Effective reduction of roadside air pollution with botanical biofiltration

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5.1 Abstract

Currently no sustainable, economical and scalable systems have been developed for the direct removal of roadside air pollutants at their source. Here we present a simple and effective air filtering technology: botanical biofiltration, and the first field assessment of three different botanical biofilter designs for the filtration of traffic associated air pollutants – NO_2, O_3 and $PM_{2.5}$ – from roadside ambient air in Sydney, Australia. Over two six month research campaigns, we show that all of the tested systems filtered NO_2, O_3 and $PM_{2.5}$ with average

single pass removal efficiencies of up to 71.5%, 28.1% and 22.1% respectively. Clean air delivery rates of up to 121 m^3/h, 50 m^3/h and 40 m^3/h per m^2 of active green wall biofilter were achieved for the three pollutants respectively, with pollutant removal efficiency positively correlated with their ambient concentrations. We propose that large scale field trials of this technology are warranted to promote sustainable urban development and improved public health outcomes.

Key words: green infrastructure; green wall; living wall; air quality; traffic pollution; urban greening

Highlights

- Botanical biofiltration of NO_2, O_3 and $PM_{2.5}$ was achieved at roadside environments.
- NO_2 was removed most efficiently, with a single pass removal efficiency of 71.5%.
- Pollutant clean air delivery rates of 40–121 m^3/h per 1 m^2 plenum were achieved.
- All pollutant removal rates were positively correlated with ambient concentrations.

5.2 Introduction

Ambient air pollution is the most significant current environmental risk to human health, with approximately 4.2 million deaths around the globe each year attributed to exposure to ambient air pollution (WHO 2019). Urban air pollution is particularly concerning, where vehicle exhaust and industrial emissions lead to elevated air pollution levels in environments inhabited by the majority of the world's population (WHO 2019). Urban air pollution is comprised of a complex mixture of suspended particles, (particulate matter; PM), and gaseous pollutants, including nitrogen oxides (NO_x), ozone (O_3), amongst other pollutants (Venkatram and Schulte 2018). Vehicular emissions, particularly in locations with high traffic densities, are the main source of harmful air pollutants in many urban areas (European Environmental Agency, 2011). Because traffic related pollutants are emitted close to ground level, elevated pollution concentrations frequently occur in 'on-road' or 'near-road' environments, whereby the urban population, including drivers, commuters, pedestrians and occupants of nearby buildings, is exposed to heightened pollution concentrations (Karner et al, 2010; Pasquier and André, 2017). Furthermore, the dispersion of ground level traffic emissions may be limited by urban geometries and structures, such as buildings, and in some

cases, tree canopies (Abhijith et al. 2017; Venkatram and Schulte 2018), thus promoting the accumulation of air pollution in zones where people are likely to be exposed.

The health effects resulting from exposure to urban air pollution are associated with huge economic impacts (Pascal et al. 2013). Therefore, work directed towards air pollutant mitigation is of the greatest importance, as are effective new technologies aimed at reducing the concentration of air pollutants in environments where human exposure is at its highest.

Botanical biofilter technology, which generally takes the form of active green walls, has been developed from an extension of the concept of phytoremediation (Irga et al. 2018). These systems have plants arranged along a vertical pane and use 'active airflow' to mechanically force an airstream through the plant foliage and growth substrate, where it exits to the ambient air (Pettit et al. 2018a). In this process, PM is mechanically filtered by the growth matrix, and gaseous pollutants such as VOCs, O_3 and NO_2 can be biodegraded by the microorganisms contained in the growth substrate or removed from the airstream by adhering to substrate adsorbents (Pettit et al. 2018b). Several studies have suggested that such systems (or similar botanical biofilters) can make functional improvements to the air quality of indoor environments (Darlington et al. 2001; Ibrahim et al. 2019; Pettit et al. 2019c; Wang and Zhang 2011).

Although active green wall research has been limited to laboratory studies and indoor air quality investigations, traditional urban forestry, such as street trees, hedges and shrubs, have been thoroughly studied for their capacity to remove urban air pollutants (Abhijith et al. 2017; Petrova 2020). Nowak et al. (2006) suggested that urban trees and shrubs remove 711,000 metric tons (US$ 3.8 billion value) of air pollution (O_3, PM_{10}, NO_2, SO_2, CO) across the United States of America each year, whereby pollutants are removed through foliar processes such as stomatal uptake and wet and dry deposition. Several studies however, have noted that in some cases, particularly in street canyons, there is potential for urban tree canopies to limit the diffusion of air pollution from sources such as traffic, and thus, increase the concentration of air pollution at ground level (Gromke et al 2008; Jeanjean et al. 2017; Salmond et al. 2013; Vos et al. 2013). Alternatively, passive green walls may be used in both street canyons and open road settings to provide improvements to air quality, primarily through hindering the dispersion of pollutants from reaching relevant exposure zones (Abhijith et al. 2017; Abhijith and Kumar 2019). Nonetheless, current technologies that attempt to mitigate ground level air pollution exposure in urban contexts, including roadside vegetation barriers and solid barriers (Gallagher et al. 2015; Tong et al. 2016), primarily work

through altering pollutant dispersion rather than reducing the pollutant load from the ambient air through filtration and bioremediation.

The use of airflow in botanical biofiltration promotes the rate at which substrate-associated pollutant removal processes operate, whilst adding the effects of bioremediation and filtration; thus removing air pollution from the ambient air rather than simply shifting pollutant dispersion, and thereby providing a promising means to considerably improve urban air quality. Additionally, the small ground and canopy footprint of green walls allows these systems to be installed in spatially constrained urban areas (Abhijith et al. 2017). Due to the extensive range of environments in which this technology can be applied and the vast range of adjunct benefits provided, including urban stormwater management, temperature reductions, acoustic attenuation and enhanced scenic landscape (Attal et al. 2017; Horoshenkov et al. 2011; Manso and Castro-Gomes 2015); the assessment of botanical biofilters for air quality enhancement is of major value for sustainable urban design, and is of international scope. Botanical biofilters have been shown to make functional improvements to the air quality of indoor environments (Darlington et al. 2001; Pettit et al. 2019c; Wang and Zhang 2011), and are beginning to be built for this purpose in urban areas, however their efficacy in outdoor environments remains untested. Here, we aim to build on indoor and laboratory research to evaluate the use of this technology as a solution to improve air quality alongside major roads.

In this investigation, we firstly assess the single pass removal efficiency (SPRE) of traffic associated air pollution achieved by botanical biofiltration. This was accomplished by conducting extensive air quality monitoring across several independent botanical biofilter arrays to assess the biofiltration efficiency for $PM_{2.5}$ (fine suspended particles with an aerodynamic diameter less than 2.5 μm), NO_2 and O_3 from the ambient air of two roadside environments in Sydney. Secondly, we consider the contribution of cleaned air produced by three biofilter designs by evaluating removal efficiencies in conjunction with airflow characteristics to determine the clean air delivery rate (CADR) for the systems when trialled *in situ*. Finally we explore the relationship between removal efficiency and ambient pollutant concentration for each of the pollutants. The combined findings demonstrate the potential for the implementation of this new technology to promote sustainable urban development areas and improved public health outcomes.

5.3 Methods

5.3.1 Site description and botanical biofilter orientation

Botanical biofiltration arrays were installed at two different roadside environments in Sydney. Sydney is Australia's most populous urban centre, with an estimated population of 5.2 million residents (Australian Bureau of Statistics 2019). Emissions from motor vehicles are a major source of air pollution in Sydney (NSW Health 2014; Paton-Walsh et al. 2019) and are the largest contributors of NO_x (Cowie et al. 2019) and $PM_{2.5}$ pollution (Crawford et al. 2017). Motor vehicles also emit VOCs, which are important precursors in the formation of ozone (NSW Health 2014). Traffic counts at both sites during the experimental period were sourced from Transurban (2020).

5.3.2 Site 1: Eastern Distributor

Two biofilter arrays were installed alongside the Eastern Distributor, situated immediately adjacent to north bound traffic so that the biofilter arrays were flush against the traffic barrier closest to the road. The Eastern Distributor Motorway (33°52'12.2"S 151°13'05.8"E) is located in the City of Sydney local government area, and is one of Australia's busiest roads and is located in one of Australia's most densely populated areas (Roads and Maritime Services 2018). To provide spatial independence, the biofilter arrays on site were separated from each other by 30 m. Sampling took place from June 2019 to November 2019.

5.3.3 Site 2: Hills Motorway

The Hills Motorway (M2; 33°46'09.6"S 151°06'58.4"E) site was located approximately 13 km north-west of Sydney's central business district within the local government area of the City of Ryde. This installation was positioned on an unused asphalt area between Southeast bound traffic on the Hills Motorway and the Christie Rd exit ramp. This area is separated from the Southeast bound traffic on the Hills Motorway by concrete ('Jersey') barriers. Three biofilter arrays were situated immediately adjacent to southeast bound traffic, on the immediate edge of the Hills Motorway's southeast bound lanes. At this site, there was at least 50 m between biofilter arrays to ensure that the effects of one biofiltration array would not confound measurements at the others. Sampling at this location took place from November 2019 to May 2020.

As it was hypothesized that the ambient pollution profile and concentration would affect filtration efficiency, the two sites were selected due to their different pollution characteristics. The Hills Motorway is comparatively more open (i.e. less urban development adjacent to the road) than the Eastern Distributor, and thus the dispersion of pollutants at this site may not be hindered to the same degree as that on the more developed Eastern Distributor. Different traffic speeds between the sites may also influence the associations between traffic volume and ambient air pollution concentration at each site. Although traffic speed was not measured in this study, the speed limit on the Hills Motorway is higher than that of the Eastern Distributor (100 km/h and 60 km/h respectively), and it is possible that faster traffic on the Hills Motorway promoted increased pollutant dispersal on the Hills Motorway (Venetsanos et al. 2001).

5.3.4 Botanical biofilters

Each of the five biofilter arrays (1 x 5 m wall surface area) held 20 biofilter modules (Breathing Wall; Junglefy Pty Ltd, Sydney, Australia) across five independent 1 m^2 plenums per array, as described in Pettit et al. (2020). Each module (0.5 x 0.5 x 0.15 m) was made from recyclable low-density polyethylene, with a front face area of 0.25 m^2 that contained 16 holes from which plants can grow. The biofilter arrays contained the following species of plants: *Westringia fruticosa* (coastal rosemary), *Myoporum parvifolium* (dwarf native myrtle), *Strobilanthes anisophyllus* (goldfussia) and *Nandina domestica* (heavenly bamboo). These species were selected for their survivability in Australian roadside environments. The internal space within the module was filled with a coconut husk-based plant growth substrate. A sheet of high-density polyethylene shade cloth lined the internal surfaces of the module to hold the plant roots and growth substrate within the module. The rear face of each module contained an opening in its centre (63.6 cm^2 cross sectional area), which was used to pull an airstream through the openings in the front face and through the growth substrate, after which it exited the module through this opening. A baffle plate was located against the internal rear face of the module to promote uniform airflow through the front face of the module. Each biofilter array was irrigated via a drip line with ~11 litres of water every 2 days. In addition to this irrigation, biofilter arrays were also exposed to rain and would have received supplementary irrigation through natural rainfall. Each biofilter module contained drainage holes allowing water to drain from each module if they were watered beyond field capacity.

To isolate the effluent airstream, modules were fixed to steel plenums, which contained fans to generate airflow. Each plenum was 1 x 1 m x 0.15 m (1 m^2 front face area) and held four botanical biofilter modules. The airstream passed into the plenum through four openings on the plenum's front face; these openings corresponded to the opening on the rear face of each of the modules. Two fans (NF-F12, Noctua; Austria) with an internal diameter of 120 mm, a volumetric flow rate of 186.70 m^3/h at 0.00 Pa of static pressure, and rated power consumption 4.32 W, were arranged in parallel on the rear face of the plenum. These generated active airflow that pulled air through the plant foliage and the front face of the module, through the opening in the rear face of the module, where the airstream then entered the plenum and exited the plenum to ambient via to vents adjacent to the fans in the rear face of the plenum. The vents matched the area of the fan outlet and used louvers to prevent rainwater from entering the plenum. Five plenums and their corresponding modules were arranged horizontally, creating 1 x 5 m biofilter arrays, which were supported on frames so that the base of the walls were ~ 1 m above the ground (Figure 27).

Figure 27. A botanical biofilter array. A) the rear view of a biofilter array showing five plenums arranged horizontally to form a 5 m^2 active green wall; B) a side view of the support structure with biofilter modules attached to the plenum; C) the front face of the biofilter array.

5.3.5 Botanical biofilter design comparisons

As this was the first time botanical biofilters had been assessed for traffic-associated air pollution removal in outdoor environments, it was unclear how some system aspects, such

as variations in airflow, would affect the overall performance. Thus, three different design iterations were used to investigate traits associated with optimum *in situ* performance (Table 7). In addition to the design iteration described above, one plenum on each biofilter array contained 4 granular activated carbon (GAC) cassettes housed within the four openings of the plenum's front face. In this design, the airstream would firstly pass through the biofilter module and then through a small cylinder (44 mm internal radius, 20 mm depth) containing GAC (GAC; EA1000 4 mm; Activated Carbon Technologies Pty Ltd, Melbourne, Australia). Although previous work has suggested that GAC can be used to enhance the SPRE of gaseous pollutants (Pettit et al. 2018b), it is unknown how it would influence the CADR in roadside environments, and for a range of behaviourally different pollutants. Lastly, one plenum on each biofilter array contained two fans with a larger volumetric flow rate (NF-A14, Noctua, Austria; 140 mm internal diameter, volumetric flow rate of 269.3 m^3/h at 0.00 Pa of static pressure, and a rated power consumption of 6.6 W. This treatment was included to test the effect of increasing volumetric airflow rate on CADR.

Table 7. The different botanical biofilter design iterations that were trialled in roadside environments.

Botanical biofilter iteration	Fan type	Fan diameter	Fan flow rate at 0 Pa static pressure (m^3/h)	Filtration components
1	NF-F12, Noctua	120 mm	186.70	Coconut husk-based plant growth substrate + 64 plants per 1 m^2
2	NF-F12, Noctua	120 mm	186.70	As for #1 with the addition of granular activated carbon cassettes
3	NF-A14, Noctua	140 mm	269.3	As for #1

5.3.6 Air quality measurement

The air velocity through each of the louvers was multiplied by the area of the louver opening to calculate the volumetric flow rate through each of the plenums. The airflow

through each of the plenums was measured with a VelociCalc Air Velocity Meter 9545 (TSI Incorporated; Shoreview, Minnesota, USA).

The concentrations of NO_2, O_3 and $PM_{2.5}$ were measured with a series of AQY1 – micro air quality monitoring systems (Aeroqual Limited; Auckland, New Zealand). Although Sydney is considered to have relatively 'good' air quality, $PM_{2.5}$ and O_3 are the air pollutants that most frequently occur in high levels (Paton-Walsh et al. 2019), while traffic emissions of NO_x account for 61.8% of the total annual NO_x emissions in the Sydney region (NSW EPA 2012). Two AQY1 instruments were located at each end of each biofilter array. These provided measurements of the proximal ambient air quality for each biofilter array. For assessment of air pollutant removal efficiency, AQY1 instruments were placed in each of the plenums, and thus detected the concentration of NO_2, O_3 and $PM_{2.5}$ in the isolated effluent airstream. Although these instruments have high detection resolutions (see Aeroqual Limited 2019) and were factory-calibrated before use, any systematic differences in the calibration of each instrument could potentially influence the accuracy of any comparisons amongst air pollution concentrations between the ambient and filtered effluent air. Thus, the locations of the instruments were randomly rotated several times throughout the experiment, both amongst plenums and ambient air detecting locations.

Average air pollution concentrations were calculated for each 5-minute period from 6:00 am to 6:00 pm. A 12-hour period overnight without fan operation provided temporal independence for each composite daily replicate of pollutant concentrations.

5.3.7 Data and statistical analysis

In order to make comparisons across treatments, the average ambient and average air pollution concentrations in the plenums of each treatment were calculated. The SPRE was calculated for each pollutant by comparing the average ambient air pollutant concentrations to the average air pollution concentrations detected in the isolated effluent airstreams of each biofilter.

Unlike assessments of air pollutant removal provided by passive vegetation, whereby phytoremediation of air pollution is usually measured as mass of pollutant removed, the use of active airflow in botanical biofiltration allows removal rates to be expressed as clean air delivery rates (CADRs). This metric is a function of the proportion of influent pollution that has been removed on a single pass through the biofilter, multiplied by the volumetric airflow

rate through the biofilter. The CADR of each pollutant thus describes the volume of 'clean' air produced by the biofilters, and is generally considered to be the best metric to evaluate air cleaning potential (Zhang et al. 2011). Further, converting the SPREs for each pollutant to CADRs facilitated valid comparisons of the treatments with different airflow rates. Differences in the CADR amongst treatments were statistically compared through ANOVA (IBM SPSS Statistic Ver 25).

Additionally, the SPRE of each pollutant was considered as a function of the ambient pollutant concentration to assess the relationship between removal efficiency and pollutant concentration. The average pollutant concentrations and biofilter SPREs from both sites at each time sample were included in this correlation, thus ensuring bivariate normality of each data point.

The ambient concentration of $PM_{2.5}$ at each site was used as a surrogate pollutant to test associations between air pollution and the traffic densities at each site. A Pearson's correlation analysis was used to test the association between the average ambient $PM_{2.5}$ concentration at each 15-minute interval and the volume of passing cars and trucks at each site.

The presence of the *Black Summer* bushfires between November 2019 – February 2020 considerably altered the ambient air quality, and thus, the contribution of traffic related emissions to the overall ambient pollution load and the corresponding temporal fluctuation of the pollutants throughout each day. Consequently, days where air quality was strongly influenced by bushfire emissions were eliminated from the data. These days were identified by using the ambient $PM_{2.5}$ concentration as an indicator variable in a time series analysis, whereby the daily variation in the $PM_{2.5}$ concentration was broken down into 'trend', 'cyclical' and 'random' components. As $PM_{2.5}$ is strongly associated with traffic emissions and contributes to a daily cyclical pattern of atmospheric $PM_{2.5}$, days where the 'random' variation in $PM_{2.5}$ exceeded that of the maximum 'cyclical' variation in $PM_{2.5}$ concentration (see Pettit et al. 2020) were defined as bushfire days and excluded from analysis, as these days were not representative of Sydney's normal air quality. Data from weekdays were used for analyses, with data from weekends excluded due to differences in traffic volumes and the presence of the 'ozone weekend effect', which commonly leads to higher concentrations of O_3 on weekends in urbanised areas due to alterations in the local atmospheric VOC to NO_x ratio (Gao and Niemeier 2007; Pont an Fontan 2001; Wolff et al. 2013).

5.4 Results

The Eastern Distributor had an average daily (6:00 am to 6:00 pm) traffic count of 33,267 cars and 1,175 trucks in the adjacent northbound lanes over the course of sampling at this site (Transurban 2020). The section of the Hills Motorway adjacent to the biofilter arrays had an average bidirectional daily traffic (6:00 am to 6:00 pm) count of 70,985 cars and 4,691 trucks over the course of sampling at this site (Transurban 2020).

At each site, ambient concentrations of all pollutants were associated with traffic density, as expected. At the Eastern Distributor the average daily ambient $PM_{2.5}$ concentration at each 15-minute interval was significantly correlated with the passing volume of cars ($r = 0.372$, $p = 0.012$, $n = 48$) and trucks ($r = 0.625$, $p = 0.000$, $n = 48$), while the daily ambient $PM_{2.5}$ concentration at each 15-minute interval was significantly correlated with the volume of passing trucks at the Hills Motorway ($r = 0.550$, $p = 0.000$, $n = 48$). At the Eastern Distributor, pollutant concentrations were generally higher and exhibited greater fluctuations throughout each day, due to greater variations in traffic volume (Figures 28-29).

The average concentrations of the three pollutants detected in the effluent of all biofiltration treatments were lower than the ambient pollutant concentrations, thus all treatments had positive SPREs for all pollutants (Figures 28-29), indicating that filtration of $PM_{2.5}$, NO_2 and O_3 from the ambient air at two different roadside environments was achieved.

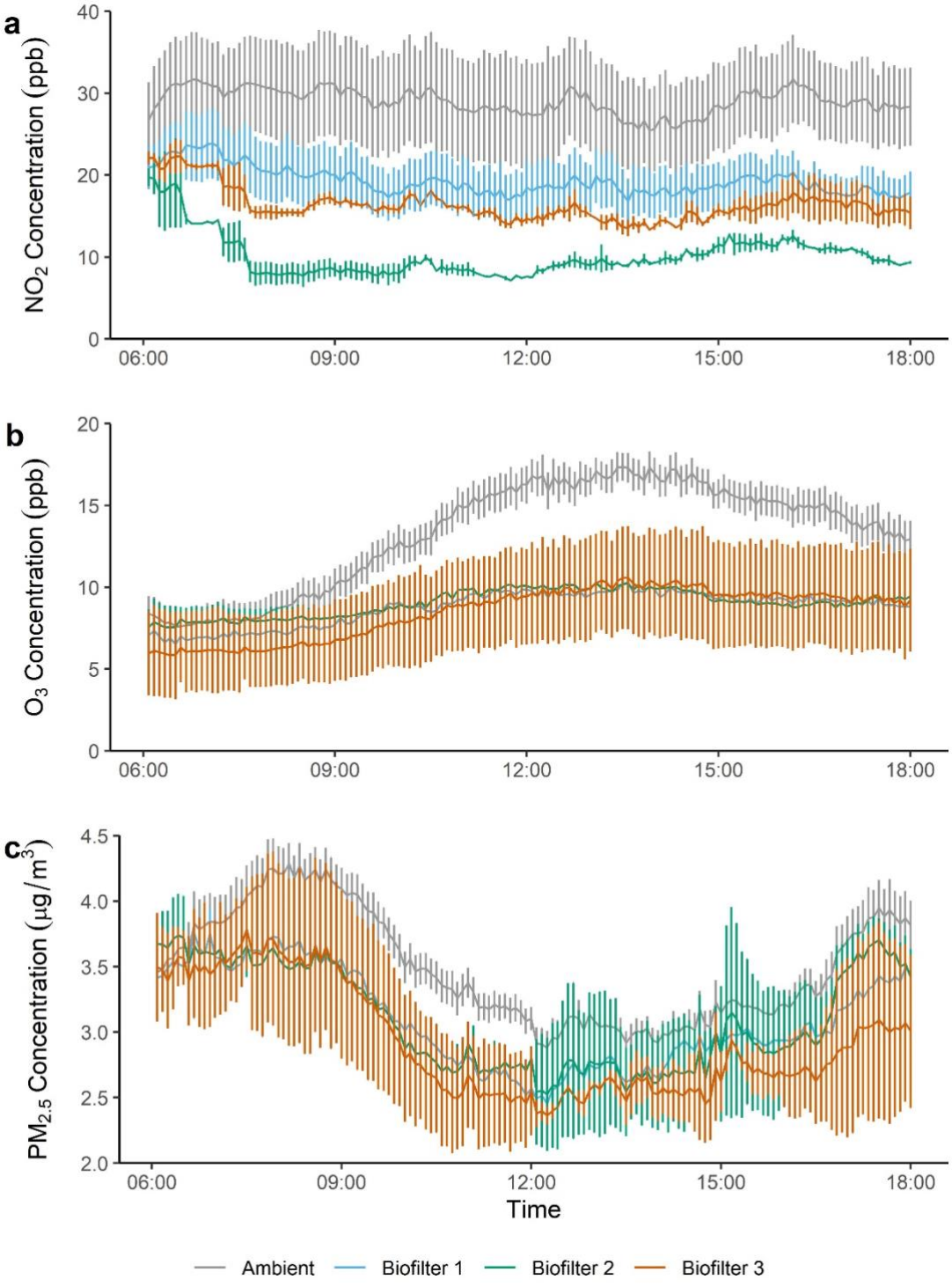

Figure 28. The average ambient and filtered effluent concentrations of air pollutants at the Eastern Distributor for each time point across the trial period of June 2019 to November 2019 (means ± SEMs). a = NO_2; b = O_3; c = $PM_{2.5}$. Biofilter 1: fans with 186.70 m^3/h flow rate at 0 Pa static pressure, Biofilter 2: fans with 186.70 m^3/h flow rate at 0 Pa static pressure + granular activated carbon cassettes, Biofilter 3: fans with flow rate of 269.3 m^3/h at 0 Pa static pressure.

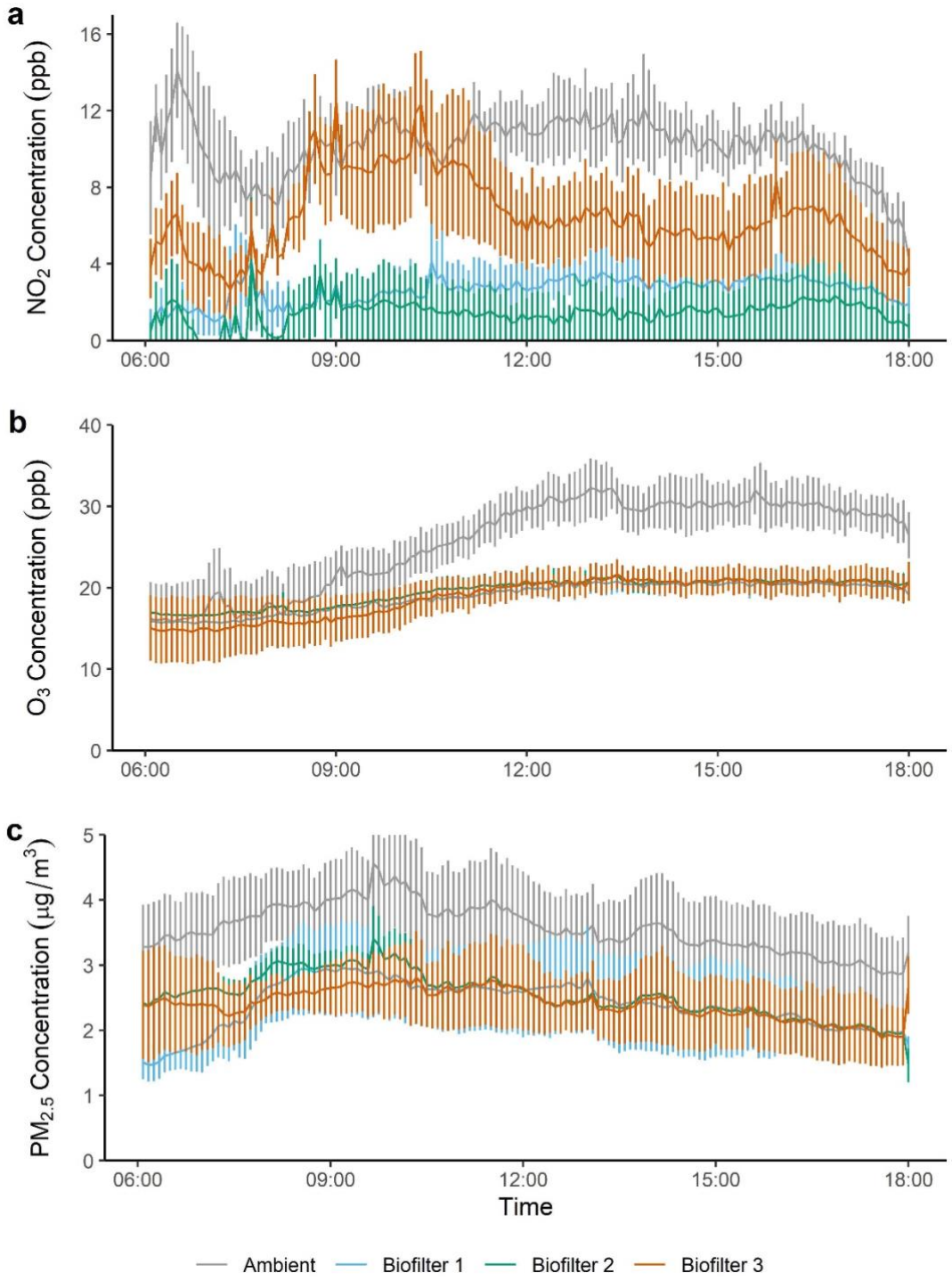

Figure 29. The average ambient and filtered effluent concentrations of air pollutants at the Hills Motorway for each time point across the trial period of November 2019 to May 2020 (means ± SEMs). a = NO_2; b = O_3; c = $PM_{2.5}$. Biofilter 1: fans with 186.70 m^3/h flow rate at 0 Pa static pressure, Biofilter 2: fans with 186.70 m^3/h flow rate at 0 Pa static pressure + granular activated carbon cassettes, Biofilter 3: fans with flow rate of 269.3 m^3/h at 0 Pa static pressure.

The average airflow through each of the plenums using 120 mm fans was 169.02 ± 4.37 m^3/h. The average airflow through plenums containing GAC was 169.01 ± 11.17 while the average airflow of plenums with 140 mm fans was 178.41 ± 22.68 m3/h.

The SPREs were taken as a function of airflow rate to calculate the CADR of each treatment (Figure 30). The plenums with larger fans and thus the highest volumetric flow rates achieved the highest CADRs for ozone and $PM_{2.5}$, while the biofilter incorporating GAC produced the largest CADR for NO_2. The CADRs of all of the pollutants however, were not statistically different amongst the biofilter treatments or sites (two-way ANOVA for each pollutant; in all cases p >0.05 for both factors; Table 8).

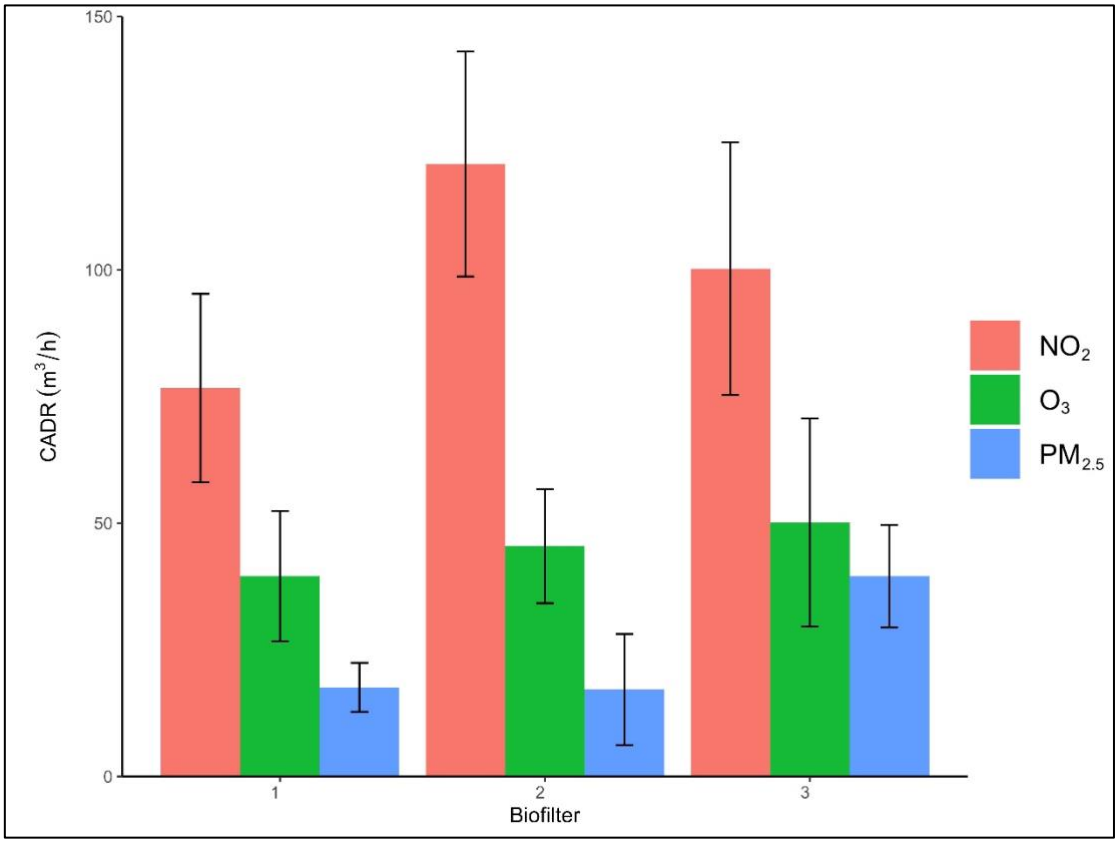

Figure 30. The average clean air delivery rates (CADRs) for 1 m^2 biofilter plenums across treatments, consolidating data from both sites (means ± SEMs). Biofilter 1: fans with 186.70 m^3/h flow rate at 0 Pa static pressure, Biofilter 2: fans with 186.70 m^3/h flow rate at 0 Pa static pressure + GAC cassettes, Biofilter 3: fans with flow rate of 269.3 m^3/h at 0 Pa static pressure (n = 14, 5 and 5 independent plenums for Biofilters 1, 2 and 3 respectively). There were no significant differences in the CADR of each pollutant amongst biofilter treatments.

Table 8. Results comparing the CADRs amongst the three biofilter treatments and the two sites. A two factor ANOVA was used for each air pollutant.

Pollutant	Source	df	*F*	*p*
NO_2	Site	1	3.597	0.076
	Treatment	2	0.541	0.593
	Site x treatment	2	0.235	0.793
O_3	Site	1	2.248	0.151
	Treatment	2	0.507	0.611
	Site x treatment	2	0.435	0.654
$PM_{2.5}$	Site	1	0.107	0.747
	Treatment	2	1.885	0.181
	Site x treatment	2	0.526	0.6

A series of Pearson's correlations assessing the association between ambient concentrations of the three pollutants and the SPREs of each treatment showed that almost all treatments exhibited statistically significant positive relationships between removal efficiency and pollutant concentration (Table 9). As the ambient concentration of all pollutants increased, the SPRE of all treatments increased as well. This trend was particularly strong for O_3 across all biofilter treatments.

Table 9. Pearson's correlation matrix of associations between SPRE and ambient pollutant concentration. n = 144 observations for each correlation. * indicates statistical significance whereby p = <0.05. Pearson's r values are shown.

Treatment	**Ambient NO_2 concentration**	**Ambient O_3 concentration**	**Ambient $PM_{2.5}$ concentration**
Plenum SPRE	0.166*	0.980*	0.203*
GAC SPRE	0.141	0.976*	0.572*
140 mm Fan SPRE	0.165*	0.946*	0.167*

5.5 Discussion

Mitigating air pollution resulting from traffic emissions is becoming increasingly problematic in urban regions, particularly so in built-up areas, where population exposure to urban air pollution is likely to increase in the next decade as urban development disproportionately occurs along main road sites (Paton-Walsh et al. 2019). Most current air pollution mitigation strategies aim to reduce source emissions, with varying effectiveness on ambient air quality (Carslaw et al. 2016; Zhang and Gu 2013), but there are no methods currently employed on a medium to large scale for the active reduction of roadside pollution *in situ*. This work represents the first field assessment of a novel botanical biofiltration system for the mitigation of NO_2, O_3 and $PM_{2.5}$ from traffic emissions. In all cases, the concentrations of these pollutants were considerably reduced by the biofilter treatments, so that the concentrations of all pollutants were lower in the effluent air stream than in the ambient air.

5.5.1 NO_2 filtration

The concentration of NO_2 in the effluent air was considerably lower than ambient, irrespective of the ambient NO_2 concentrations, with average SPREs across all sampling periods ranging from 57.81-75.63%, depending on the treatment. While there were clear differences in the ambient concentration profile of the pollutants between the two sites, the average daily temporal pattern of NO_2 was consistent within sites, with neither site showing clear fluctuations in NO_2 concentration related to traffic volume or sunlight intensity.

When standardised by substrate volume, the NO_2 CADRs recorded in this study are substantially higher (by ~20-30%) than those detected under elevated NO_2 concentrations in Pettit et al. (2019b), most likely due to the use of different systems and pollutant inlet concentrations between the studies. The volumetric airflow rate has been a critical parameter for determining the optimal CADR of biofilters (Guieysse et al. 2008). This has most commonly been explored through the removal of VOCs, whereby larger airflow rates lead to reduced SPREs but often increased CADRs by increasing the volume of air that is processed (e.g. Wang and Zhang 2011). In this case however, the different airflow rates provided by different fans did not lead to significant differences in the NO_2 CADR amongst the treatments, and it is likely that greater variation in volumetric flow rates will be required to produce significant differences in CADRs. Additionally, the use of GAC did not significantly

increase the NO_2 SPRE, in contrast to previous studies where activated carbon has been used successfully to filter NO_2 from contaminated air streams (Yoo et al. 2015). Nonetheless, the GAC augmented biofiltration treatment used in this experiment did not considerably reduce the airflow rate (i.e. volumetric airflow rates where very similar to that of the plenums without GAC cassettes), and thus did not compromise the CADRs. The use of different activated carbon-based adjunct filter designs (modifications to GAC type and volume) requires further exploration to thoroughly determine whether effects similar to that observed in laboratory studies (Yoo et al. 2015) can be achieved.

As this work did not measure the ambient or filtered concentrations of VOCs, this remains an important consideration for future research. Previous work conducted in laboratory scale experiments (Pettit et al. 2019a; Treesubsuntorn and Thiravetyan 2018) and indoor trials (Darlington et al. 2001; Pettit et al. 2019c; Wang and Zhang 2011) has highlighted that botanical biofilters are efficient at filtering a range of different VOCs, however it remains unknown how such systems can filter specific VOC mixtures and concentrations associated with traffic emissions. Furthermore, it is important to monitor any possible VOC emissions emitted by the biological components of the system as there is potential for VOCs to react with NO_2 to lead to the formation of O_3 (Atkinson 2000).

5.5.2 O_3 filtration

The ambient concentration of O_3 generally increased through the day at both sites – as is commonly observed in urban areas (Pancholi et al. 2018; Warmiński and Bęś 2018). Although the concentration of NO_2 was higher at the Eastern Distributor site than the Hills Motorway, the concentration of O_3 was higher at the Hills Motorway than the Eastern Distributor, which may reflect the seasonal differences in sampling periods between the two sites (Warmiński and Bęś 2018). In all cases, the concentration of O_3 in the effluent air stream generally started out equal to the 6 am ambient O_3 concentrations, and remained at this level, while the ambient concentration rose throughout the day. Although it is possible that there is a threshold concentration of O_3 that cannot be filtered with the system tested here, the different concentrations of O_3 at each site, in both the ambient and effluent air streams of all biofilter treatments suggests such possible effects may be concentration dependent. Both NO_2 and O_3 are photo-chemically sensitive under sunlight conditions (Atkinson 2000). As the plenum intercepted sunlight, it is difficult to determine what effect

the plenum alone may have had on these pollutants, however the contribution of any possible effects on the NO_2 or O_3 concentrations resulting from shading are likely to be minimal due to the short residence time of effluent gas within the plenums (~2 s).

Although the botanical biofiltration of NO_2 and O_3 has been observed in laboratory studies using spiked pollutant concentrations (Pettit et al. 2019b), this work represents the first instance whereby the continuous removal of traffic sourced pollutants by botanical biofiltration has been recorded. The *in situ* measurements from this study provide a more accurate estimate of the air cleaning potential of botanical biofiltration than scaled up estimates from laboratory studies, and reflect their likely performance for their intended purpose. Nonetheless the decay rates observed in the laboratory studies resulting from a spiked pollutant concentration are difficult to compare to the filtration effects demonstrated here from a continuous emission of pollutants.

The fate of the filtered pollutants, and their ramifications for the biofiltration system, remains unclear. Previous work has noted the potential production of nitric acid within the growth substrate, as NO_2 combines with irrigation water to produce nitric acid and NO (Zheng et al. 2016). Alternatively, the co-biofiltration of O_3 and NO_2 may affect a form of pH control due to the generation of alkaline products from O_3 biofiltration (Maldonado-Diaz and Arriaga 2015). Although it was not the intention to assess filtration products within the media in this study, any changes in substrate pH were insufficient to visibly affect plant health or influence system performance.

5.5.3 $PM_{2.5}$ filtration

The average $PM_{2.5}$ CADRs through the botanical biofilters were lower than those of the gaseous pollutants. Irga et al.'s (2017b) laboratory study used a spiked dose of particles from combusting diesel fuel, and observed greater botanical biofilter $PM_{2.5}$ SPREs than this study (~48%). It is unknown whether the chemical composition and size distribution of particles differ between these studies, and it is possible that variation in these characteristics may have led to these discrepancies, as larger particles are removed with greater efficiency (Pettit et al. 2017). Nonetheless, the SPREs presented in the current work reflect the removal of particle compositions encountered in roadside environments. Although there were no significant differences in the $PM_{2.5}$ CADR amongst the treatments using different airflow rates in this study, Irga et al. (2017b) found that the rate constant of $PM_{2.5}$ concentration

decay increased with volumetric flow rate through the filter until a threshold airflow rate was reached. It is possible similar effects were not observed in this experiment due to the relatively small differences in airflow rates amongst the treatments. The current findings also show that the $PM_{2.5}$ SPRE will vary throughout the day, as the concentration of $PM_{2.5}$ in the effluent airstreams closely mirrored the fluctuating pattern of the $PM_{2.5}$ inlet concentration at both sites.

While the methods employed in this experiment simply detected reductions in the $PM_{2.5}$ concentration from filtration, passive green walls have demonstrated potential to accumulate particles on their foliage surfaces. The degree to which plant foliage intercepts particles has been linked to both leaf scale traits such as stomatal density, presence of trichomes, ridges and grooves (Weerakkody et al. 2018a; 2018b), and the structure and topography provided by grouping of plants (Weerakkody et al. 2019). It is plausible that these same mechanisms would apply to active green walls, and particle filtration by the plant foliage should be considered in other studies. While this work has demonstrated plant foliage can accumulate particles, it is unclear what effect this is likely to have on the ambient air quality. Research into the air quality effects of active and green walls should aim to quantify this in future studies and establishing an understanding of the contribution of each air cleaning mechanism in a green wall system would enable appropriate plant species selection and enable targeted design improvements.

Particles were removed at different efficiencies to that of the gaseous pollutants, highlighting the clear differences in the chemical and physical properties of each pollutant. It is likely that NO_2 was removed with greatest efficiency due to its ability to interact with water. Interestingly, the composition of particles can vary depending on their source and it is possible that $PM_{2.5}$ of different chemical compositions may be removed with different removal efficiencies.

5.5.4 Incorporation into urban design and future developments

The results from this study demonstrate proof of concept for *in situ* botanical biofiltration, and suggest that botanical biofilters may be an effective solution to help mitigate air pollution exposure. With the tested biofilter systems, however, the pollutant reduction effects are unlikely to impact the ambient air quality outside of the zone immediately adjacent to the biofilter array. The implementation of larger arrays in targeted locations will thus be

required to have such an effect, and while the relationship between CADR and wall size is clear, the relationship between wall size and ambient air quality effect remains untested at this stage. There is considerable potential to implement large green walls, since such infrastructure consumes relatively little space at street level. In the case of the current experiment, the size of the green walls could be considerably increased by extending their height; in this regard, the green wall would consume the same ground footprint yet have a larger area and filtration capacity.

Careful site selection will likely be needed to obtain effective biofiltration, and thus realize the greatest benefits in ambient air quality enhancement. While the ambient pollution profile may influence filtration efficiency, the urban geometry and airflow characteristics of the site will affect both the dispersion of air pollution emissions (Di Sabatino et al. 2013) and the dispersion of filtered air. Environments where the dispersion of air pollution emissions is limited, such as car parks and traffic tunnels, promote the accumulation of air pollution, and thus the use of botanical biofilters may be of considerable value in such locations. Additionally, botanical biofilters may find value in environments where other forms of greening, such as trees, cannot be used. Nonetheless, the positive association between removal efficiency and ambient pollution concentration detected in the current research suggests that botanical biofilters are most effective in those environments where they are most needed. Although positive associations between SPRE and ambient concentrations were detected across the range of ambient pollution concentrations observed in this study, previous work testing SPREs at higher pollution concentrations has shown inverse relationships between these variables (Pettit et al. 2020), and further work is still required to understand the complex relationship between biofilter pollutant removal efficiency across the range of relevant ambient concentrations.

It is clear that different forms of urban greening are associated with different effects on ambient air pollution concentrations. Passive green walls have been recommended as a suitable green infrastructure for reducing PM concentrations through the deposition of PM onto plant foliage, without affecting the air exchange between the street canyon and air above it (Abhijith et al. 2017; Litschke and Kuttler 2008). Furthermore, passive walls are able to alter the flow and dispersion patterns of air pollutants, so that pedestrian pollutant exposure may be reduced in open road conditions (Abhijith et al. 2017). The air quality reductions detected in our study were simply the result of biofiltration, and future work, with the use of modified and larger active botanical biofilters, is needed to determine the effect of these combined mechanisms on ambient pollutant concentrations. While the behaviour of air

pollution in the atmosphere is commonly modelled, the concept of modelling the dispersion and behaviour of 'clean air' is a novel concept and thus *de novo* research is necessary to truly assess biofilter effects on ambient air quality.

This work has demonstrated the potential for botanical biofilters to filter traffic associated air pollutants – NO_2, O_3 and $PM_{2.5}$ – from roadside environments. Clean air delivery rates of up to 121 m^3 /h, 50 m^3 /h and 40 m^3 /h per m^2 of active green wall biofilter were achieved for the three pollutants respectively, with pollutant removal efficiency positively correlated with their ambient concentrations. On the basis of this research, several infrastructure-scale systems are planned for installation in critical locations around Australia. Future work will thus aim to assess the influence of these systems on the general ambient air quality conditions experienced by populations residing proximal to the biofilters.

5.6 Funding

This work was supported by Transurban Ltd and Jobs for NSW [F19 7192]. T. Pettit and R. Fleck are supported by Australian Government Research Training Program Scholarships. P.J. Irga is supported by the University of Technology Sydney (UTS) Chancellor's Postdoctoral Research Fellowship scheme, facilitated through The Centre for Green Technology.

5.7 Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Preface: Chapter 6

In addition to assessing the biofiltration of traffic associated pollutants, the Black Summer wildfire that affected Australia over the summer or 2019-2020 provided a novel opportunity to assess the biofiltration of bushfire associated pollutants. This chapter thus describes the first trial of an outdoor, infrastructure scale filtration system of any type to ameliorate high concentrations of wildfire associated pollutants.

The work presented in this chapter has been published in the *Journal of Hazardous Materials Letters*:

Pettit, T., Irga, P.J. and Torpy, F.R., 2020. The botanical biofiltration of elevated air pollution concentrations associated the Black Summer wildfire natural disaster. *Journal of Hazardous Materials Letters*, *1*, p.100003.

This chapter is written verbatim to this article.

Author Contributions:

Thomas Pettit: Conceptualization, methodology, software, formal analysis, investigation, data curation, writing - original draft, visualisation, project administration, funding acquisition. **Peter J. Irga:** Methodology, investigation, writing - review & editing, visualisation, supervision, project administration, funding acquisition. **Fraser R. Torpy:** Conceptualization, methodology, investigation, writing - review & editing, visualisation, supervision, project administration, funding acquisition.

Chapter 6

6. The botanical biofiltration of elevated air pollution concentrations associated the Black Summer wildfire natural disaster

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6.1 Abstract

The '*Black Summer*' wildfires that affected Australia over the 2019-2020 summer have led to concern over the health effects of exposure to wildfire emissions, and generated a need for means to reduce exposure. Recently, active green infrastructure has been implemented in cities to assist in the removal of urban air pollution, however the filtration of wildfire emissions has not been previously tested. Here, we field trial botanical biofiltration for the reduction of elevated air pollutant concentrations associated with *Black Summer*. Two active green walls were installed in outdoor environments in Sydney over *Black Summer*, with the concentrations of NO_2, O_3 and $PM_{2.5}$ in ambient and filtered air streams monitored over 14 days with elevated air pollution concentrations due to wildfire emissions. Average pollutant single pass removal efficiencies of 63.17%, 38.79% and 24.84% for NO_2, O_3 and $PM_{2.5}$ respectively were recorded, with clean air delivery rates of 558.90 m^3/h, 343.19 m^3/h and 219.77 m^3/h for NO_2, O_3 and $PM_{2.5}$ respectively for each 5 m^2 biofilter wall. Weak negative associations were observed between the removal efficiency of NO_2 and $PM_{2.5}$ and their corresponding ambient concentrations. Strategic employment of botanical biofiltration may thus be of value in reducing wildfire emissions in sensitive populations.

Keywords: botanical biofilter; green wall; living wall; green infrastructure; bushfire

Highlights:

- Active green walls demonstrated removal of NO_2, O_3 and $PM_{2.5}$ from wildfire smoke.
- NO_2 was removed most efficiently, with a single pass removal efficiency of 63.17%.
- Clean air delivery rates of 220-559 m^3/h were achieved for all pollutants.
- NO_2 and $PM_{2.5}$ removal rates were negatively correlated with ambient concentrations.

6.2 Introduction

Over recent decades, fire weather seasons have increased in frequency and intensity across a quarter of the earth's vegetated surface, and the global burnable area affected by long season fire has doubled (Jolly et al., 2015). This trend will likely be associated with an increase in population exposure to wildfire smoke and corresponding health impacts. Strong correlations have been identified between wildfire smoke exposure and both respiratory morbidity and all-cause mortality, and have been attributed to an estimated 339,000 annual deaths worldwide (Analitis et al. 2012; Johnston et al. 2012; Stauffer et al. 2020). These effects are likely to be more pronounced in wildfire 'hot spots' such as Australia, wherein recent climatic shifts have been associated with considerably increased wildfire frequencies, particularly during dry summers (Dutta et al. 2016).

Wildfire smoke contains a mixture of harmful pollutants. Fine particulate matter ($PM_{2.5}$: particles with an aerodynamic diameter less than 2.5 μm) is a major constituent of wildfire emissions (Vicente et al. 2013), and has well-known harmful properties (Xing et al. 2016). Additionally, wildfire smoke contains nitrogen dioxide (NO_2; Mebust et al. 2011) and ozone (O_3; Jaffe and Wigder 2012) which are both strong oxidants associated with respiratory symptoms and diseases (Latza et al. 2009; Nuvolone et al. 2018)

The *Black Summer* wildfire natural disaster that affected Australia over the summer between December 2019 and February 2020 (Borchers Arriagada et al. 2020; Vardoulakis et al. 2020; Walter et al. 2020; Yu et al. 2020) burned an estimated 17 million hectares of land across New South Wales, Victoria, Queensland, Western Australia, South Australia and the Australian Capital Territory (Parliament of Australia 2020), with smoke plumes extending as far New Zealand (NASA 2020). The scale and duration of population exposure to wildfire emissions were unprecedented (Walter et al. 2020), and have been associated with 417

deaths, 1124 hospital admissions for cardiovascular symptoms, 2027 hospital admissions for respiratory symptoms and 1305 emergency department attendances for asthma symptoms (Borchers Arriagada et al. 2020). With the predicted increases in severity and frequency of wildfires, and increasing awareness of the adverse health effects of wildfire smoke, questions are now being raised on what effective actions can be taken to reduce exposure.

Over the past two decades, a range of active botanical biofiltration systems has been developed to mitigate ambient air pollution (see Irga et al. 2020 for descriptions of several systems). These systems use mechanically generated, active airflow — usually supplied by low power fans — to pass a contaminated airstream through a vertical plant growth substrate and foliage (Pettit et al 2018a). As the air stream passes through the system, a range of air pollutants can be removed through physical, biological and chemical mechanisms; particulate matter (PM) is filtered by the substrate and root system (Pettit et al. 2017) and gaseous pollutants, such as volatile organic compounds (VOCs; Pettit et al. 2019a), NO_2, and O_3 (Pettit et al 2019b) adhere to specialised substrate adsorbents (Pettit et al 2018b) or become degraded by the plants' root zone microbial community (Pettit et al 2018a). Previous work has demonstrated the capacity of active botanical biofilters to effectively remove pollutants from indoor environments (Wang and Zhang 2011; Pettit et al. 2019c). Consequently, a range of commercial active green infrastructure designs have been implemented in urban settings to assist in the removal of urban air pollutants (Irga et al. 2020). Previous work has focused on the biofiltration of anthropogenic pollutants; however there has been no assessment of the biofiltration of wildfire-associated air pollutants in open, outdoor environments. The *Black Summer* wildfires provided a unique opportunity to assess the biofiltration of wildfire emissions by such systems. The air pollution from *Black Summer* has been compared to that of the most polluted mega cities (Vardoulakis et al. 2020), consequently research that contributes towards the understanding of how these systems perform in highly polluted environments is of considerable value.

The aim of the current research was thus to assess the capacity of an active green wall biofilter to filter NO_2, O_3 and $PM_{2.5}$ from wildfire polluted ambient air, and thus to provide 'clean air' during wildfire events, and secondly, to examine the effect of ambient pollutant concentration on filtration efficiency during wildfire events.

6.3 Methods

6.3.1 Active green wall description

The active green walls (Figure 31) used in this experiment were comprised of five plenums (1 x 1 m, depth 0.15 m; Figure 31), providing a front face surface area of 5 m^2. Each plenum had four openings on its front face (63.6 cm^2 cross sectional area), that were each connected to a modular botanical biofilter (*Breathing Wall;* Junglefy P/L, Sydney Australia). Biofilter modules were made from recycled low-density polyethylene containing a coconut husk-based growth substrate. There were 16 holes on the front (polluted air inlet) face of these modules into which plants of the following species were grown: *Westringia fruticosa* (coastal rosemary), *Myoporum parvifolium* (dwarf native myrtle), *Stobilanthes anisophyllus* (goldfussia) and *Nandina domestica* (heavenly bamboo). These species were selected for their survivability under normal Sydney environmental conditions. Internal linings of high-density polyethylene shade cloth retained the roots of the plants and the plant growth substrate within the modules. The outlet face of the modules had central ports that connected them to the plenums. Air was driven through the plant foliage, growth substrate and the plenum by two fans per plenum (NF-F12, Noctua, Austria; volumetric flow rate 186.70 m^3/h; internal diameter 120 mm; power consumption 4.32 W) located on the rear face of each plenum. These fans were chosen as they provided a volumetric flow rate similar to Irga et al.'s (2017b) optimised $PM_{2.5}$ SPRE flow rate when systems were standardised by filter area. Fans were operated from 6:00 am to 6:00 pm with a period without fan operation overnight providing temporal independence for daily samples. Two identical active green wall systems were used, located near a roadside (Hills Motorway) in Sydney, Australia. The walls were separated by >50 m to provide spatial independence. As these green walls were located outdoors, they were exposed to ambient air pollutant concentrations comprised of both vehicular exhaust and wildfire smoke.

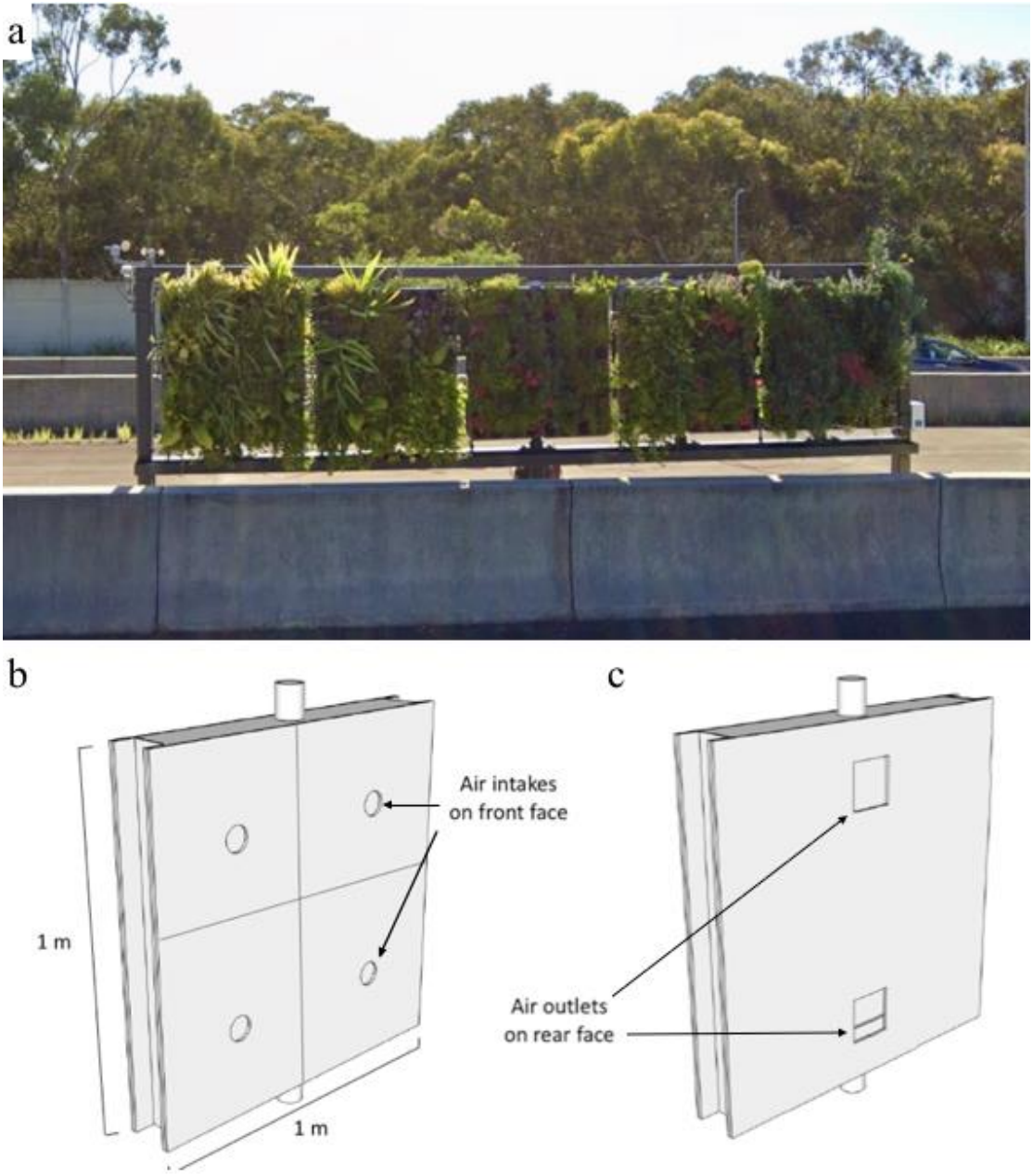

Figure 31. a = One of the active green walls used in this study; b and c = Plenum used to hold the active green wall modules and isolate the effluent airflow. b) shows the front (polluted air inlet) face of the plenum without planted modules attached. c) shows the rear (filtered air outlet) face. Fans were housed within the air outlets to produce active airflow. Five plenums were placed side-by side horizontally to create 5 m^2 active green walls.

6.3.2 Wildfire events

As traffic emissions are normally the major contributors to NO_x and $PM_{2.5}$ pollution in Sydney (Cowie et al. 2019; Crawford et al. 2017; Paton-Walsh et al. 2019), diurnal variability in ambient pollution concentrations was influenced by temporal fluctuations in traffic volume independent of wildfire emissions. Variation in traffic thus represented a cyclic pattern in the ambient pollutant concentration, whereby contributions from wildfire emissions followed a random pattern, predominantly influenced by fire and wind characteristics. A time series analysis was thus conducted using the ambient $PM_{2.5}$ concentration recorded at each wall (see *2.3 Sampling regime*) as a surrogate variable for general air pollution, as it is strongly associated with both traffic and wildfire emissions (Forehead et al. 2020). The 14 days where the random residual variation in $PM_{2.5}$ concentration exceeded the maximum cyclical variation were thus deemed to be 'wildfire days' (Figure 32). To ensure the emissions detected on these days were primarily sourced from wildfires, the data was cross-checked against the average 24 h $PM_{2.5}$ concentration collected from the New South Wales Government Department of Planning Industry and Environment (see Appendix 2) and historical air quality data (Johnston et al. 2011). The average $PM_{2.5}$ 24 h concentrations across the NSW DPIE's Sydney air quality-monitoring network on these days were all within the 99^{th} percentile of historical data from 1994-2007. Over this 13 y period, all days with $PM_{2.5}$ concentrations at this level were attributable to landscape fire (hazard reduction burns and wildfire) smoke, with a single exception caused by a dust storm (Johnston et al. 2011). Additionally, the wildfire days identified in *Black Summer* were also cross-checked with announcements from the NSW Rural Fire Service, which all reported fires in close proximity to Sydney on these days.

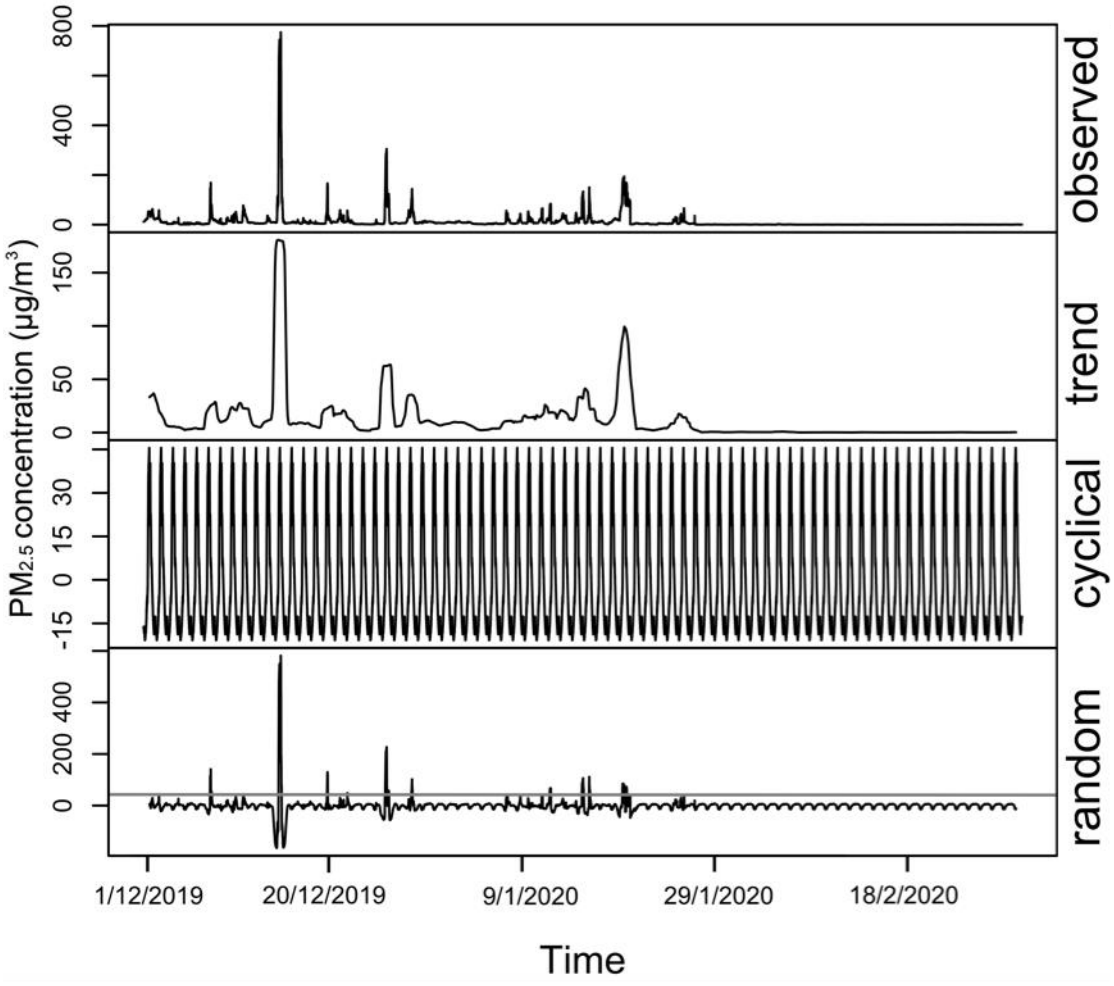

Figure 32. The observed and decomposed time series of the $PM_{2.5}$ concentration (µg/m^3). The grey line across the 'random' variation represents the maximum cyclical variation in $PM_{2.5}$ concentrations. Wildfire days were readily identified from the 'random' trend.

6.3.3 Sampling regime

The concentrations of NO_2, O_3 and $PM_{2.5}$ were detected by a network of Aeroqual AQY1 micro air quality monitoring systems (Aeroqual, Auckland, New Zealand). One AQY1 system was placed on the end of each active green wall and these measured the ambient pollutant concentrations throughout the experiment, and provided a spatially-relevant baseline against which to compare filtered air pollutant concentrations. AQY1 units were also placed inside each of the five plenums within each green wall. As the plenums isolated the filtered effluent airstream, these instruments recorded pollutant concentrations in the filtered effluent air streams from each independent plenum. Each instrument logged the average

concentrations of NO_2, O_3 and $PM_{2.5}$ every five minutes across the entire *Black Summer* experimental period (December 2019-February 2020).

The airflow through each of the plenums was quantified with a VelociCalc Air Velocity Meter 9545 (TSI Incorporated; Shoreview, Minnesota, USA). The air velocity through each of the effluent vents which was multiplied by the cross sectional area of the vent openings to calculate the volumetric flow rate through each of the plenums.

6.3.4 Data analysis

Pollutant single pass removal efficiencies (SPREs) were calculated by comparing the ambient pollutant concentrations to those in the isolated effluent air stream from time-matched samples. SPREs were taken as a function of the volumetric flow rate to estimate the clean air delivery rates (CADRs) of each pollutant provided by the 5 m^2 active green walls (CADR = SPRE x biofilter airflow rate).

To assess the monotonicity of the relationship between SPREs and ambient concentrations, Spearman's correlations were conducted for each pollutant.

6.4 Results

Pollutant concentrations in the ambient and filtered airstreams for wildfire days are shown in Figures 33a-c. In all cases, lower pollutant concentrations were observed in the effluent air streams than in ambient air, however the magnitude of these differences were not consistent across pollutants. Ambient concentrations of all pollutants varied widely, and frequent, dramatic changes in concentrations occurred, likely a consequence of the meteorological influences on smoke transportation from the wildfires. Across the whole sampling period, maximum five-minute-average-concentrations of 178.6 ppb, 59.4 ppb, and 774.7 $\mu g/m^3$ were detected for NO_2, O_3 and $PM_{2.5}$ respectively. Given Sydney's normally good air quality, these values were extraordinary.

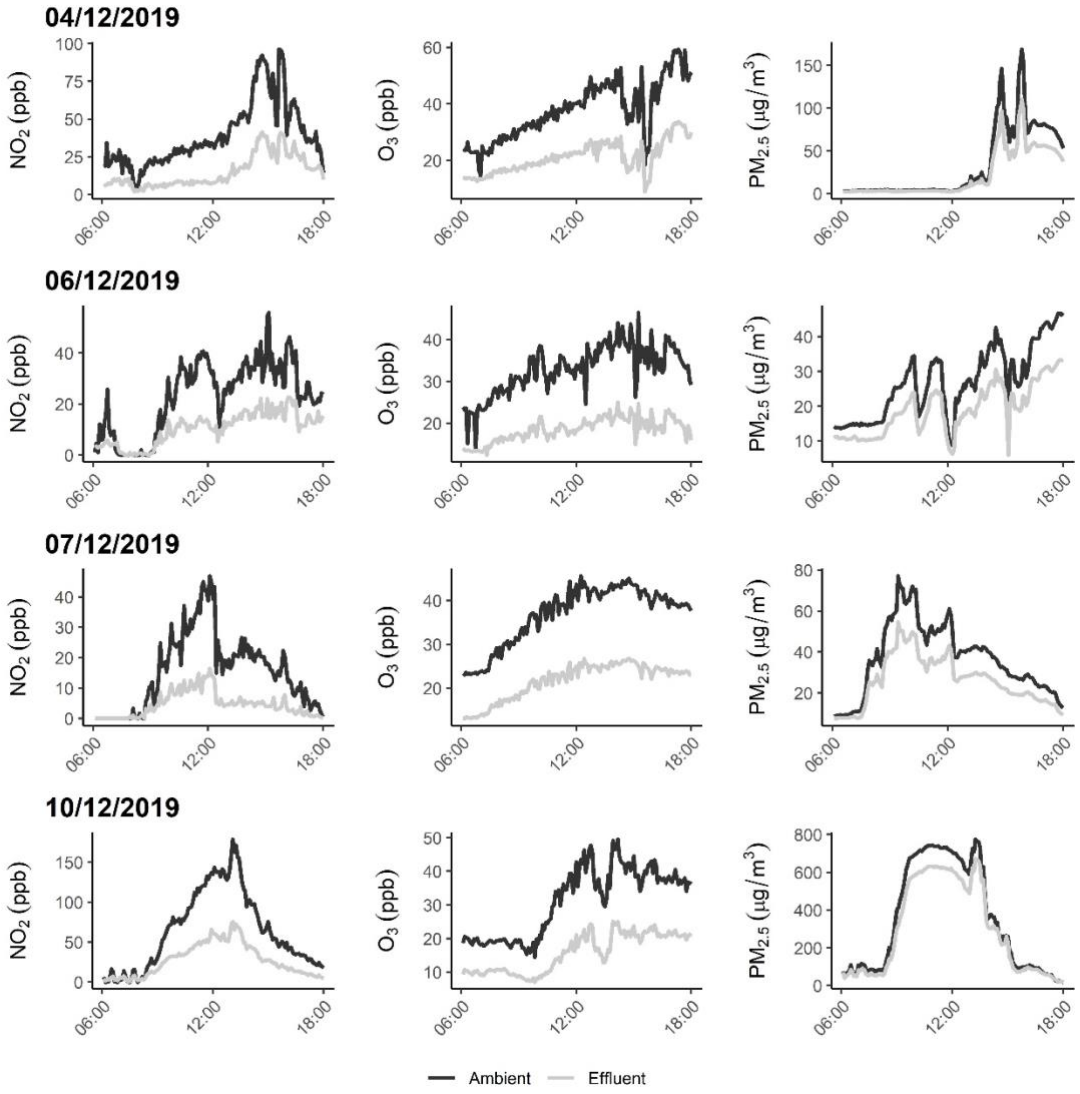

Figure 33a. The concentrations of NO_2, O_3 and $PM_{2.5}$ on days with elevated pollutant concentrations due to wildfire emissions. Average concentrations are shown for the ambient pollutant concentrations and the concentrations in the filtered effluent airstream.

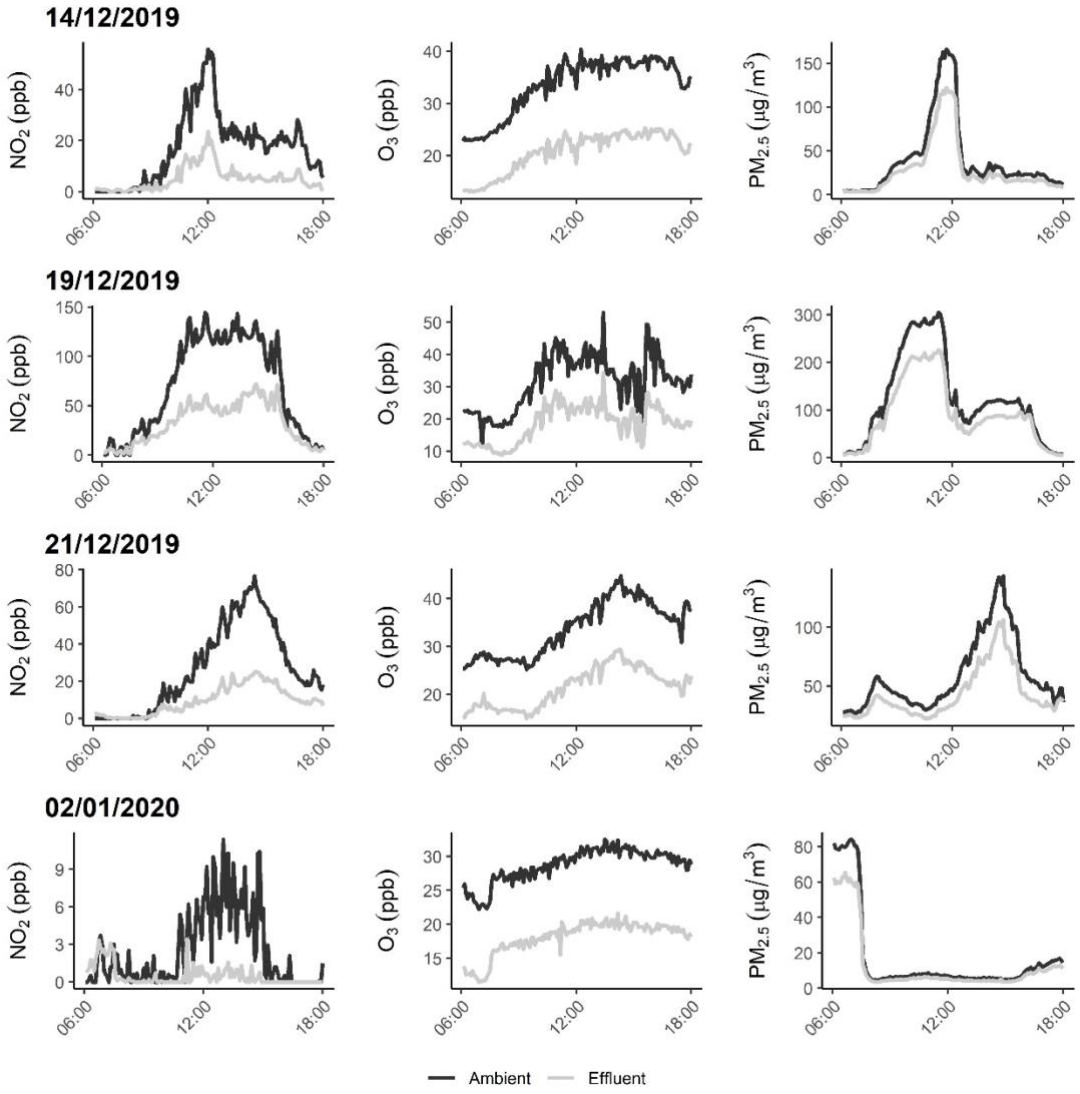

Figure 33b. The concentrations of NO_2, O_3 and $PM_{2.5}$ on days with elevated pollutant concentrations due to wildfire emissions. Average concentrations are shown for the ambient pollutant concentrations and the concentrations in the filtered effluent airstream.

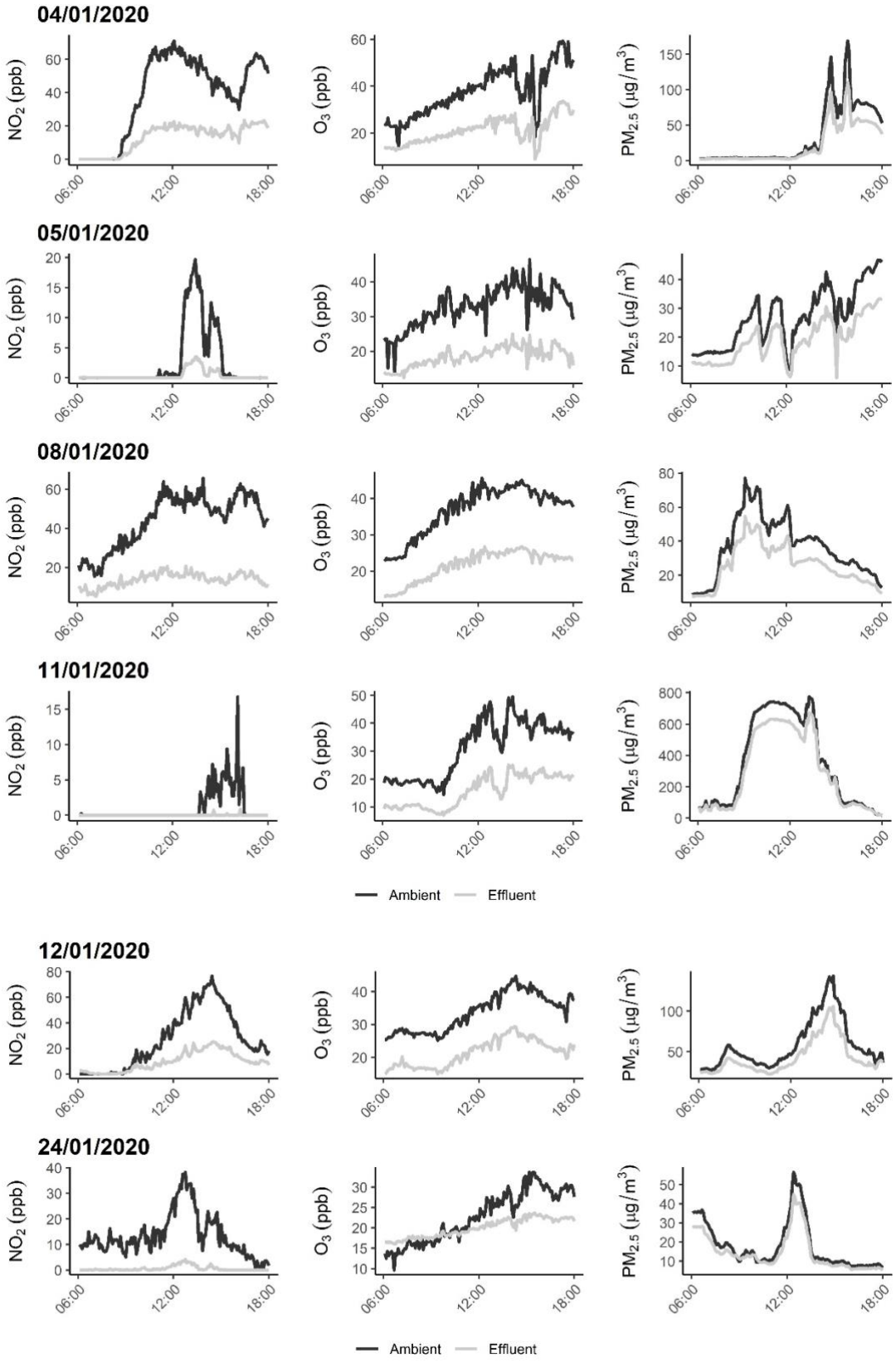

Figure 33c. The concentrations of NO_2, O_3 and $PM_{2.5}$ on days with elevated pollutant concentrations due to wildfire emissions. Average concentrations are shown for the

ambient pollutant concentrations and the concentrations in the filtered effluent airstream.

As the focus of this work was to assess the removal of wildfire emissions, lower limit thresholds were assigned to each pollutant to exclude data from the analysis that was unrepresentative of elevated pollutant concentrations associated with wildfires. For NO_2 and $PM_{2.5}$, data where the ambient concentrations were less than 19 ppb and 25 $\mu g/m^3$ respectively were excluded. These values represent the World Health Organisation's recommended annual NO_2 exposure and 24-hour $PM_{2.5}$ exposure limits (World Health Organisation 2018). As Sydney usually experiences ozone concentrations much lower than the WHO recommendations (Paton-Walsh et al. 2019), a lower limit threshold of Sydney's annual mean O_3 concentration of 18.5 ppb was used (Paton-Walsh et al. 2019). All subsequent analyses used only data where ambient pollutant concentrations were greater than these corresponding thresholds.

NO_2 was removed most efficiently by the active biofilters, with an average SPRE of 63.17%, while O_3 and $PM_{2.5}$ were removed with lower removal efficiencies of 38.79% and 24.84% respectively. These were converted to clean air delivery rates by multiplying the SPRE by the volumetric flow rate, which was 884.8 m^3/h through each 5 m^2 active green wall, producing average CADRs of 558.9 m^3/h for NO_2, 343.2 m^3/h for O_3, and 219.8 m^3/h for $PM_{2.5}$.

Spearman's rank correlations were used to assess the monotonicity of the relationships between the ambient concentrations and the SPREs of each pollutant (Figure 34). Although we detected no association for O_3, NO_2 demonstrated a weak negative association ($p = < 0.01$, $\rho = -0.158$, $n = 919$) as did $PM_{2.5}$ ($p = < 0.01$, $\rho = -0.251$, $n = 1075$).

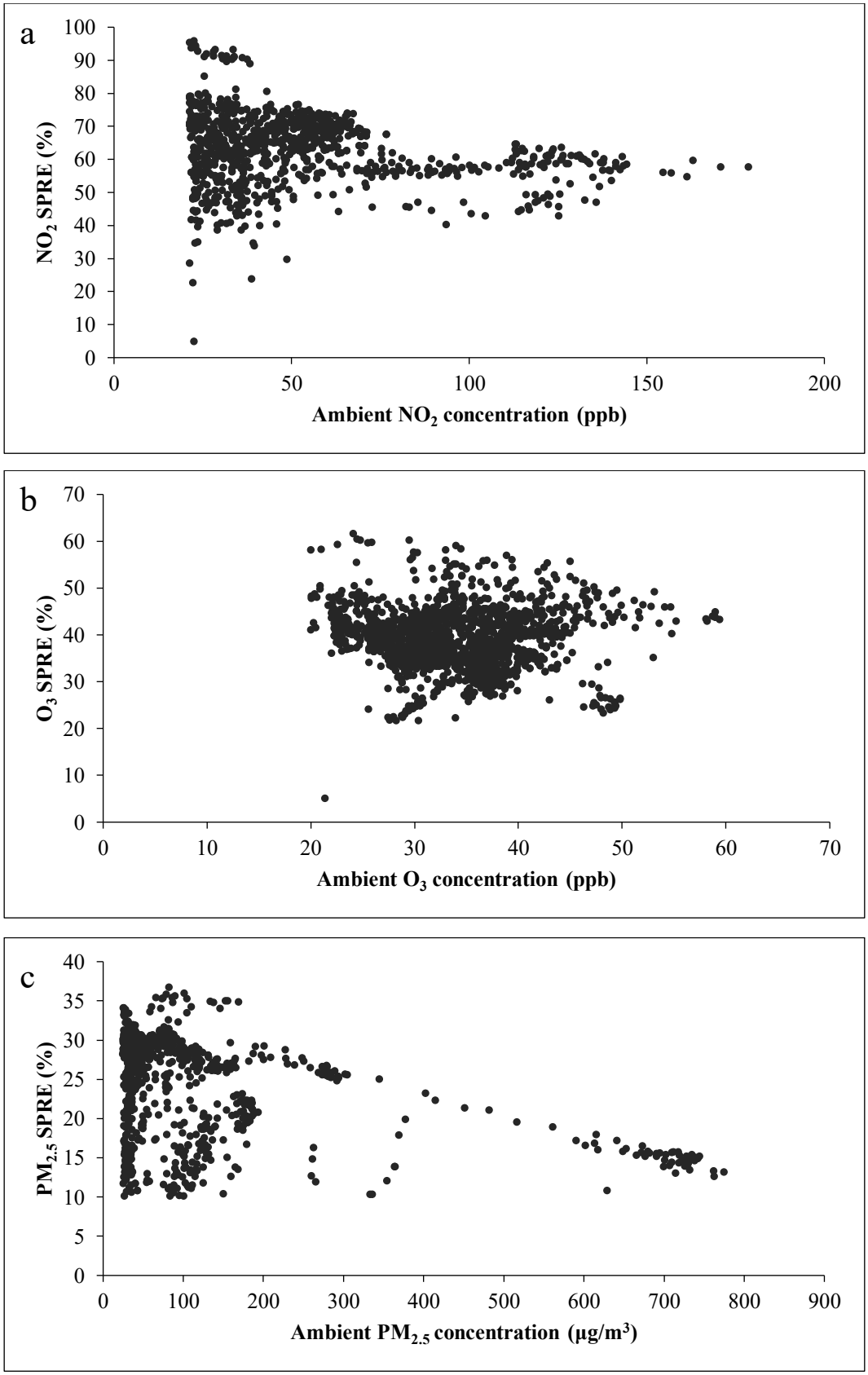

Figure 34. The ambient concentration of pollution against the corresponding SPRE of a = NO_2; b = O_3; c = $PM_{2.5}$.

6.5 Discussion

This work represents the first trial of an outdoor, infrastructure scale filtration system of any type to ameliorate high concentrations of wildfire-associated air pollutants. The pollutants were removed with different removal efficiencies, and whilst the mechanisms of pollutant removal still require further research, it is probable that the contribution of each removal mechanism varies with the chemical and physical properties of each pollutant, as well as the biotic and abiotic components of the biofilter system (Pettit et al. 2019a). The way in which the pollutants interact with the aqueous phase of the filtration matrix may play an important role; although O_3 and NO_2 are both soluble in water, NO_2 hydrolyses readily in water (Zheng et al. 2016), and this may have ramifications for the filtration of NO_2. Of the three pollutants assessed, NO_2 was removed most efficiently, with an average SPRE of 63.17%. Although the SPRE of NO_2 was more variable at lower ambient concentrations, whereby small differences in the NO_2 concentration in the influent or effluent had a disproportionately large impact on the SPRE, the removal efficiency was relatively consistent throughout the range of observed ambient concentrations. Comparatively, O_3 was removed less efficiently, at an average SPRE of 38.79%. Although the botanical biofiltration of NO_2 and O_3 has been observed in laboratory studies using spiked concentrations of pollutants (Pettit et al. 2019b), this work represents the first observation whereby a constant removal of wildfire associated pollutants from a naturally generated influent air stream by active green wall biofilters has been demonstrated. While gaseous pollutants are removed by several processes, usually beginning with dissolution in to the aqueous phase of the filtration matrix, the fate of the filtered pollutants, and their ramifications for the active green wall system, remains unclear. Previous work has noted the potential production of nitric acid within the growth substrate as NO_2 combines with irrigation water (Zheng et al. 2016). The simultaneous biofiltration of O_3 and NO_2 may have enhanced pH control due to the generation of alkaline products from O_3 biofiltration (Maldonado-Diaz and Arriaga 2015). Although it was not our intention to assess filtration products in this study, any changes in substrate pH were insufficient to visibly affect plant health or influence system performance.

When standardised by substrate volume, the NO_2 and O_3 CADRs observed in this study were substantially higher than those observed in the laboratory (Pettit et al. 2019b), most likely due to the use of different ventilation systems and pollutant inlet concentrations between the studies, with the current measurements likely providing a more accurate estimate of the *in situ* air cleaning potential of the green wall biofilters.

The $PM_{2.5}$ SPRE was lower than that reported in laboratory studies. Irga et al. (2017b) reported a $PM_{2.5}$ SPRE of 48% for diesel smoke for an equivalent active green wall biofiltration system. The composition of the tested $PM_{2.5}$, including both the size-distribution of particles and chemical composition, is likely to have caused these differences. Pettit et al. (2017) found that larger particles, 1–2.5 μm in diameter, were filtered much more efficiently by green wall biofilters than smaller particles in the 0.3–1 μm diameter class. The instruments used in the current study did not facilitate the discrimination of particles smaller than $PM_{2.5}$, however, detection of smaller size fractions and understanding the ambient size distribution within the $PM_{2.5}$ particle size class in wildfire emissions would allow for a more critical assessment of particulate filtration. Although less efficient than laboratory estimates, the PM CADRs observed in this study are nevertheless of value, as they demonstrate the practical removal of particle compositions from a real urban environment. $PM_{2.5}$ biofiltration by active green walls has been demonstrated in indoor environments (Pettit et al. 2019c), however such work has been limited to the short-term (< 1 h) removal of spiked or ambient PM. The current trials build on this work, and demonstrate that successful, prolonged biofiltration is possible. Although the $PM_{2.5}$ SPRE reported in this study were less efficient than laboratory estimates achieved by a similar active green wall system and a Minimum Efficiency Reporting Value (MERV) 11 pleated panel HVAC (heating ventilation and air conditioning) filter (Irga et al. 2017b), the $PM_{2.5}$ SPRE observed in this study is highly valuable as it reflects the *in situ* treatment of a unique source of PM. As seen in heavy vehicle diesel particulate filters, the impact of ash and soot accumulation in filters, both independently and as a mixture, potentially compromises the filters efficiency (Kimura et al. 2006). When soot pollutants accumulate in filters, these air pollutants can potentially be regenerated.

Previous work has revealed that PM is filtered by the matrix created by the plant growth substrate and plant root system (Pettit et al. 2017), however the effects of long term PM filtration, particularly at high concentrations, are yet to be tested. The dynamic nature of the system, including irrigation regimes and plant and microbial activity, make it difficult to estimate the possible effects on biofilter airflow rates that may results from long-term PM accumulation within the matrix.

The CADRs of all pollutants indicate that even relatively small active green wall systems can provide considerable volumes of filtered air, which could provide realistic improvements in environmental quality if such systems are strategically deployed, and the filtered airstream is managed in such a manner so as to delay atmospheric dilution.

Although the removal efficiencies of NO_2 and $PM_{2.5}$ were negatively associated with their respective ambient concentrations, the strength of these associations was weak in both cases, and is it likely that other variables that were not measured in this study may have stronger associations with removal efficiency. The moisture level of the plant growth substrate is an aspect that is associated with removal rates of some pollutants (Abdo et al. 2019; Pettit et al. 2019a), and as these active green walls were exposed to rain and subject to a particular irrigation regime, it is likely that the substrate moisture level varied throughout the trial period, and may have influenced filtration efficiency. Other temporal effects including plant growth and PM accumulation over time may have altered the substrate matrix and be linked with variability in pollutant removal efficiency, however no long term *in situ* studies of the simultaneous botanical biofiltration of NO_2, O_3 and $PM_{2.5}$ are available. As this experiment focused on the removal of wildfire emissions under ambient *in situ* conditions, ambient temperature and humidity were not manipulated throughout the experiment. It is possible that variations in temperature and humidity may have led to variations in SPREs throughout the trial, and these effects would be worth including in future laboratory studies. While pollutant removal remains a complicated process influenced by a range of physical, chemical and biological properties and processes, it is possible that at higher concentrations there is a saturation effect whereby the removal efficiency is reduced. Nonetheless, the ambient pollutant concentration remains an important consideration of system performance, and should be explored in conjunction with temporal effects in future research. In some cases in the current trials, pollutant concentrations in the effluent air stream were greater than in the ambient air stream, however in all cases where this occurred, the ambient concentrations of pollutants were generally very low and absolute differences in pollutant concentrations between the filtered and ambient air were comparatively small.

In extreme air pollution events such as *Black Summer*, any air pollution mitigation strategies are clearly of value. The current findings suggest that active green walls in targeted locations may be a valuable adjunct to the wearing of facemasks and staying indoors. The use of indoor air cleaners during wildfire events has been identified as an effective means by which to reduce exposure to emissions (Barn et al. 2016), and the use of active green walls in indoor settings may offer a similar effect. Although this trial occurred in an outdoor setting, wherein the rate of pollution removal was small compared to the rate of emissions, the use of active green walls in indoor settings may be a more appropriate means of providing enhanced air quality and reducing occupant exposure to wildfire emissions. These strategies may be particularly useful in indoor environments that remain susceptible to wildfire smoke

infiltration, as the protection provided by a building is dependent upon building construction and the degree of infiltration of outdoor air (Barn et al. 2016).

While the air pollution profile generated by wildfire emissions differ greatly from those that are anthropogenically-derived, the gross pollution concentrations observed in this study are comparable to ambient environments in highly polluted mega cities (Vardoulakis et al. 2020), and thus the removal rates reported in this study may also be achievable in these locations. The critical need for air quality improvements in some highly polluted urban areas has led to the development of several novel air purifying towers (i.e. see Cao et al. 2014 and Smisek 2018) and this has highlighted the potential of up-scaled systems to impact the surrounding ambient air quality. Upscaling active green walls in hotspot locations within large, polluted cities and assessing their influence on the ambient air quality (in addition to their other environmental benefits, see Perini and Rosasco 2013) is a valuable area of future research. The low cost of these systems compared to conventional air filtration devices, along with their 'green credentials' favours the scalability of these systems. Increasing the size of active green walls in open urban contexts would not only proportionately increase the CADR provided by each wall, but may, in some cases, create a barrier between the emission source and the relevant receiver on the leeward side of the wall (Abhijith et al. 2017). No study to date has measured the combined synergistic impact of the barrier effect and CADR on the surrounding ambient air quality and this remains an important consideration in subsequent studies.

6.6 Conclusion

Between December 2019 and February 2020, Australia experienced elevated air pollution due to extensive emissions from the *Black Summer* wildfires. The research presented here demonstrated that a green wall biofilter with active air flow drawing untreated air through the plant foliage and growth substrate was able to filter NO_2, O_3 and $PM_{2.5}$ during periods of high pollution levels associated with wildfire emissions. Across the observed pollutant concentrations, NO_2 was removed with greater efficiency than O_3 and $PM_{2.5}$. As these pollutant concentrations are comparable with those in mega cities with poor air quality, future work should trial such systems in these environments and assess the impacts of filtration on the ambient air quality.

6.7 Funding

This work was supported by Transurban Ltd and Jobs for NSW [F19 7192]. T. Pettit is supported by an Australian Government Research Training Program Scholarship. P.J. Irga is supported by the University of Technology Sydney (UTS) Chancellor's Postdoctoral Research Fellowship scheme, facilitated through The Centre for Green Technology.

6.8 Acknowledgements

The authors would like to acknowledge Ellery Johnson and Zarah Fath for their assistance in preparing the figures.

7. Chapter 7

7.1 General discussion

The aim of the combined findings of this thesis was to investigate the air cleaning potential of active green walls and their capacity to provide clean air to the surrounding environment. A series of laboratory experiments, indoor trials and outdoor trials were conducted to test several aspects of air pollution botanical biofiltration by active green walls. Firstly, laboratory studies indicated that active green walls can filter out a range of different VOCs, however, removal efficiency is strongly dependent upon the specific chemical properties of each VOC. Prior to this experiment, previous work had used a limited subset of VOCs to assess removal efficiency, however comparisons of removal rates amongst different VOCs remained unexplored. This experiment has revealed that small molecular weight, highly dipole VOCs are removed with the greatest efficiency and provides a model to estimate the removal efficiency of untested VOCs.

Building upon this work, indoor trials were conducted to assess the removal efficiency of VOCs and PM *in situ* using active green walls of appropriate scale for their respective room sizes. Two indoor environments were used in these trials: one comparing the VOC and PM concentrations provided by different phytoremediation technologies (namely potted-plants, a passive green wall, an active green wall and a control treatment); and another comparing the VOC and PM removal effects provided by an active green wall to that of an HVAC system. Firstly, amongst the tested phytosystem technologies, the active green wall was the only treatment to provide significantly lower concentrations of VOCs and PM when compared to the control, with the active green wall maintaining significantly lower concentrations of TVOCs throughout the experimental period (average TVOC concentration 72.5% lower than the control), with a similar trend observed for PM. Secondly, the active green wall reduced the average TVOC concentration by ~28% over a 20 min testing period compared to levels with no green wall and a filtered HVAC system in operation. The average ambient PM concentration in the classroom with the HVAC system operating was 101.18 $\mu g/m^3$, which was reduced by 42.6% by the active green wall.

The strong effect sizes identified in these indoor trials attracted considerable interest from commercial green wall providers with a keen interest in implementing infrastructure-scale active green walls in outdoor environments to provide enhanced air quality, amongst

other environmental benefits. As VOCs are often the most concerning pollutant in indoor environments, the literature has focused on investigating how this class of pollutants can be treated by potted-plants and green walls. In outdoor environments however, different pollutants become increasingly relevant due to their relatively high concentrations in the ambient air near outdoor sources such as traffic emissions. In particular, nitrogen dioxide has been problematic in several ambient environments, however it was unknown whether active green walls could treat NO_2, and secondly whether exposure of NO_2 to the planted system would result in the production of O_3. Thus a series of laboratory experiments were conducted to assess the capacity of replicate active green walls to filter NO_2 at both ambient and elevated concentrations within a closed-loop flow reactor, while the concentrations of NO and O_3 were simultaneously monitored. Both tested biofilter species (*Spathiphyllum wallisii* and *Syngonium podophyllum*) demonstrated exponential decay for the biofiltration of all three pollutants at ambient concentrations. Additionally, biofilters demonstrated considerable pollutant removal under elevated concentrations of NO and NO_2 with average NO_2 clean air delivery rates of 661.32 and 550.8 $m^3 \cdot h^{-1} \cdot m^{-3}$ of biofilter substrate for *Spathiphyllum wallisii* and *Syngonium podophyllum* respectively.

Whilst this work provided evidence that effective filtration of NO_x is possible with green wall technology, it remains unknown how NO_2 and O_3 would be treated under prolonged ambient *in situ* conditions, whereby complex mixtures of VOCs, NO_2 and O_3 may be present in varying concentrations under varied UV exposure. Nonetheless, these results provided promising potential for the botanical biofiltration of these pollutants in ambient outdoor environments. Such a development is valuable to enhanced environmental quality as there is currently no sustainable, economical and scalable system that has been developed for the direct removal of roadside air pollutants at their source.

A follow up study represented the first field assessment of three different botanical biofilter designs for the filtration of traffic associated air pollutants – NO_2, O_3 and $PM_{2.5}$ – from roadside ambient air in Sydney, Australia. This work was conducted across two different roadsides with six-month research campaigns at each site. During these campaigns, all of the tested systems filtered NO_2, O_3 and $PM_{2.5}$ with average single pass removal efficiencies of up to 71.5%, 28.1% and 22.1% respectively. Clean air delivery rates of up to 121 m^3/h, 50 m^3/h and 40 m^3/h per m^2 of active green wall biofilter were achieved for the three pollutants respectively, with pollutant removal efficiencies positively correlated with their ambient concentrations.

While this trial was occurring, severe wildfires occurred over a large proportion of Australia, which dramatically affected the air quality at the trial site. The *Black Summer* wildfires that affected Australia over the 2019-2020 summer have led to concern over the health effects of exposure to the growing problem of wildfire emissions in Australia, and generated a need for a means by which to reduce exposure. This event presented a novel opportunity to assess the botanical biofiltration of air pollutants associated with the *Black Summer* wildfires. In this experiment the ambient concentrations of NO_2, O_3 and $PM_{2.5}$ were measured at a site containing two active green walls in Sydney, Australia. Additionally, the concentrations of these pollutants were also measured in the active green wall's filtered air stream. Across this period, 14 days with highly elevated air pollution concentrations due to wildfire emissions were identified. Average pollutant single pass removal efficiencies of 63.17%, 38.79% and 24.84% for NO_2, O_3 and $PM_{2.5}$ respectively were recorded, with clean air delivery rates of 558.90 m^3/h, 343.19 m^3/h and 219.77 m^3/h for NO_2, O_3 and $PM_{2.5}$ respectively for each 5 m^2 biofilter wall. Weak negative associations were observed between the removal efficiency of NO_2 and $PM_{2.5}$ and their corresponding ambient concentrations. These effects suggest that implementing botanical biofilters in carefully selected sites may have the potential to reduce the concentration of wildfire emissions and thus provide reduce exposure in sensitive populations.

7.2 Implications

The combined results presented in this thesis provide empirical evidence that active green walls may be a valuable technology for mitigating harmful air pollutant concentrations in a range of different environments. In indoor applications, active green walls may be implemented so as to treat air circulating within the room, and thus reduce the reliance upon HVAC systems for indoor air quality management. This is significant as the energy expenditure of HVAC systems is considerable, with HVAC in Australian office buildings accounting for approximately 40% of total building energy consumption (Department of the Environment and Energy 2013). It is thus critical that future work makes energy use comparisons between different technologies, in conjunction with air quality comparisons to ensure that active green walls are developed, and used sustainably. The balance between energy use reduction and air quality enhancement suggest that active green walls are most suitable in certain indoor environments. Firstly, active green walls may be a preferable technology to HVAC systems when there is a large temperature differential between the

ambient outdoor air and the desired indoor air temperature, as greater temperature differential require greater energy use by HVAC systems (NSW Office of Environment and Heritage 2015). In such cases, active green wall technology can treat indoor air by recirculating the air within the building rather than flushing out 'dirty' indoor air with 'clean' air from outside as HVAC systems do. This has the capacity to reduce the extent to which HVAC systems are used and thus reduce their energy consumption.

Secondly, environments with high outdoor pollution levels might make active green walls a favourable technology for indoor use. As HVAC systems maintain indoor air quality by diluting indoor pollutants with 'clean' outdoor air, high ambient outdoor pollutant concentrations both lead to a major load on the filtration capacity of the HVAC, and an unavoidable transfer of pollution to the indoor environment. Most HVAC systems have a filtration component that filters out a proportion of the suspended particles (PM), however outdoor sourced gaseous pollutants are admitted with ventilation air for most systems. Thus reliance on HVAC systems for indoor air quality management in environments with high ambient outdoor air pollution is problematic. In this event, the use of other technologies for indoor air management that do not transfer outdoor generated pollutants to the indoor environment, such as active green walls, will be beneficial. This was highlighted in the field study in Beijing (Chapter 3) where the air quality provided by the active green wall was superior to the air quality provided by the building's HVAC system.

At this stage is unknown whether an active green could effectively replace an HVAC system and provide equivalent air quality in all conditions, however careful use of HVAC in conjunction with active green wall technology may be able to considerably reduce building energy consumption and provide enhanced air quality.

After demonstrating the potential of active green walls to provide enhanced air quality to indoor environments, a collection of active green walls were trialed assessed in outdoor environments, all demonstrating the capacity to filter NO_2, O_3 and $PM_{2.5}$ from traffic and wildfire emissions. Despite observing positive SPREs and CADRs, it is difficult at present to determine what effect this would have on the surrounding air quality. It is likely that careful site selection will be needed, along with green walls of considerable size to observe major effects on the surrounding air quality. Several site-specific considerations are paramount for the maximization of potential active green wall impacts, including proximity to source, ambient pollutant concentration, dispersion of polluted and filtered air and their interaction with localised meteorological conditions and other effects such as traffic. As the cleaned airflow from the active green walls could easily be subsumed by ambient airflow through

sites by natural wind flow, it is likely that sites with limited wind and other dispersal mechanisms will be most suited to active green walls.

Despite the current absence of quantifiable effects from botanically biofiltered air on the surrounding air pollution concentrations, commercial interest has led to the installation of several systems in outdoor environments (Figure 35.; Irga et al. 2020). Quantifying the effects that large infrastructure scale active green walls have on the ambient air quality is a logical step for further research.

Figure 35. An outdoor active green wall (Junglefy *Breathing Wall*™) installed by Junglefy, in St Leonards, NSW, Australia. Figure from Junglefy (2018).

Regardless of indoor or outdoor application, most *in situ* designs make use of a plenum to guide airflow. Although laboratory systems have been optimised to enhance air pollutant removal, plenum design, and its effect on airflow and pressure drop, has yet to be studied in detail. For bespoke green walls, the architectural and engineering requirements of

each site may lead to variations in plenum design, which could in turn influence the airflow of the system. These effects may make future designs complex.

Plant health and survival remains another key aspect for successful green wall implementation. Selecting plant species that first and foremostly will survive in their environment is vital to ensuring green wall success. This is particularly the case for outdoor environments, whereby factors such as temperature, light levels and humidity, are generally more variable than for their indoor counterparts. The plant species chosen for outdoor environments will have to be robust to these climatic variances. In this regard, plant species that are used in one area may not necessarily be suitable for use in another, i.e. plant species used in the outdoor active green wall trials in this work (*Westringia fruticosa*, *Myoporum parvifolium*, *Stobilanthes anisophyllus* and *Nandina domestica*) will not be suitable choices for use in most European climates. Furthermore, the long-term effects of elevated pollutant concentrations on many green wall plants are not thoroughly understood, particularly when active filtration is involved. Long term filtration of some chemicals in high concentrations, such as NO_2, may have the capacity to alter the chemical properties of the substrate, and it is not fully understood how this could affect the plants or the system's microbial community.

7.3 Future Directions

7.3.1 Energy comparisons

The results from this research have presented the potential for active green walls to be used in buildings as an indoor environmental management system. Buildings consume 29% of Australia's total energy, with 40% of this energy used for the temperature control of ventilation airstreams; in an increasingly energy conscious work, it is clear that these figures have to be reduced. There is a clear need for air cleaning technologies that are capable of effectively cleaning a comprehensive range of pollutants in an energy efficient manner. The findings of this research suggest that botanical and biotechnological developments may play a significant role in achieving this goal and help our urban centres move towards smart 'eco-efficient' built environments (Pacheco-Torgal 2020). Growing evidence indicates that biofilter technology may be an effective and sustainable means to maintain habitable buildings in a low energy, sustainability-focussed future. In addition to the air pollutants reductions observed in this research, botanical biofilters can influence atmospheric air temperature and humidity (Pérez-Urrestarazu et al. 2016), while sufficient lighting allows CO_2 reductions through plant photosynthesis (Torpy et al. 2017). As the botanical based

systems are likely to influence the indoor CO_2 balance through photosynthesis and respiration, it is critical that system properties such as substrate moisture level and plant species selection influence indoor CO_2 concentrations (Gubb et al. 2018; 2019; Treesubsuntorn and Thiravetyan 2018). Comprehensive trials in the indoor environment and comparative energy assessments between botanical biofilters and standard indoor environmental quality management technologies would be a valuable progression of this research field. Future research should thus trial and quantitatively performance-evaluate botanical biofilters for *sustainable* total indoor environmental quality management.

7.3.2 Effect on ambient air quality

In addition to indoor air quality effects, the CADRs of the tested systems provide evidence that it may be possible for active green walls to improve the ambient air quality of particular outdoor or semi outdoor urban environments. To greater understand this however, further research will need to thoroughly assess the ambient air quality proximal to active green walls and make relevant comparisons to assess the contribution of botanical biofiltration to the surrounding air quality. Modelling the dispersion of *filtered air* would also be a valuable pathway of further research to understand how active green walls can contribute to enhanced air quality. Large-scale field trials in appropriate environments will be needed to accurately estimate these parameters.

7.3.3 Removal mechanisms and fate of pollutants

Decades of research demonstrating VOC removal by potted-plants indicates that the rhizospheric microbial community plays a major role in degrading these pollutants. It is not well understood how active airflow influences each VOC removal mechanism, or the mechanisms by which active green walls remove other gaseous pollutants such as NO_2 and O_3. Inoculating botanical systems with specific microbes has shown promising increases in the removal of particular pollutants (Khaksar et al. 2016a), however the extent increased pollutant removal under exposure to complex mixtures of pollutants associated with *in situ* concentrations and conditions remains unclear. Experiments that assess these factors may uncover pathways to enhance these systems' removal efficiencies for some pollutants, and will provide a greater understanding of the fate of the treated pollutants, and their ramifications for the active green wall system. Additionally, it is unclear how the dynamic

nature of the system, with its inherent variations in substrate moisture level and plant size, influences the biofiltration of polluted air.

7.4 Conclusion

This thesis has demonstrated that active green walls can filter out a comprehensive range of pollutants, including VOCs, PM, NO_2, and O_3, from a contaminated air stream, although removal efficiencies are clearly pollutant dependent. The filtration capacities demonstrated in this work suggests that active green walls can make a functional improvement to the air quality of some indoor environments. Implementing active green walls in indoor environments as an indoor environmental management system and comparing the energy use and indoor environmental quality between that of the active green wall and other conventional technologies is an exciting area of future research, with the results potentially contributing to sustainable building design.

Active green walls have also demonstrated the removal of NO_2, O_3 and $PM_{2.5}$ from the ambient air in outdoor environments. Similar removal efficiencies and clean air provisions were observed whether these pollutants were emitted from vehicular traffic or wildfires in very high concentrations. Infrastructure scale active green walls in select outdoor environments offer a promising means to improve air quality at sites that suffer from high air pollution and limited dispersion. The cumulative findings of this thesis reveal that active green walls may play an important role in enhancing air quality and reducing exposure to air pollution.

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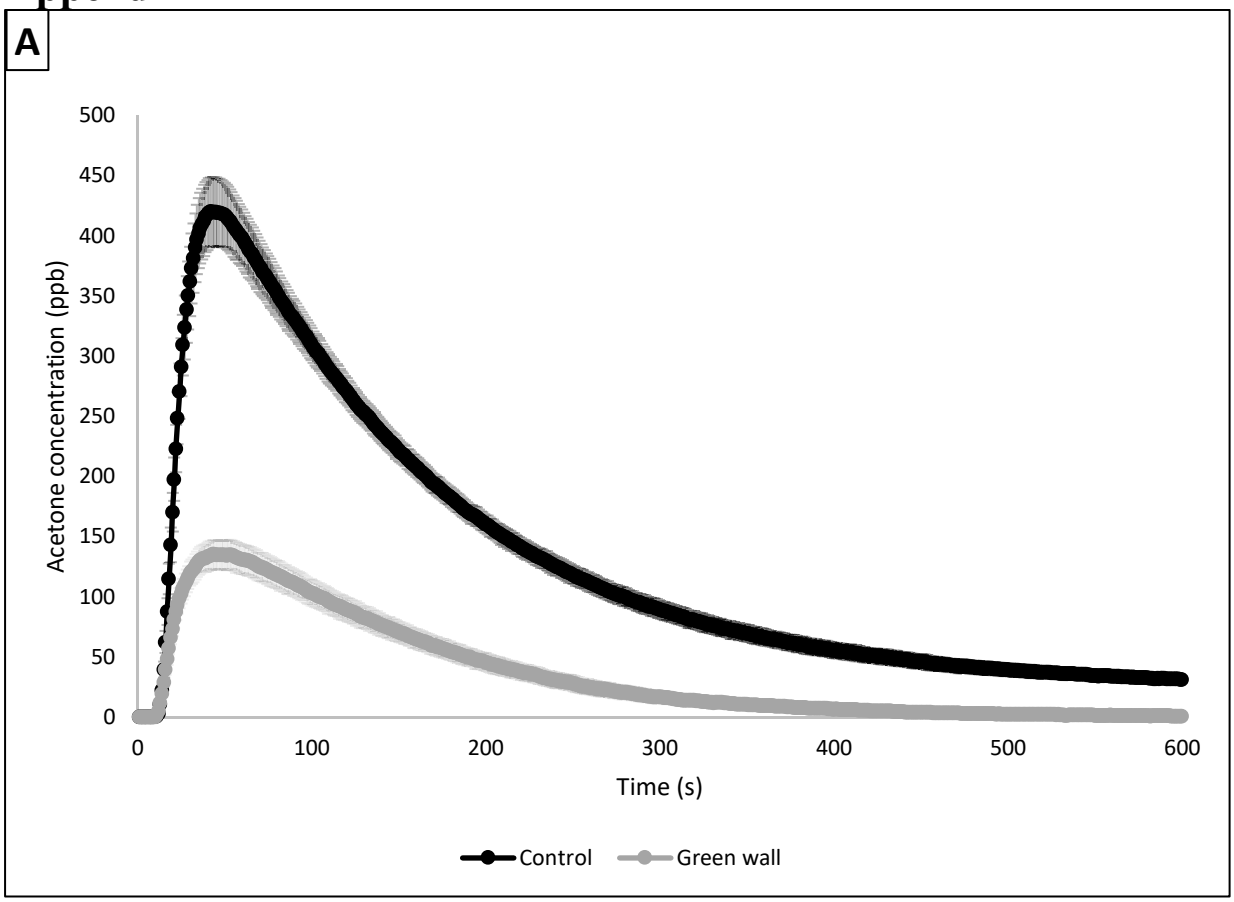
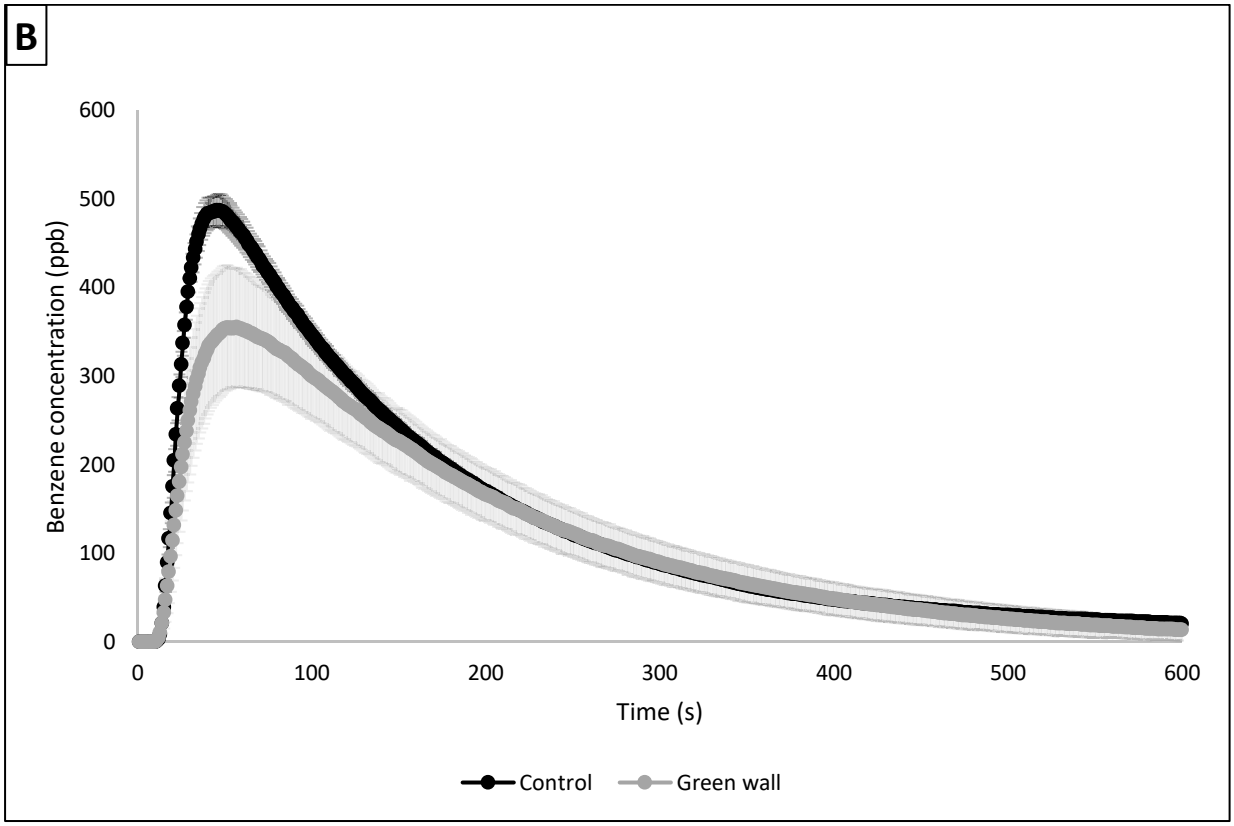
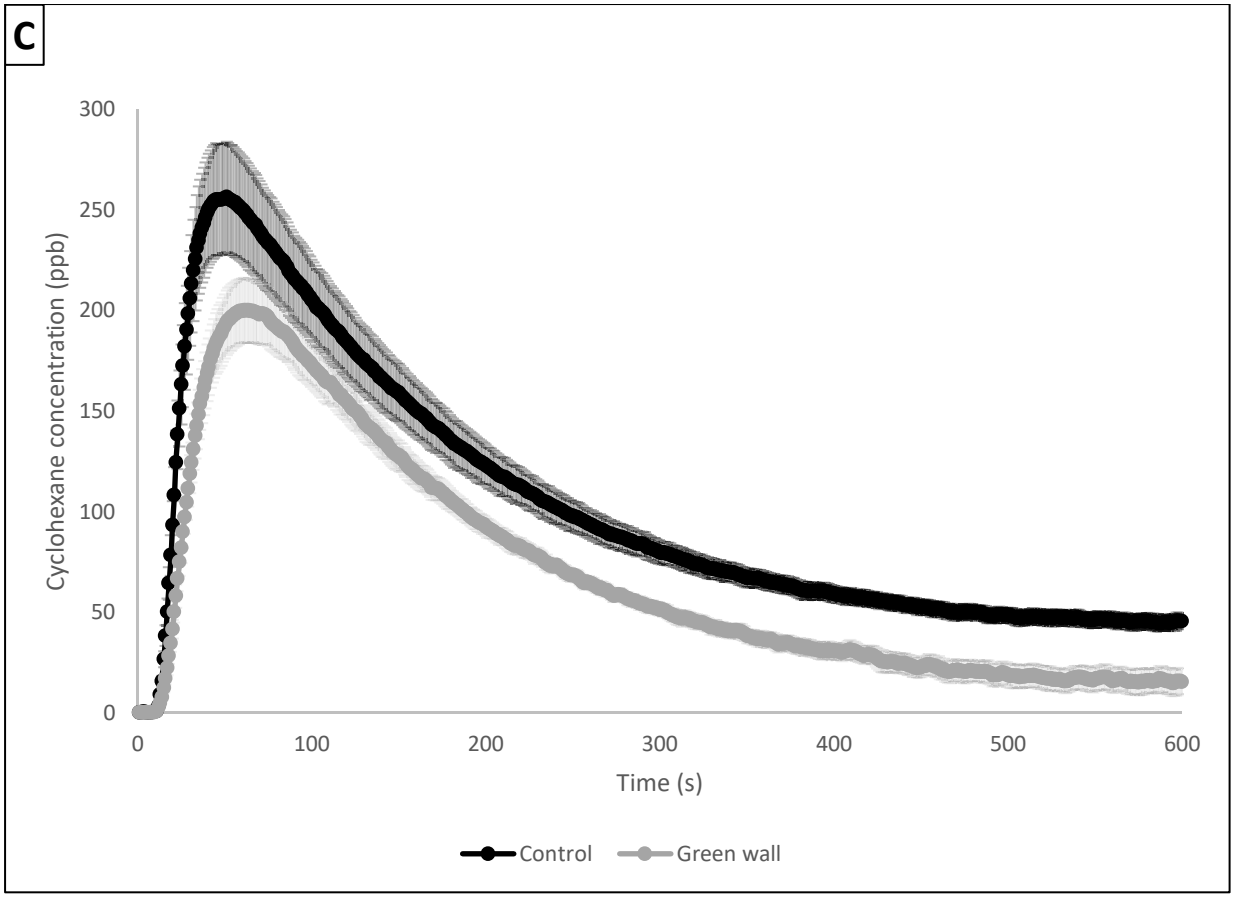
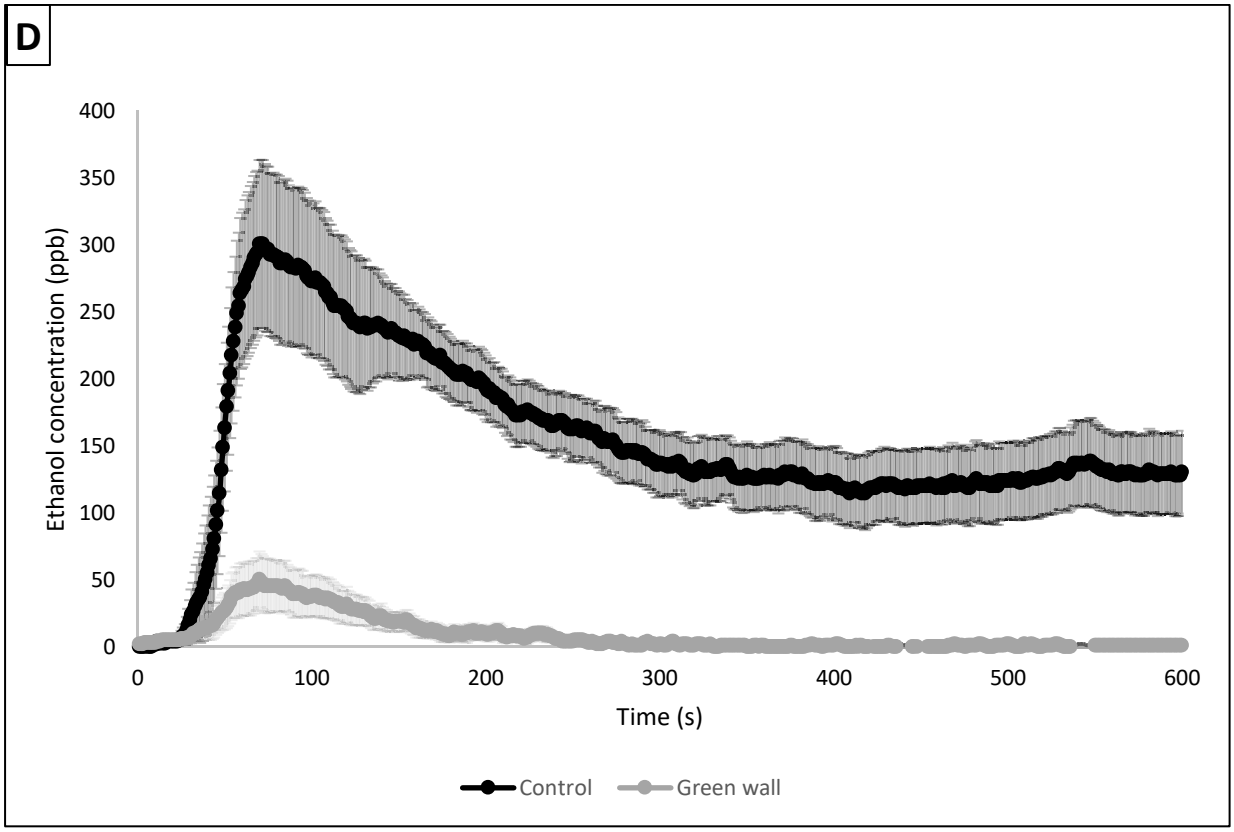
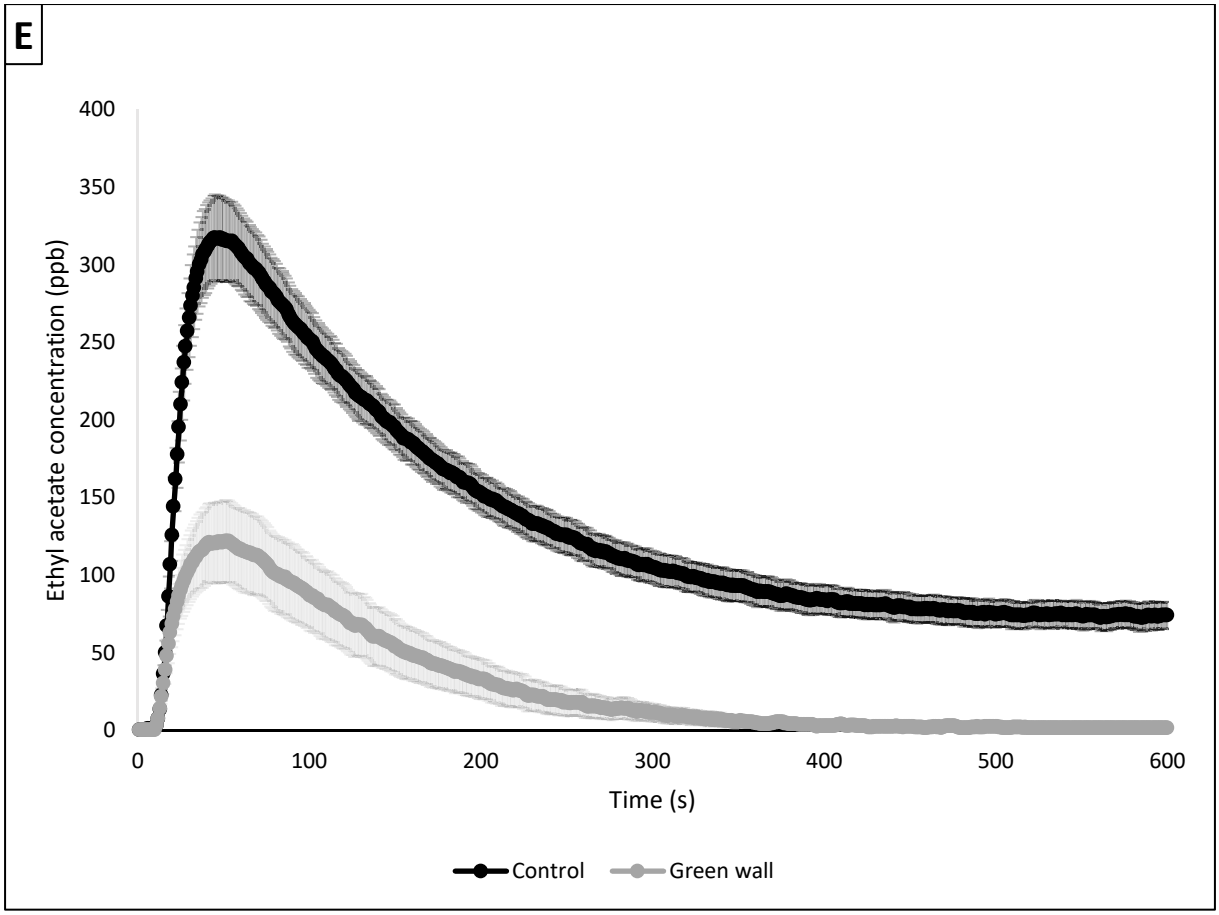
Appendix

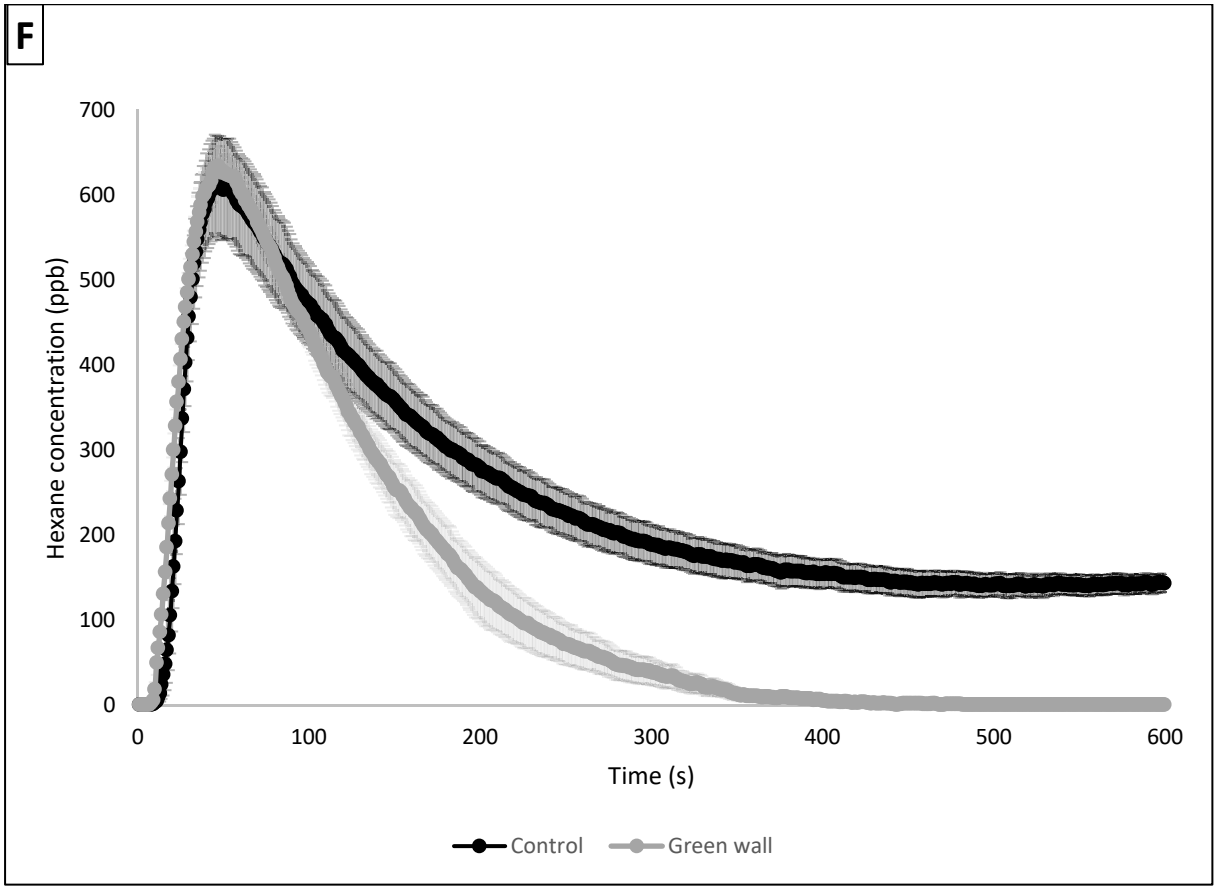

A
Acetone concentration (ppb)
500
450
400
350
300
250
200
150
100
50
0
0
100
200
300
400
500
600
Time (s)
Control
Green wall

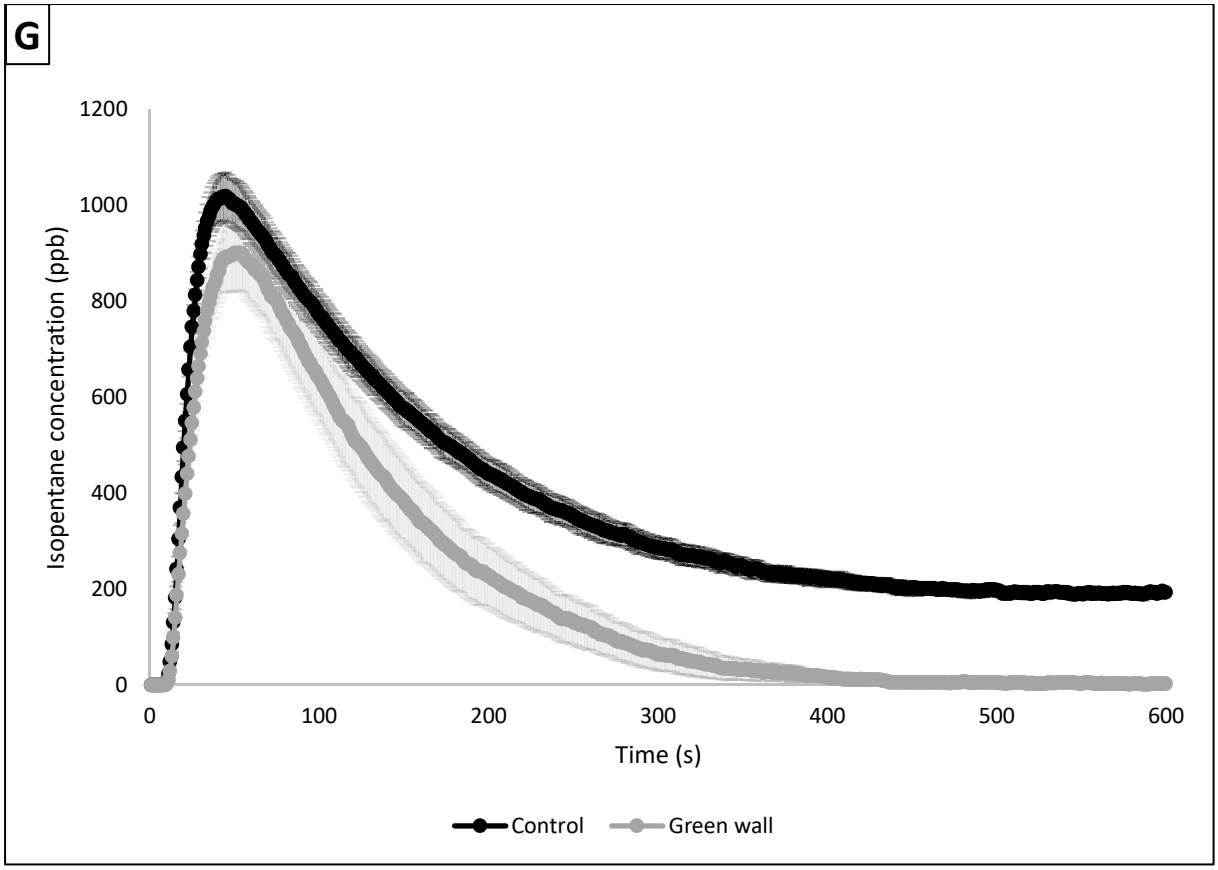

B
Benzene concentration (ppb)
600
500
400
300
200
100
0
0
100
200
300
400
500
600
Time (s)
Control
Green wall

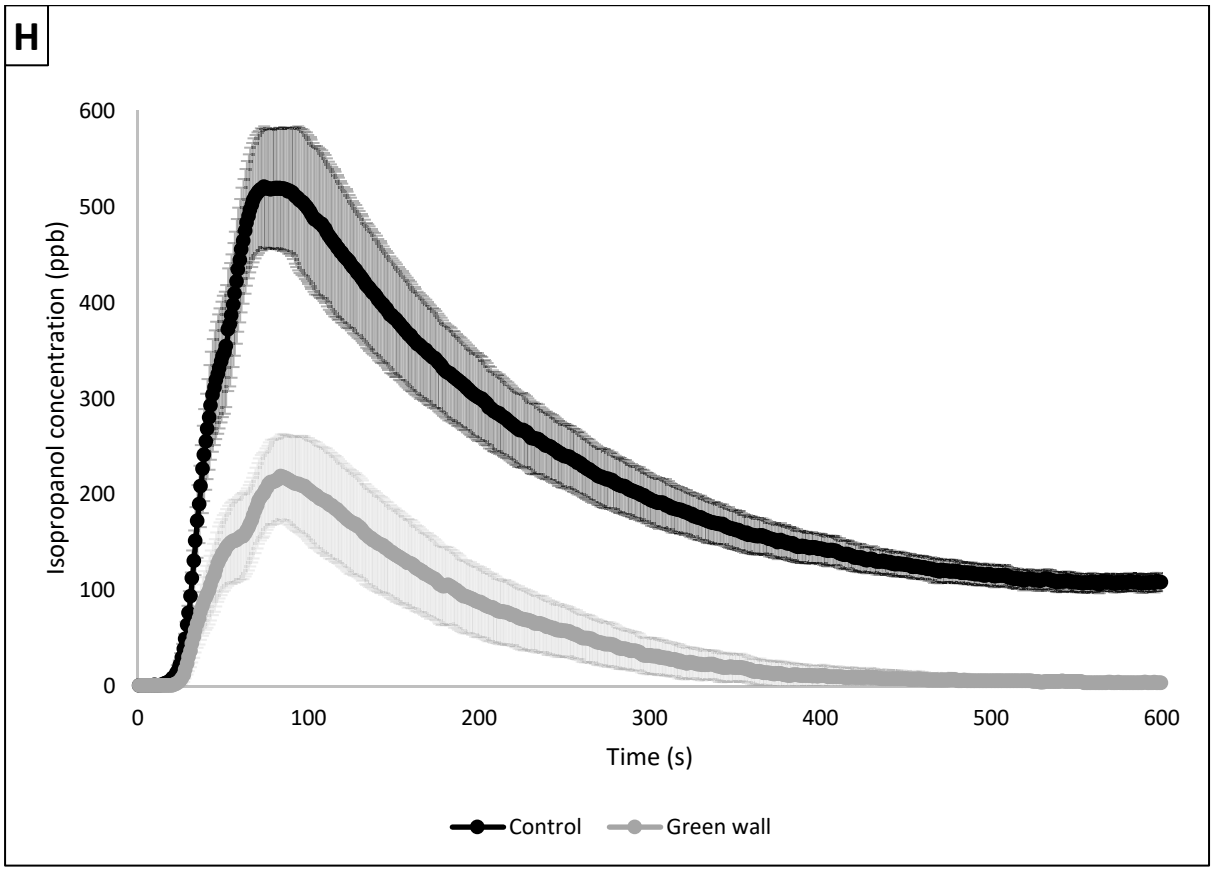

C
300
250
200
150
100
50
0
Cyclohexane concentration (ppb)
0
100
200
300
400
500
600
Time (s)
Control
Green wall

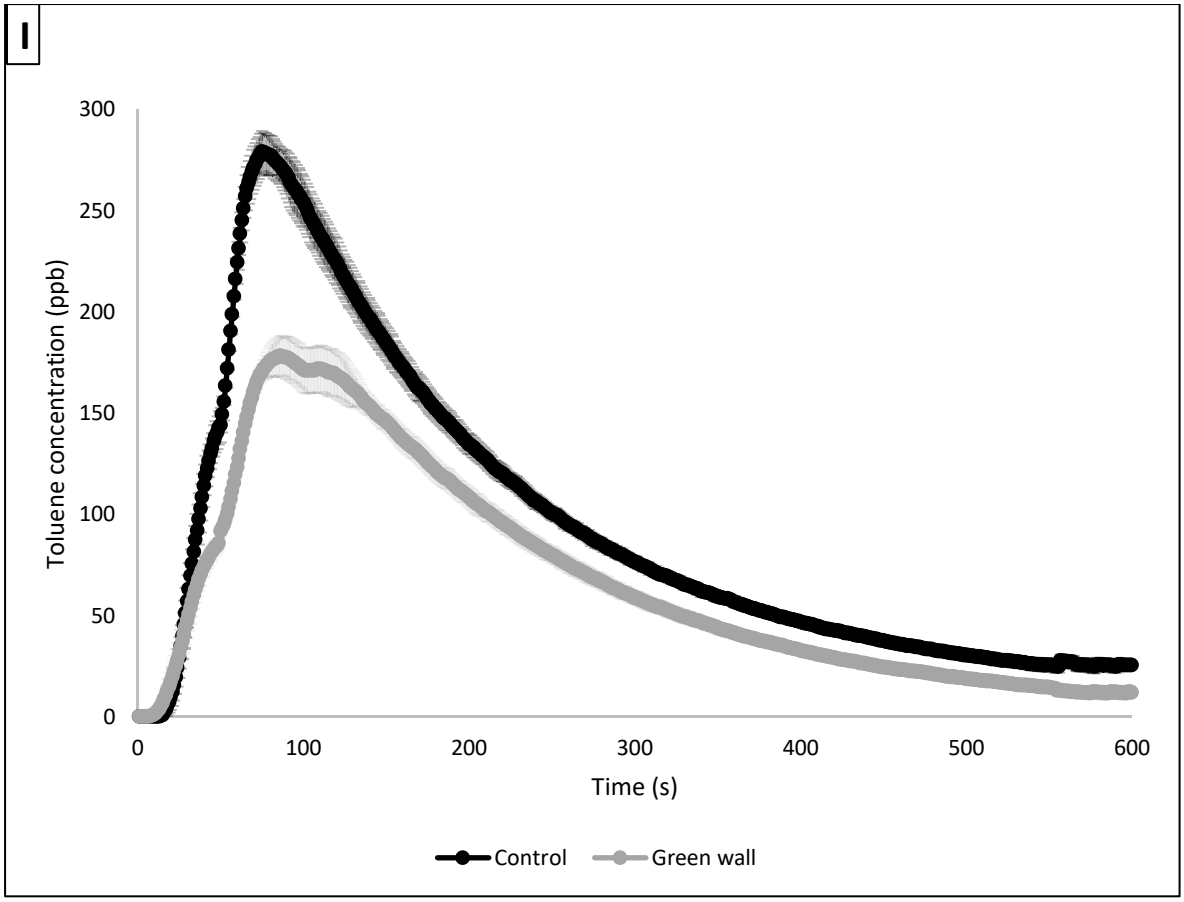

D
400
350
300
250
200
150
100
50
0
Ethanol concentration (ppb)
0
100
200
300
400
500
600
Time (s)
Control
Green wall


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


F
Hexane concentration (ppb)
700
600
500
400
300
200
100
0
0
100
200
300
400
500
600
Time (s)
Control
Green wall


G
1200
1000
800
600
400
200
0
Isopentane concentration (ppb)
0
100
200
300
400
500
600
Time (s)
Control
Green wall


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



Appendix 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.

Appendix 2. The air pollutant concentrations detected by the NSW DPIE's Macquarie Park air quality monitoring station. Colours indicate the air quality classification by NSW DPIE: blue = very good; green = good; yellow = fair; orange = poor; maroon = very poor; red = hazardous.

Day count	Date	Max 1 hr average	Max rolling 4 hr average	Average 24 hr concentration
		NO_2 (ppb)	O_3 (ppb)	$PM_{2.5}$ ($\mu g/m^3$)
4	4/12/19	12	87	42.2
6	6/12/19	22	50	32.3
7	7/12/19	3	54	29.4
10	10/12/19	24	103	152
14	14/12/19	4	53	25.7
19	19/12/19	21	105	62.2
21	21/12/19	10	72	39.2
33	2/01/20	5	28	18.5
35	4/01/20	12	86	30
36	5/01/20	2	47	31.5
39	8/01/20	6	61	77.8
42	11/01/20	21	26	29.2
43	12/01/20	6	23	39.9
55	24/01/20	9	37	34.2