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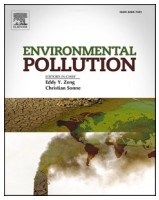

Fuel fumes and foliage: The fate of speciated gasoline VOCs during phytoremediation and their impact on the bacterial phenotype☆

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ABSTRACT

The capacity of indoor plants including green walls to capture, deposit and remediate individual volatile organic compounds (VOCs) has been well documented. However, in realistic settings, plant systems are exposed to a complex mixture of VOCs from highly varied various emission sources. Gasoline vapour is one of the major sources of these emissions, containing high concentrations of the carcinogens benzene, toluene, ethylbenzene and xylene (BTEX). Using both solid phase micro extraction (SPME) and quick, easy, cheap, effective, rugged and safe (QuEChERS) sampling techniques, we assessed the dynamics of individual speciated gasoline VOC phytoremediation from the air and uptake within green wall plant species and growth substrates within a small passive green wall system, along with quantifying the phenotypic changes within the plant-associated bacterial communities resulting from gasoline exposure. Over 8 h the green wall system achieved 100% removal of atmospheric benzene, 1,2,3-trimethyl, eicosane and hexadecane, benzene 1,3-diethyl-; 1,3,5 cycloheptatriene,7-ethyl and carbonic acid eicosyl vinyl ester. All plant species tested demonstrated the accumulation 45 petrochemical VOCs (pVOCs) with *Spathiphyllum wallisii* successfully accumulating the majority of pVOC functional groups after 24 h of gasoline exposure. Within the plants phyllospheric bacterial communities, changes in both cellular complexity and granularity appeared to increase as a result of gasoline exposure, while cell size diminished. This work provides novel findings on the VOC removal processes of botanical systems for realistic and highly toxic VOC profiles.

1. Introduction

Volatile organic compounds (VOCs) are carbon-based chemicals, characterised by high vapour pressure at room temperature. Within the urban environment, VOCs are primarily associated with anthropogenic pollutant sources such as vehicle emissions and the off gassing from a broad array of synthetic building materials and cleaning products (Irga et al., 2018; Jia et al., 2008). These VOCs can accumulate within poorly ventilated indoor spaces and commonly exceed outdoor ambient concentrations by 3–5 times (Jafari et al., 2015). These contaminants often persist below the range of human perception; however, they have been associated with negative health outcomes including discomfort, irritation and respiratory disease (Meciarova & Vilcekova, 2016; Wolkoff, 2013), having serious impact on the productivity of workplaces (Fiedler et al., 2005). Of the broad range of VOCs routinely detected indoors, the most problematic are benzene, toluene, ethylbenzene and xylene (BTEX) due to their class 1 (benzene) and 2 (toluene, ethylbenzene & xylene) carcinogenic classifications (Deng & Deng, 2018).

Several studies have determined that a significant contributor to indoor VOC contamination is the emission of gasoline (motor spirit, benzine, petrol) derived compounds (Jia et al., 2008). A literature review conducted on BTEX exposure by gasoline station workers from 16 countries over 20 years by Edokpolo et al. (2014) concluded that the surveyed individuals were exposed to BTEX concentrations ranging from 0.6 to 896 ppb, with concentrations regularly exceeding WHO

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Abbreviations

BTEX –	Benzene, toluene, ethylbenzene and xylene
GC-MS –	Gas chromatography–mass spectrometry
ACN -	Acetonitrile
HVAC –	Heating, ventilation, air and conditioning
PM –	Particulate Matter
ppb –	parts per billion by volume
pVOC –	Petrochemical volatile organic compounds
TIC –	Total Ion Chromatogram
TVOC –	Total Volatile Organic Compounds
VOC –	Volatile Organic Compounds
WHO –	World Health Organisation
QuEChERS -	Quick, Easy, Cheap, Effective, Rugged and Safe
SPME	Solid Phase Micro Extraction

guidelines (Godoi et al., 2013). An additional study by Demirel et al. (2014) observed significant elevation of BTEX levels within indoor environments within a radius of 500 m of gasoline stations, subsequently resulting in a 3–21% increased risk of cancer for these individuals (Karakitsios et al., 2007). Chronic exposure to BTEX has been associated with serious health outcomes including acute non-lymphocytic leukaemia and myeloid leukaemia, as-well as associated risks for chronic lymphocytic leukaemia and multiple myeloma (Hamid et al., 2019; Warden et al., 2018). Conventional air cleaning technologies such as heating, ventilation, and air conditioning (HVAC) systems are effective for particulate filtration, however they are incapable of gaseous pollutant capture (W. Chen et al., 2005) and are thus reliant on dilution with outdoor air for the removal of these pollutants, a process which is dependent on the intake airstream itself being unpolluted.

It is well known that plants can remediate a variety of gaseous pollutants and have been previously shown to be effective at addressing poor indoor air quality (Matheson et al., 2023a). Nonetheless, removal of gaseous contaminants by the phyllosphere (stomatal uptake and endo/epiphytic bacterial degradation) is understudied and may be an area for active bio-enhancements (Cornejo et al., 1999; Jin Kim et al., 2010, 2014; Soreanu et al., 2013; Wood et al., 2002). It is generally considered that the driving force for the removal of VOCs by plant systems is the rhizospheric microbial community, which exists in a symbiosis with the host plants which provide structure and chemical signalling(Irga et al., 2013; Shao et al., 2020). The above-ground plant parts play a role by pollutant adsorption, adhesion and translocation through the plants vascular system via the phloem to the rhizosphere to facilitate the degradation process by which VOCs are detoxified via the microbial metabolism pathways (Gupta et al., 2017; Prigioniero et al., 2021; Teiri et al., 2022).

To date, nearly all studies on VOC degradation pathways have been conducted on potted plant systems in relation to single analytical VOC exposures (Dela Cruz et al., 2023), however, to the best of our knowledge, research on plant/growth media interactions during the remediation of realistic, complex indoor contaminants such as gasoline vapour has not been explored. As *in-situ* pollution characteristics are highly variable it is important to understand the physiology underlying the biological responses of these systems when exposed to 'real-world' azeotropic VOC mixtures. The profiling of microbial communities and building an understanding of the metabolic changes within these systems that are associated with phytoremediation processes may lead to the potential for microbial biostimulation or augmentation to further increase degradation efficiencies of plant systems for significant indoor pollutants.

Here we investigate the specific plant/growth medium interactions for three plant species within a commercial green wall system when exposed to gasoline vapour, recording the speciated removal of gasoline derived VOCs. Examination of changes to rhizospheric and phyllospheric bacterial communities resulting from exposure to gasoline vapour was also explored, aiming to identify changing functional traits of the bacterial communities in different stages of the phytoremediation process.

2. Materials and methods

2.1. Green wall modules

In this study, 9 independent, small scale, commercial passive green wall modules (Ambius 'Small Live Green Wall', Ambius Pty Ltd Australia; Fig. 1) were assessed for the removal of petrochemical derived VOCs (pVOCs). These systems contained 3 plant species with randomised configurations, including *Peperomia clusiifolia* (Jacq.) Hook. (Fig. 2A), *Scindapsus aureus* (Linden & André) Engl (Fig. 2B). and *Spathiphyllum wallisii* (Regel) (Fig. 2C) (plant species names are according to IPNI, 2023). The plant species were selected as they are all common indoor ornamental plants and have been previously shown to reduce VOC concentrations (Sriprapat & Thiravetyan, 2013). Each green wall unit contained 2.46 L of 'all-purpose blend' potting mix (Hortico, Dulux Group Australia Pty Ltd, Padstow, Australia) consisting of composted hardwood sawdust, composted bark fines, and coarse river sand (2:2:1) with 0.6 $g.L^{-1}$ bulk density and 30% air-filled porosity. In addition, 1.25 g of slow release Total all-purpose fertiliser (Osmocote, Scotts Australia Pty Ltd, Baulkham Hills, Australia) was mixed in to the substrate (N:P:K = 19.4:1.6:5). The green wall systems utilised a small water reservoir (1 L capacity) with a geotextile wick to maintain substrate moisture

Fig. 1. Experimental small-scale green wall biofilters maintained within climate-controlled research glasshouse. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

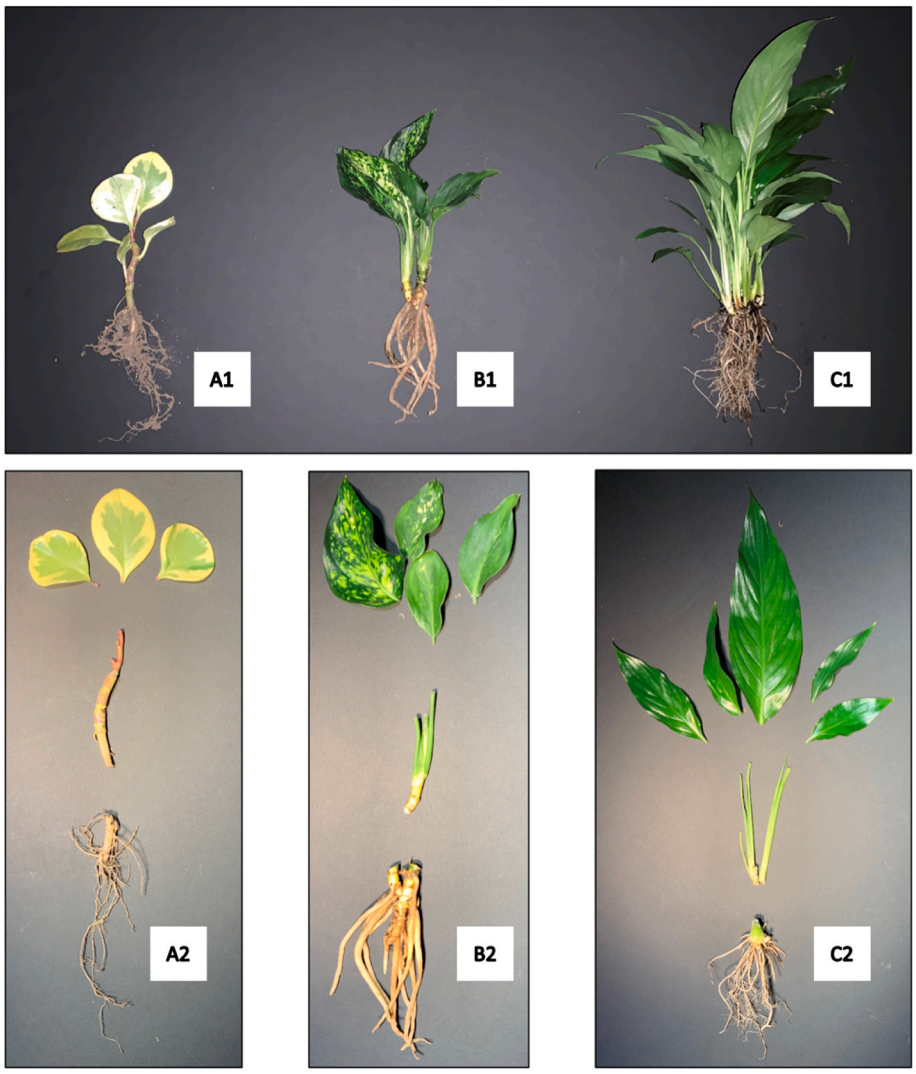

Fig. 2. Green wall plant species used in the current experiments. Photographs depict both intact plants (top from left to right plant species are; A1) *Peperomia clusiifolia*; B1) *Scindapsus aureus*; C1) *Spathiphyllum wallisii*), and plants dissected into leaf, stem and root constituents (bottom from left to right plant species are; A2) *Peperomia clusiifolia*; B2) *Scindapsus aureus*; C2) *Spathiphyllum wallisii*.). From left to right plant species are: A2) *Peperomia clusiifolia*; B2) *Scindapsus aureus*; C2) *Spathiphyllum wallisii*). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

content at 0.206 m^3 m^{-3}. All green wall units were maintained in a research glasshouse prior to experimentation to allow for growth within a standardised environment for 4 weeks and were tested across a two-week period to minimise effects of plant age and size difference between replicates. The glasshouse conditions were as follows: temperature of 23.7 ± 3.6 °C (mean ± standard deviation), relative humidity of 68.1 ± 16.0%, and a maximum mid-day irradiance of 90 ± 10 μmol $m^{-2}.s^{-1}$.

2.2. Gasoline vapour trials

Green wall moduleswere exposed to pVOCs within a sealed Perspex chamber, previously described within (Pettit et al., 2019), (0.6 x 0.6 × 0.6 m; 216 L). For each plant trial, 250 μL of a composite gasoline sample was placed in a heated bead bath (Sheldon manufacturing, USA) at 80 °C and sealed in the chambers with the respective experimental green wall treatments. Gasoline vapour was a composite mix (1:1:1 ratio) of ethanol-free, 91 RON (Research Octane Number: USA equivalent is 87 Anti-Knock Index (AKI)) unleaded petrol sourced from three locations within the Sydney metropolitan area. When heated in the chamber, gasoline samples completely evaporated within 30 min, at which point gas samples were collected using solid phase microextraction (SPME) fibres. SPME fibres were composed of 30 μm polydimethylsiloxane (PDMS) which has been used previously to detect gasoline constituents in water (Kim et al. 2012). After the 30 min gasoline evaporation window a SPME fibre was inserted through the chlorobutyl septum and left for 1 h to all pVOCs in the chamber to adsorb. Each fibre was replaced every hour for an 8-h trial, representing a common office working day. To ensure plant specific VOC removal capacity results were not confounded by chamber leakage, chemical degradation or adhesion to the chamber surfaces, an empty chamber control ('no biofilter', $n = 6$) was employed as-well. After removal from the chambers, SPME fibres were analysed immediately by gas chromatography-mass-spectrometry (GC-MS; ISQ™ 7610 Single Quadrupole GC-MS, ThermoFisher, USA) to quantify specific pVOC removal. Specific GC-MS analysis parameters are outlined in section 2.4.

The green walls then remained in the chamber for a total of 24 h before being disassembled for QuEChERS extraction. Chambers were illuminated with two 41 W Parscan LED spotlights (ERCO Lüden¬scheid, Germany) to simulate typical indoor lighting conditions (Dominici et al., 2021). This yielded 5–50 μmol m^{-2}. s^{-1} of light on the leaf surfaces, where the lower irradiances were detected on the shaded understory of the green wall plants. The CO_2 concentration, temperature and humidity were monitored and were consistent amongst all experimental

trials, and thus any influence they might have had on VOC removal was eliminated from the experiment. All experimentation was conducted under laboratory conditions at ~22.1 °C.

2.3. Sample extraction and preparation

After 24 h within the chamber, the plants in each green wall were dissected into root, stem, leaf, and substrate components (Fig. 2; A2, B2 and C2). Substrate samples consisted of a mixed sample taken out of the centre of each top and bottom plant holders to limit cross over effects between the plant species. Two subsamples of each plant part were made by dividing the materials with a scalpel, with one sample being soaked and agitated in MilliQ water for subsequent bacterial extraction and analysis (described within section 2.4), and the other used for the QuEChERS analysis.

Analysis of residual pVOC concentrations in each plant part was carried out using the QuEChERS method (Fig. 3). The determination of VOCs within plant and soil samples is hampered by the complexity of the matrices and the trace-level concentrations and high volatility of the compounds, thus the trials within this work used the novel solvent-minimised QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction procedure. QuEChERS can determine both non-polar and polar compounds and has been previously used for the determination of pesticides and VOCs (L. Chen et al., 2010; De Mastro et al., 2022a, 2022b; Anastassiades et al., 2003; García Pinto et al., 2011; Lesueur et al., 2008; Pinto et al., 2010). For each replicate, plant parts and soil were macerated to homogeneity in a MilliQ rinsed mortar and pestle, an average of 2 g of material was added to individual polypropylene centrifuge tubes (50 mL) along with 4 mL of MilliQ water. Acetonitrile was added at a ratio of 1:2.5 mL alongside the 10 g QuEChERS extraction kit satchel (4 g $MgSO_4$, 1 g NaCl; Agilent Technologies, Inc.) to facilitate the separation of organic material and solution (De Mastro et al., 2022a).

The centrifuge tubes were vigorously shaken for 1 min using a vortex shaker (Thermoline Scientific, Australia) and centrifuged at 4000 rpm (Hettich GmbH & Co. Germany) for 5 min. For sample clean-up, 1 mL of the liquid layer was transferred into the 2 mL QuEChERS AOAC dispersive centrifuge tubes (50 mg PSA, 150 mg $MgSO_4$; Agilent Technologies, INC) which were vortexed for 30 s and centrifuged at 4000 rpm (Eppendorf AG 230V, Germany) for 5 min. Following centrifugation, the remaining liquid layer was transferred into 1.5 mL screw cap vials and analysed by gas chromatography-mass spectrometry (GC-MS; ISQTM 7610 Single Quadrupole GC-MS, ThermoFisher Scientific™) to quantify VOC contents within each plant part. Non-gasoline exposed plant material controls were extracted, analysed and used as a blank control to distinguish gasoline influenced VOC build up within the plant parts.

2.4. VOC speciation with GC-MS

A Single Quadrupole ThermFisher Scientific™ gas chromatography-mass spectrometer with a WPS oven, autosampler and DB-5MS UI column and helium as carrier gas at a flow rate of 1.0 mL/min (25 m × 0.25 mm I.D, 0.25 μm film) was used for data acquisition. 1 μL of each sample was injected, the injection and ion source temperature were 270 °C with a MS transfer line temperature of 250 °C. The column oven temperature was set at 40 °C for 4 min, ramping to 150 °C at a rate of 5 °C per min, and then at 40 °C per min to a final temperature of 220 °C, which was held for 5 min. The total retention time was 32.75 min. For analysis of SPME fibres exposed to airborne pVOCs, the fibres were desorbed in splitless mode for 1 min, and pVOCs were separated in a HP-5MS capillary column, all other parameters remained the same as liquid analysis.

Mass-spectrometry was run with a classical ionisation method with scans beginning after 1 min and a scan range of 40–200 atomic mass units (amu) and a scan time of 0.5 s. Compounds were identified using the full scan mass spectra with a >85% similarity match to the National Institute of Standards and Technology (NIST23) mass spectra library (V.2.3). This GC method/Retention Index Database provides retention indices and gas chromatographic conditions for 180,618 compounds, which includes non-polar, semi-polar on polar stationary phases from the literature and NIST laboratories acquired on packed and open tubular columns (Babushok V. I et al., 2007; Stein Stephen et al., 2007; Zenkevich I. G et al., 2009). In addition, HPLC grade deuterated benzene (Sigma Analytical Science & Technology, St. Louis, MO, USA) was used as an internal standard for benzene and its derivatives. Concentrations

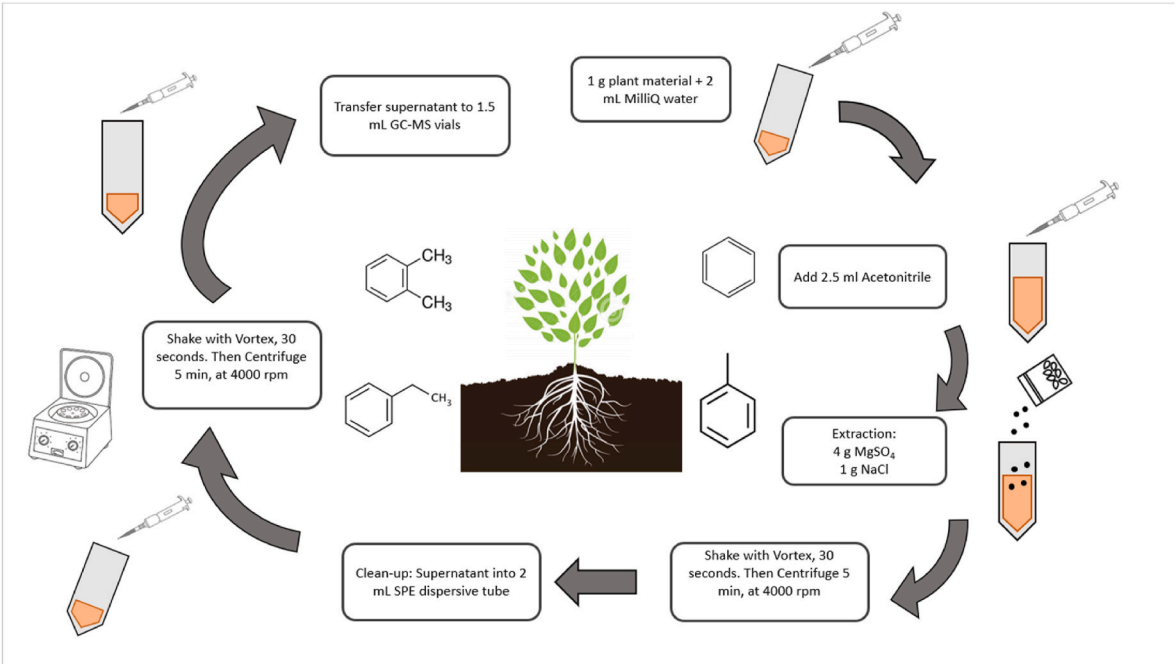

Fig. 3. Schematic presentation of the QuEChERS method for the extraction of petrochemical VOCs from green wall plant parts and growth substrate. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

ranging from 0.1 to 5.0 μg/L were analysed using the classical ionisation method stated above, and analyte retention times were averaged to be used for formal compound identification during the analysis of experimental samples. The areas of each VOC peak in the total ion chromatograph (TIC) were used to assess relative differences in VOC concentrations amongst treatments.

2.5. Bacterial enumeration with flow cytometry

Dissected plant parts and substrate samples were washed and agitated within 100 mL of MilliQ (18.2 Ω, MilliQ, Germany) water. Then, 1.6 mL of 'wash liquid' was transferred into individual cryotubes containing 200 μL of paraformaldehyde (PFA) and stored at −80 °C. The experimental samples consisted of; i) treatments that had been exposed to no petroleum vapour, ii) treatments that had 24 h of petroleum vapour exposure, and iii) 2 h of petroleum vapour exposure. This 2 h exposure time treatments were included as this has been shown to be the period in which peak degradation of petroleum VOCs for these types of systems occurs (Matheson et al., 2023b). The flow cytometer (Cytoflex LX, Beckman Coulter, USA) was operated in plate mode with Milli-Q water as the sheath fluid using the proprietary software, CytExpert (Beckman Coulter, Inc, USA). Prior to bacterial analysis, a machine deep clean with detergent was performed as is standard operating procedure (FlowClean Cleaning agent, Beckham Coulter Inc., USA). Calibration of the flow cytometer was carried out prior to analysis using a suspension of fluorescent microspheres (CytoFlex Daily QC Fluorospheres, Beckham Coulter Inc., USA) within Milli-Q water (3 drops into 1 mL).

Using methods described by Partensky et al. (1999), bacterial sub samples (40 μL) were stained within 96-well flat-bottom cell culture microplates (200 μL working volume, Corning Costar, USA) containing filtered (0.22 μm) TE buffer (10 mM Tris-HCL, 1 mM disodium EDTA, pH = 8.0, Sigma-Aldrich, USA) and SYBR Green I (1:20,000 dilution, SYBR Green I Nucleic Acid Gel Stain-10,000X concentrate in DMSO, Introgen, USA). Control samples consisted of 100% 0.22 μm filtered TE buffer which was stained ('stained buffer'), as well as unstained sample water and diluted unstained filtered (0.22 μm) TE buffer for each individual plant part/substrate from each species ('unstained samples'). These controls set the gating threshold for background green

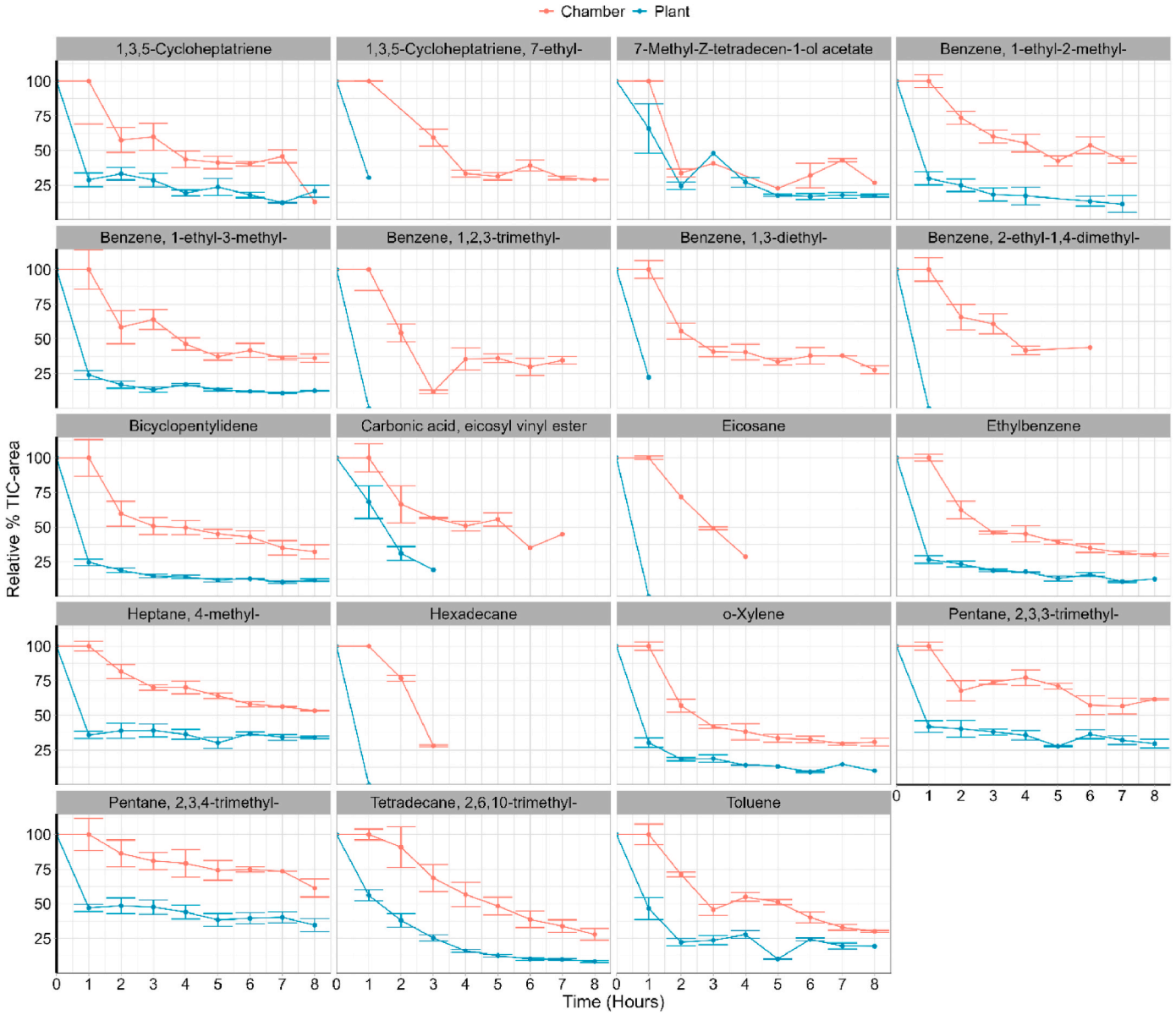

Fig. 4. Relative decay curves of speciated airborne pVOCs for chamber control and green wall treatments over 8 h of exposure. Error bars represent standard error of mean (SEM). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

fluorescence. The green fluorescence signal (>1200 threshold to minimise contributions from unstained particles) triggered acquisition and was enumerated at a flow rate for 1 min (10 μL min ^{1}). Analysis plates were prepared in batches of 2 samples at a time to ensure the stain remained active during acquisition. Within cytograms, bacterial populations were gated into high DNA (HDNA) and low DNA (LDNA), with HDNA bacteria representing more active (dividing/metabolising) bacterial communities (Jellett et al., 1996). This method exclusively enumerated heterotrophic bacteria, and thus no autotrophs nor eukaryotic organisms were included in the data.

2.6. Statistical analysis

Relative airborne pVOC decay curves were generated by plotting peak mean Total Ion Chromatogram (TIC) areas of speciated VOCs over time and fitting each with a polynomial function. Decays is expressed as a percentage removal from the initial mean TIC area, represented on the graphs as timepoint 0. An analysis of similarity percentages (SIMPER) was used to identify which pVOC species were driving differences in the cross-VOC removal patterns between the empty chamber and the green wall treatments. SIMPER was performed at timepoints 1h and 8h on a Bray-Curtis dissimilarity matrix of TIC-area comprising all pVOC species depicted in Fig. 4.

To visualise the relative concentrations of speciated pVOC in the different plant parts and substrates, bar plots were used to depict the mean TIC areas across all tested species. Multiple identified pVOCs were found within non-exposed control green wall samples. The experimental glasshouse where the green walls were maintained is a semi-indoor environment located on the roof of building 4 within the city campus at the University of Technology Sydney in Ultimo, New South Wales. While these controls were not directly exposed to gasoline the presence of fuel vapour within residential buildings is well documented. Petrochemical VOCs are also emitted from a variety of synthetic solvents and cleaning materials (Irga T J Pettit F R Torpy, 2018; Jia et al., 2008) as well as significantly produced during start-up of gas-powered engines (Wang et al., 2022). These factors may have exposed control samples to trace levels of petroleum vapour during green wall growth phase. Thus, the area TICs found within the control samples were used as a blank and subtracted from the area TICs experimentally exposed samples (García Pinto et al., 2011).

To identify differences in pVOC presence and relative concentrations amongst plant parts/substrates between the plant species, a Permutational Multivariate Analysis of Variance (PERMANOVA) using a Bray Curtis dissimilarity matrix was performed on the TIC Area data set, subsequent pairwise comparisons were performed to identify specific significant differences between plant species and plant parts. Benjamini-Hochber (BH) adjustments were made for multiple comparisons to ensure the robustness of the results. For data processing of flow cytometric traits, the abundance of microbial communities was determined by the number of events per unit volume (cells.mL ^{1}) falling within the previously described gates (section 2.4). The phenotypic traits of bacteria this method included were: cell granularity/complexity (Violet SSC-A) and metabolic activity (B525-40-A). These were divided by the median value of the quality control calibration beads to produce a normalised standardisation across different runs. To determine if the 'integrated phenotype' combined effect of all traits had changed between exposure treatments and exposure times, changes in the phenotype were visualised using non-metric Multidimensional Scaling (NMDS) with environmental vectors fitted to the ordination using the envfit(1) function from the vegan package to show maximum correlations with phenotypic traits. Changes in integrated phenotype were verified with tests of homogeneity of dispersions (PERMDISP) and permutational analysis of variance (PERMANOVA), testing differences in geometric spread and central location of the groups; respectively. All analysis was performed using a dissimilarity matrix calculated by Bray Curtis distance on normalised trait data with 999 permutations. An analysis of similarity percentages (SIMPER) was used to identify which bacterial phenotypes were driving differences between the bacterial plant part communities across the various gasoline exposure protocols (no exposure, 2 h exposure and 24 h exposure). SIMPER was performed on a Bray-Curtis dissimilarity matrix.

All statistical analysis and graphics were performed in R and the following packages: ggplot2 (R Core Team, 2022), tidyr (Wickham, 2020), ggpubr (Kassambara, 2018), dplyr (Wickham, 2022), vegan (Oksanen et al., 2020), pairwiseadonis (Martinez Arbizu, 2022).

3. Results and discussion

3.1. Speciated removal of airborne VOCs

After 1 h of residence time within the test chamber, GC-MS speciation detected 19 pVOCs within the empty chamber control (Fig. 4) (consisting of: 8 benzene derivatives, 5 alkanes, 2 cycloheptanes, 2 esters and 1 halide) and only 14 within the green wall treated chambers (6 benzene derivatives; 3 alkanes; 2 cycloheptanes, 2 esters and 1 halide). This indicates that three pVOCs: benzene, 1,2,3-trimethyl, eicosane and hexadecane, were removed by the green walls to below detection limits of the GC-MS within the first hour. These VOCs were the major contributors to the dissimilarity between the VOC removal of the empty chamber control and the green walls ($p = 0.006$, 0.037 and 0.036; respectively). The green wall treatments were also able to remove several other pVOCs to undetectable GC-MS limits compared to the chamber control before the 8-h sampling time. Notably, benzene 1,3-diethyl-; 1,3,5 cycloheptatriene,7- ethyl and carbonic acid eicosyl vinyl ester. Over 8 h of exposure, the green wall treatment removed several additional pVOCs to a significant degree more than the empty chamber control, these pVOCs were, benzene-1-ethyl-2-methyl ($p = 0.001$), ethylbenzene ($p = 0.003$) and σ-xylene ($p = 0.035$) (Fig. 4). While considerable reductions of toluene were observed, this pVOC did not contribute significantly to the overall dissimilarity in SIMPER analysis, most likely due to its overall removal being less than the previously mentioned significant pVOCs. Nonetheless these results show the capability of green walls to remediate benzene derivatives and TEX compounds within gasoline vapour, a group of known class 1 and 2a carcinogens imposing great health risks to persons that are exposed (Edokpolo et al., 2014; Neghab et al., 2015).

3.2. Fate of the individual speciated pVOCs in green wall plant components and growth substrate

The below findings demonstrate the differences in pVOC uptake by the various plant parts of the green wall plant species. All plants demonstrated the ability to absorb pVOCs over the 24 h test period but exhibited significant differences in removal between plant species aswell as differences in the deposition of specific pVOCs. GC-MS speciation detected 90 different VOCs above a certainty of 75% across both control and pVOC exposed samples. Of these, 45 individual pVOCs were identified (Fig. 5) and grouped into 10 functional groups (Table S1). A significant difference in pVOC TIC area was observed between the plant species and plant parts ($F = 5.95$, $p = 0.001$; $F = 26.81$, $p = 0.001$, respectively).

Interestingly, GC-MS failed to reveal any aromatics, which are a major component of gasoline at ~30.5% (U.S. Department of Health and Services, 1995), within any of the exposed plant or substrate samples after 24-h. The absence of these compounds within the plant parts is surprising, as benzene derivatives were shown to be actively removed by the green walls within 8 h of exposure (Fig. 4), suggesting that some aromatics should be present within the exposed plants after 24 h. It is likely that the lack of detectable aromatics within our samples may be a result of biodegradative metabolism: the degradation of BTEX compounds starts with ring cleavage to form compounds that undergo deep oxidation in order to enter the plants tricarboxylic acid (TCA) cycle

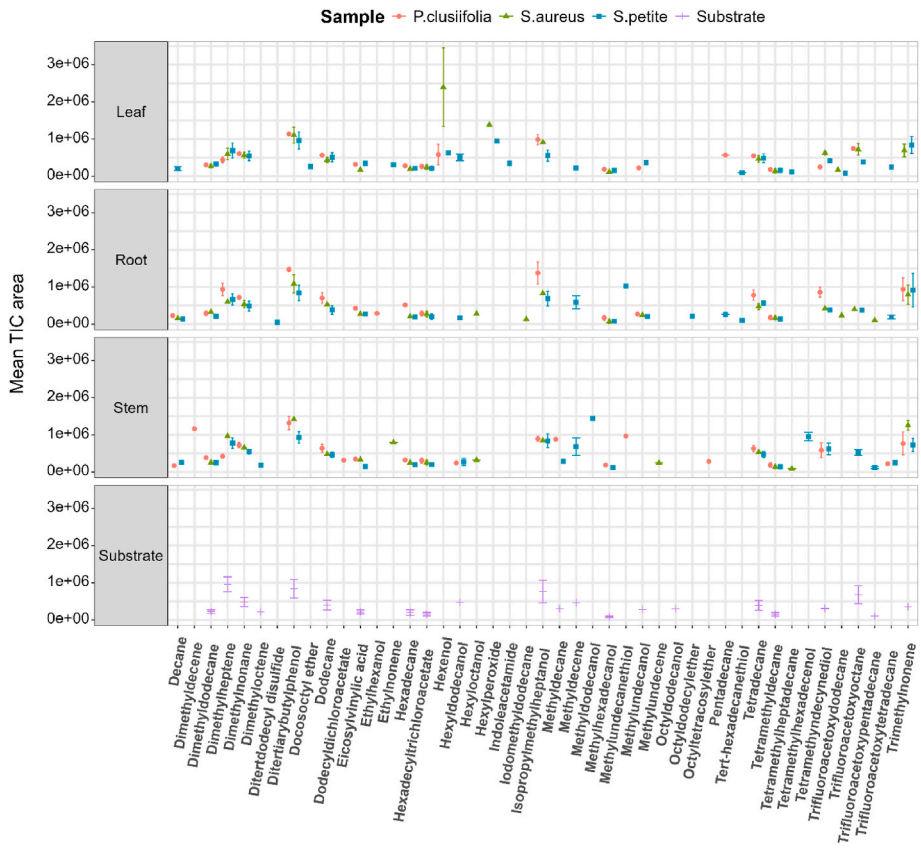

Fig. 5. Mean TIC Area of pVOCs detected in plant parts for each plant species (*P. clusiifolia*, *S. aureus*, *S. wallisii*), as well as the substrate treatment after exposure to gasoline vapour for 24 h. Error bars represent SEM.

(Giese et al., 1994; Sangthong et al., 2016). It is thus possible that after 24 h of exposure, the aromatic hydrocarbons present within petroleum vapour have undergone ring cleavage and oxidation, metabolically transforming them into various non-aromatic compounds. While it is feasible that aromatic VOC biodegradation could yield compounds including the aliphatic compounds detected in the current work (Fig. 5), identifying and testing the specific pathways and products involved would require detailed biochemical studies not within the scope of the current work.

When comparing the uptake of pVOCs between the various plant species and their parts, all plants had an affinity to uptake branched alkanes (~32% of Gasoline) within all structures (leaf, stem, root), particularly dimethyl nonane; tetramethyldecane; dimethyl dodecane; tetramethyl heptadecane; trimethyl octane; trimethyl dodecane; methyltridecane and methyldecane. This was also apparent across the alcohol, alkene, ester and phenol functional groups (specific chemical identities are listed in Table S1). Interestingly, pairwise comparisons identified *Spathiphyllum wallisii* as the most efficient in overall pVOC species uptake significantly outperforming *S. aureus* and *P. clusiifolia* (p. Adjusted <0.05). Specific plant part comparisons saw significantly better pVOC uptake in the roots of *S. Pettite* then *S. aureus* (p. adjusted $=$ 0.042) and in the leaf and stem compared to *P. clusiifolia* (p. adjusted $=$ 0.047, 0.027; respectively). This may be due to its larger foliage surface area compared to *P. clusiifolia* and *S. aureus* (Fig. 2, C1). Whilst previous work has reported an absence of significant correlation between leaf area and TVOC removal (Suárez-Cáceres et al., 2021), those studies have primarily focused on removal of individual VOC types rather than a large, heterogeneous VOC profile as studied within the current work. It may be the case that plants with larger foliage surface areas facilitate a greater capture of multiple VOC types through deposition. Across all the plant species, various pVOCs were recorded within their leaf parts that were not also detected in stem and root systems from the same plants. This was most noticeable with hexanol, which was only recorded in high quantities within the leaves of all plant species. Once inside the leaf, pollutant gases diffuse into the spaces between the leaf cells, where they are either detoxified and/or translocated to the roots and rhizosphere via the phloem (Noctor et al., 2011; Singh & Tripathi, 2007). It is thus logical that pVOCs found in the leaf should be present throughout the whole plant system as was observed for volatile alkanes in the current work. The difference between alkane and hexanol distribution recorded here may be due to the much higher concentrations of alkanes, which make up most of gasoline by volume (National Center for Biotechnology Information, 2023), resulting in their more rapid uptake and translocation to the root system (Oyabu et al., 2003) compared to hexanol.

Various pVOCs were also recorded within stem and root samples while not appearing within the leaves of the same species, specifically, *Spathiphyllum wallisii's* stems contained dimethyloctane; methyldecane; methyldodecanol; tetramethylhexadecanol and trifluoroacetoxypentadecane and in the root samples we detected methylundecanethiol; octyldodecylether and pentadecane, none of which were present in leaf samples. *Scindapsus aureus* had ethylnonene; methlundecane and tertramethylheptadecane in the stem and decane; methylundecanol; trifluoroacetoxypentadecane in the root but not leaf samples, while *Peperomia clusiifolia* contained dimethyldecene; dodecyldichloracetate; hexyldodecanol; methyldecane; methylundecanethiol; octyltetracosylether and trifluoroacetoxypentadecane) in the stem and ethylhexanol in the roots only. This phenomenon of VOCs only being detected within the plants' stems and roots may be due to a rate limiting step in plant VOC removal (Baduru et al., 2008). According to Fick's first law of diffusion, gasses pass into plant tissues by diffusing down a concentration gradient (Wei et al., 2017): this may explain the presence of pVOCs solely within the stem, as preferential absorption of other VOCs may lead to high volatile gas densities in the leaves, preventing the uptake of less readily absorbed species. As such,

the stem may begin to absorb other VOCs from the air, however due to the lack of stomata on the plant stem, pVOCs accumulate and gradually penetrate through to the phloem before they can be translocated down to the roots (Kirkham, 2014).

The soil samples were a composite mixture taken from all planted areas within each green wall. The substrate was outperformed by all plant species for pVOC uptake (p. adjusted = 0.06 for all respectively), after 24 h of exposure there was no evidence of the amide, ether, peroxide, sulphides, and thiol pVOC groups within the substrate (Fig. 5). This may be explained by the system's passive nature. While substrate adsorption has been considered a primary sink for pollutant removal by green wall systems (Prodanovic et al., 2017, 2018), this pathway may pertain more to active systems where polluted air streams are forced through the growing media. It may be the case that within passive green wall systems most pollutant removal is achieved through foliar uptake where it is then translocated via the phloem to rhizospheric bacteria around the root system (Wood et al., 2006). Here pVOC excretion may occur from the plant's roots into the substrate (Kim et al., 2016). This hypothesis is backed by the presence of alcohols, alkanes, alkenes, esters, and phenols within the substrate as these functional groups were detected in each plant species and plant parts while those absent functional groups saw minimal to no detection within the root systems of the plant species. As such root excretion of these pVOCs into the substrate was minute and possibly at concentrations that were undetectable through GC-MS analysis (Wei et al., 2017). A secondary possibility is that these VOCs were degraded by bacteria in the substrate before samples were taken. It is thus suggested that future work test samples collected at a finer time scale to determine which of these possibilities is true.

3.3. VOC exposure influences plant-associated bacterial community phenotypes

Non-metric Multidimensional Scaling (NMDS) with environmental vectors fitted to the ordination indicated a stress value of 0.05, represent accurate visual representation of the changes of integrated phenotype across different exposure treatments and times (Fig. 6). An analysis of plant and substrate-associated heterotrophic bacteria was performed in concert with the VOC analysis to determine whether there were large scale microbial patterns that interacted with VOC fate. PERMANOVA

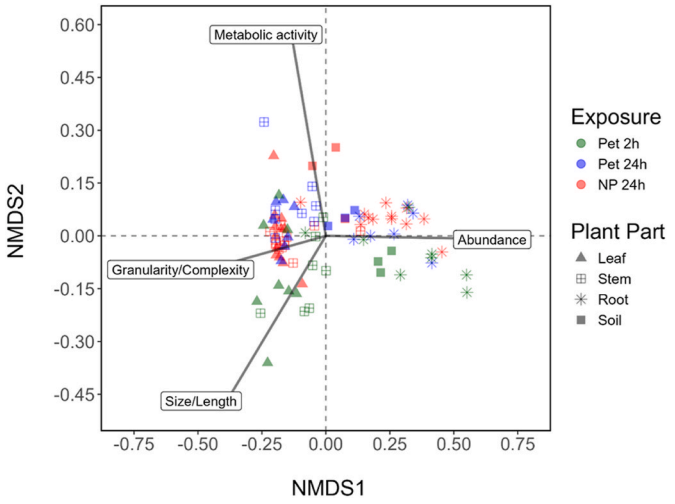

Fig. 6. nMDS ordination of bacterial 'integrated phenotype' data in relation to pVOC exposure and plant part accumulation. Vectors display maximum correlations between observations and phenotypic traits. Ordination is based on Bray-Curtis dissimilarity with a stress value of 0.051. Pet 2 h: samples exposed to gasoline vapour for 2 h. Pet 24 h: samples exposed to gasoline vapour for 24 h. NP: 24 h chamber controls.

indicated that plant part, gasoline exposure and exposure time had significant effects on the recorded bacterial phenotype ($p = 0.001$), with significant interactions between plant part and gasoline exposure ($p = 0.009$). Plant species was not found to have significant effects on bacterial phenotype, thus this variable was omitted for the SIMPER analysis.

Subsequent SIMPER analysis found cell abundance was the largest contributor to dissimilarity amongst the plant parts, with the root samples exhibiting significantly higher bacterial cell abundance than both leaf and stem samples ($p = 0.001$ in both cases). Along with the far greater access to water and nutrients in the rhizosphere, soil also provides a more stable environment compared to the phyllosphere (Bulgarelli et al., 2013), with bacterial epiphytes in the phyllosphere far more directly exposed to acute fluctuations in temperature and humidity, along with the lethal effects of UV irradiation (Vorholt, 2012). PVOCs were detected within the plant root zones after 24 h (Fig. 5), for rhizospheric bacteria the exposure was associated with a significant decrease in cell abundance ($p = 0.045$), and in metabolic activity ($p = 0.005$) based on measurements of cell specific HNA or LNA, with HNA corresponding to cells which are more metabolically active (Jellet, 1996). Several previous studies have observed notable increases in the rate of VOC removal efficiency over repeated exposure in passive botanical systems and have associated this effect with the specific biostimulation of bioremediating microbial communities (Orwell et al., 2006; Torpy et al., 2013a; Wood et al., 2006). It is possible that the short-term testing period in the current study could have led to similar microbial community changes at a detectable scale, however, future work should focus on detailed microbial profiling and understanding of metabolic pathways to shed light on the effects of VOCs on rhizospheric microbial communities. It should be noted that previous work within this field has been limited VOC exposure to single or at most two VOCs, which may have led to the focussed stimulation of a narrower group of bacteria than the complex VOC mix used in the current work.

Similar observations were also made when comparing the no petroleum exposed rhizosphere to the 2-hr exposed petroleum rhizosphere samples, however, with more significantly pronounced p-values (metabolic activity decrease $p = 0.001$ and abundance decrease $p = 0.030$). Recent research focused on the botanical degradation of petroleum vapour has indicated that peak pVOC degradation occurs at approximately 2 h after initial exposure (Matheson et al., 2023b). It is likely that this is when innate pVOC degradation enzyme systems within the phyllospheric bacterial community are in the process of active mobilization in response to the petroleum vapour resulting in the increased metabolic activity and granularity seen in this work (Fig. 6).

Phyllospheric bacteria are those residing on the leaf and stem structures of the plants. For these communities under no petroleum exposure both the microbes in the leaf and stem displayed significantly larger cell size then those in the root ($p = 0.009$) while cell abundance in the rhizosphere was larger ($p = 0.001$). Following petroleum exposure after 24 h the phyllosphere bacteria in the leaf became significantly more complex/granular ($p = 0.004$) while bacteria on the stem saw an indication of increased DNA metabolic activity ($p = 0.002$). Internal granularity is a side scatter measurement of cellular components (i.e. nucleus, granulocytes, monocytes). Petroleum contamination has been shown previously to positively influence inorganic nitrogen and hydrocarbon degrading bacteria within soil environments (Nie et al., 2011) which may be equivalent to the effects recorded here, as bacterial populations are being exposed to high concentrations of petroleum vapour they require higher metabolic activity for degradation as-well as larger vacuoles for nitrogen storage (Walecka-Hutchison & Walworth, 2007).

Interestingly after petroleum exposure phyllospheric communities where no longer statistically different in cell size to the non-exposed rhizospheric community, indicating possible reductions in phyllospheric cell size. Additionally, although the rhizosphere remained statistically larger in abundance ($p = 0.004$, $p = 0.015$) there was a statistical shift suggesting possible increases in abundance of the

phyllospheric communities. Similar observations were also apparent in the 2-hr exposed samples. It is known through studies related to the bacterial cell cycle that nutrient-rich conditions lead to a decrease in mass doubling time and an increase in cell size, whereas nutrient-poor conditions curtail growth and reduce cell size (Fantes & Nurse, 1977; Schaechter et al., 1958). The hypothesised bacterial cell responses to petroleum exposure proposed within this work may be the result of processes that bacterial cells utilise to access the newly introduced hydrophobic nutrient source. Oso et al. (2019) investigated the ability of 21 phyllospheric bacterial strains to grow on diesel fuel. The bacteria tested were not selected for their abilities to degrade hydrocarbons. Of the 21 strains, 9 were found to require several days before any increase in growth was detected, and no strains exhibited an exponential growth phase — this was thought to be due to carbon limitation resulting from the surface of oil droplets in the solution. An equivalent effect may be apparent to a lesser degree in this work, as initial exposure to high concentration gasoline vapour possibly resulted in the death of non-hydrocarbon degrading bacteria, while the surviving bacterial cell's access to nutrients were slowed because of hydrophobic gasoline vapour contaminating surface water droplets, thus reducing diffusion to the bacteria (Schreiber et al., 2005). It is reasonable to suggest that the initial decreases in cell size and length would not persist over longer time periods as hydrocarbon degrading bacteria begin to produce surfactants which would increase the bioavailability of hydrocarbons by reducing water surface tension and thus increasing the surface area of oil droplets (Banat et al., 2010; Patel et al., 2019; Ron & Rosenberg, 2014; Silva et al., 2014).

When observing the bacterial communities within the soil of the green walls without petroleum exposure, both leaf and stem communities exhibited significantly higher cell complexity and cell size ($p = 0.002$, $p = 0.043$; respectively), while root communities only contained an increased abundance of cells $p = 0.050$. Following petroleum exposure after 24 h the leaf communities maintained higher cell complexity $p = 0.004$ and saw increased metabolic activity $p = 0.002$, while stem communities only saw significantly higher metabolic activity $p = 0.012$ interestingly there was no longer a statistical difference in cell size, comparisons to root communities saw no statistical differences at all. Overall these results indicate a propensity for gasoline exposure to favour smaller less complex/lower DNA bacteria within rhizosphere and substrate communities and more complex higher DNA bacteria in phyllospheric communities. Here, we present novel findings related to the phenotypic changes within green wall rhizospheric and phyllospheric bacterial communities resulting from to exposure to a 'real world' azeotropic VOC pollution source. The experimental conditions within this work only observed short term changes; future work should test the microbial responses to long term exposure to azeotropic VOC mixtures, as well as utilising exact microbial profiling and characterising techniques such as 16s rNA amplicon sequencing approaches coupled with real-time PCR on amplified DNA targeting expression of BTEX degrading enzymes. This will provide greater understanding of the metabolic pathways, genes and enzymes involved in microbial remediation within botanical systems, and could facilitate improved screening of plant species to advance the pollutant removal efficiency of these systems.

4. Conclusion

This study provides novel insights into how a passive green wall system removes, contains and deposits speciated VOCs which make up gasoline vapour, along with community level bacterial changes that occur with exposure. Differences amongst the plant species in the green wall were recorded, with *Spathiphyllum wallisii* being the only species to contain all pVOC functional groups, while different pVOCs were found across all the plant parts within the green walls, the leaf areas were revealed to capture several pVOCs that were not present in other parts of the green wall plants. While aromatics were not found within the plant's parts and substrate of the green wall after 24 h, SPME analysis over 8-h showed the green wall was able to significantly remove Benzene derivatives, ethylbenzene and xylene from the atmosphere. Exposure to pVOCs was found to invoke phenotypic changes within the phyllospheric bacterial communities leading to increased metabolic activity and cellular granularity while diminishing cell size. While communities within the rhizosphere did not demonstrate phenotypic changes, this was most likely due to their belowground environment, and it is possible that repeated VOC exposure over a longer time period would lead to detectable effects. This research has significant implications given the highly toxic nature of the BTEX group found within gasoline vapour, which poses a considerable risk to human health, and the high efficiency by which plant-based systems can remediate these pollutants.

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CRediT authorship contribution statement

Stephen Matheson: Writing – review & editing, Writing – original draft, Formal analysis, Data curation, Conceptualization. **Robert Fleck:** Methodology, Writing – original draft, Writing – review & editing. **Thomas Lockwood:** Resources, Software. **Raissa L. Gill:** Data curation, Formal analysis, Visualization, Writing – review & editing. **Luowen Lyu:** Visualization, Writing – review & editing. **Peter J. Irga:** Funding acquisition, Supervision, Writing – original draft, Writing – review & editing. **Fraser R. Torpy:** Funding acquisition, Supervision, Writing – original draft, Writing – review & editing.

Declaration of Competing Interest

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.envpol.2024.125199.

Data availability

Data will be made available on request.

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