

ELIMINATION OF PRIORITY INDOOR VOLATILE ORGANIC COMPOUNDS BY ACTIVE BOTANICAL BIOFILTERS: EXPERIMENTAL AND MODELING APPROACH

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Abstract

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Indoor air

Multiphysics modeling

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This master's dissertation investigates the elimination of priority volatile organic compounds (VOCs) by active botanical biofilters through a combined experimental and modeling approach. The research focuses on the removal of benzene, toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde (BTEXFA) compounds, which represent indoor air pollutants posing a realistic threat to human health.

The experimental approach employed an active botanical biofilter (ABB) and microbial biofilters (MBs) to evaluate VOC removal performance under varying boundary conditions. First a study on ABB acclimatization was conducted. Once fully operational and removing VOCs, an airflow variation study was performed to document removal at varying airflow rates. Simultaneously, a novel 3D multiphysics model based on computational fluid dynamics was developed to characterize MB substrate aerodynamics, VOC transport, and removal phenomena.

The effects of acclimatization on VOC removal varied depending on the specific VOC, with different patterns evident between BTEX, formaldehyde, and acetaldehyde. Furthermore, it was demonstrated that acclimatization by repeated VOC exposure significantly enhanced BTEX removal efficiency. The airflow variation study revealed a complex mix of effects influencing ABB performance, with many distinct reactions to airflow increase between VOCs. An aerodynamics submodel was successfully validated with experimental data, while the full preliminary model left room for improvement.

This research advances the understanding of botanical biofiltration mechanisms and provides practical insights for optimizing ABB-based indoor air purification systems, contributing to sustainable urban bioscience engineering applications.

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List of Abbreviations

ABB: Active Botanical Biofilter

BB: Botanical Biofiltration

BTEX: Benzene, Toluene, Ethylbenzene, and Xylene

BTEXF: Benzene, Toluene, Ethylbenzene, Xylene and Formaldehyde

BTEXFA: Benzene, Toluene, Ethylbenzene, Xylene, Formaldehyde and Acetaldehyde

DALYs: Disability-Adjusted Life Years

DBAF: Dynamic Botanical Air Filtration

ERV: Energy Recovery Ventilation

FA: Formaldehyde and Acetaldehyde

FDH: Formaldehyde Dehydrogenase

FTDH: Formate Dehydrogenase

GAC: Granular Activated Carbon

HEPA: High-Efficiency Particulate Air

HRV: Heat Recovery Ventilation

IARC: International Agency for Research on Cancer

IAQ: Indoor Air Quality

LMM: Linear Mixed Model

MB: Microbial Biofilter

MFCs: Microbial Fuel Cells

NBPI: Corona Discharge and Needlepoint Ionization

OQAI: Indoor Air Quality Observatory

PCO: Photocatalytic Oxidation

PM: Particulate Matter

SBS: Sick Building Syndrome

SO₂: Sulfur Dioxide

TVOC: Total Volatile Organic Compounds

U.S. EPA: United States Environmental Protection Agency

UV: Ultraviolet

VOC: Volatile Organic Compound

VVOC: Very Volatile Organic Compound

WHO: World Health Organisation

I Literature Study

i Prelude: The Life, The Death, and The Breath

Air pollution was recognized early in ancient times. The connection between the air we breathe, and the vitality of life is intricately explored in the classical texts of Aristotle and Hippocrates ^[1,2]. Aristotle argued that the interconnection between life, death, and breath is explained by the exchange of particles in the air. He observed that air contains particles essential for the mind and soul, emphasizing the critical nature of breathing in sustaining life. He argued that life and death are bound up with the taking in and letting out of the breath ^[1]. Hippocrates, on the other hand, connected the quality of air with the health of individuals, noting that impure air can lead to diseases, particularly in urban environments that lack cleansing air flow ^[2]. Their observations indicate an early recognition of how environmental conditions and human activities can impact the atmosphere and, consequently, the health of urban inhabitants ^[1,2]. These ancient perspectives on air quality and health remain relevant today, a time characterized by rapid urbanization. As more people move to cities, new challenges emerge, including the often-overlooked issue of poor indoor air quality (IAQ) ^[3].

ii Indoor and outdoor air quality

Air quality is typically considered an outdoor problem, receiving more attention historically than indoor air ^[3]. Likewise, the health effects of indoor air pollutants have not been studied to the same extent as those of outdoor air pollutants ^[3]. Yet it is estimated, particularly in contemporary Western societies, that urban populations usually spend more than 80–90% of their time inside buildings, according to their activity patterns ^[4]. The latter has been exacerbated during the COVID pandemic ^[5]. Indoor spaces such as office buildings, schools, malls, and households can be several times more contaminated than outdoors, particularly by Volatile Organic Compounds (VOCs), which have the majority of their sources indoors (section 1.4) ^[3,5]. For instance, at the time of initial occupancy, office buildings can harbour indoor air with total volatile organic compound (VOC) concentrations that are 50 to 100 times greater than those in the outdoor air ^[3]. With the rise in the global urban population, individuals are increasingly spending more time indoors, resulting in prolonged exposure to increasing indoor air pollution ^[5–7]. This situation presents a serious risk to human health. The array of air pollutants that contribute to poor IAQ is extensive, including particulate matter (PM), ozone, heavy metals, sulfur dioxide (SO₂), nitrogen dioxide (NO₂), and VOCs, among others ^[5,8]. A growing body of research suggests that indoor air pollutants are significant contributors to health issues experienced by individuals in built environments ^[9]. These health challenges can subsequently affect public health on a larger scale ^[8].

iii Indoor air quality from a socioeconomic perspective

Indoor air pollution is a major concern worldwide ^[3,5,6]. Apart from particulate matter, high-income countries are mostly affected by VOCs ^[3,5]. Modern energy-efficient buildings are often sealed tightly, controlling indoor-outdoor air exchanges and recirculating much of the indoor air ^[3]. This leads to high concentrations of pollutants such as VOCs over time, even if their emission rates are low ^[3]. Feigin et

al., (2016) state that 10.2% of high-income countries are already affected by exposure to indoor air pollution^[10]. This is in the form of respiratory and cardiovascular diseases in their inhabitants ^[5,10]. While this is 33.7% for middle and low-income countries, it still shows that IAQ concerns all economic classes.

In low- and middle-income countries like Haiti and Guatemala (Central America and Caribbean Region) or Mali, Niger, Ethiopia (African Region) polluting solid fuels are used for cooking and heating impacting the indoor air quality ^[3,11]. According to WHO data, above 50% of households in the aforementioned countries use solid fuels to meet their basic needs ^[12]. Pollutants, like benzene, toluene, and PM, mentioned in Table 1, are produced by inefficient and incomplete solid fuel combustion ^[5]. If the indoor environment is occupied and poorly ventilated, it aggravates the IAQ ^[3]. According to the World Health Organisation (WHO), over 3.2 million people died prematurely from indoor air pollution caused by cooking with solid fuels in 2020 ^[13,14]. This included countries like; India, China, Russia, Nigeria and Indonesia having the highest death tolls ^[13,14].

iv Indoor sources of pollutants and the focus on VOC's

IAQ is mainly determined by indoor emission sources due to the small air volume of the indoors and its associated reduced ventilation rate ^[3]. This way small emissions easily result in the build-up of unhealthy concentrations. Though, IAQ is also affected by outdoor air pollutant concentrations according to the present ventilation rate. Many indoor air pollutants have their emission source within the indoor environment ^[3]. Table 1 shows these pollutants and main indoor sources ^[5]. The most abundant and harmful group of these (indicated in red) are Volatile Organic Compounds (VOCs). These substances have a high vapor pressure and low boiling point at room temperature, leading to a large number of molecules easily evaporating into the surrounding air ^[5]. VOCs are widespread indoors due to their use in various household products, such as paints, cleaning agents, adhesives, and building materials ^[8,15]. Consequently, occupants are exposed to these substances. Numerous VOCs are linked to various negative health impacts, such as respiratory problems, neurological harm, and an elevated likelihood of developing certain types of cancer ^[8].

The most common VOCs found in the air include formaldehyde, benzene, toluene, ethylbenzene, and xylene (collectively referred to as BTEX) ^[3,5]. These substances represent a considerable portion of the Total Volatile Organic Compounds (TVOC) concentration ^[3,5]. When formaldehyde is added to the BTEX list (resulting in BTEXF), these primary indoor VOCs are believed to contribute to what is known as "sick building syndrome" ^[5]. Due to all the alarming characteristics and effects above, VOCs and BTEXF more specifically will become the main problem factor on which we will focus in the upcoming study [16]. Sick Building Syndrome (SBS) refers to a condition where individuals inside a building experience health and comfort issues that are not attributed to a specific illness ^[16]. This encompasses various mucosal, skin, and general symptoms linked to work environments in certain buildings. It's the employees who show symptoms due to elevated contamination levels, while the building itself is deemed "sick" due to its indoor environment or services being the culprit ^[17]. Buildings are categorized as sick based on their symptom index, a measure determined by the number of work-related symptoms reported per occupant.

Table 1: Priority indoor volatile organic compounds (VOCs), their emission sources, health effects and threshold values [5,8].

Indoor air pollutant	Indoor Emission Source	Health Effects/Risks	IARC (classification) [18]	IARC IUR value (cancer potency) [18]	Belgian limits: selected reference value [µg/m³] [18]	Flemish Indoor Air Target Guidance Value [µg/m³] [18]	Flemish Indoor Air Intervention Guidance Value [µg/m³] [18]	Other recommended limits [µg/m³]
Polycyclic Aromatic Hydrocarbons (PAHs)	solid fuel combustion							
Volatile Organic Compounds (VOCs) - BTEXF	furniture, carpets, building materials, cleaning products	sick building syndrome	/		200-300 (total VOC) [18]	300	1000	200-300 (total VOC) [18]
Benzene	combustion devices, new or renovated buildings, building materials such as paints, carpets, solvents, various plastics, and wooden furniture	Chronic exposure: carcinogenic-, blood-illnesses, reproductive problems, neurological problems. myeloid leukemia [5]	Group1	6×10^{-6}	10 (ATSDR,2007)	/	0.4	0: no safe exposure threshold [8]
Toluene	paints, gasoline, resins, cosmetics, adhesives and coatings, renovated buildings, combustion devices, tobacco smoke, fingernail polish, other household products	Long-term exposure: respiratory diseases, can affect the central nervous system	Group 3	/	260 (WHO,2000)	5000	14000	/
Ethylbenzene	paints, plastics, solvents, combustion, dyes, polymers, lacquers, insecticides, cleaning products, pharmaceuticals, adhesives	Higher concentration and long-term exposure: problems related to dizziness, headache, the gastrointestinal, central nervous systems, leukemia, respiratory and reproductive system	Group 2B	/	260 (ATSDR)	/	/	/
Xylene			Group 3	/	200 (ATSDR,2007b)	/	/	/
Formaldehyde	wood products made with adhesives	skin irritation, respiratory issues, linked to nasopharyngeal cancer [8]	Group1	/	100 (WHO,2010)	/	100	100 (WHO) [8]
Acetaldehyde		Respiratory symptoms [18]	Group 2B	2.2×10^{-6}	140 (OEHHA,2008)	160	480	/
Heavy Metals	dust, paint, plumbing							
Sulfur Dioxide (SO2)	fossil fuel combustion							
Nitrogen Dioxide (NO2)	gas stoves, heaters							
Black Carbon	incomplete solid fuel combustion							
Carbon Monoxide (CO)	gas appliances, heating systems							
Ozone	electrinics, photocopiers							
Particulate Matter (PM2.5, PM10)	dust, combustion processes							
Biological pollutants	pollen, animals, pathogens, humidifiers							

v International, Belgian, and Flemish Guidelines

To address the health risks associated with exposure to various indoor air pollutants, organizations like the WHO, US EPA and European Environment Agency formulate guidelines to establish safe limits within the indoor environment ^[8]. However, each country may adapt their safety limits, like in the case of Belgium. Priority indoor air pollutants, maximum allowed indoor concentration, and main health effects are shown in Table 1.

Air quality-related health effects represent a significant cost on society both in the form of economic pressure on healthcare systems and in terms of lost healthy life years ^[18]. In 2017, the Superior Health Council of Belgium elaborated an advisory report on indoor air quality at the federal level, given the need to harmonize data, provide recommendations for research and policy implementation. Data was collected on IAQ in Belgium, and it was shown that the TVOC limit was exceeded in 95% of the locations tested. Following the report's conclusions, plans were made to do an exploratory study of the socio-economic cost of the IAQ, including accurate calculation of DALY's ^[18]. As of now (2025), the Superior Health Council of Belgium has given no updates on this matter. Also, the Flemish region has adopted its own target and intervention guidance values for indoor air in building ^[19]. These values indicate desired reference concentrations and a more stringent level when action should be taken to reduce exposure to a substance, respectively. These values are applied for VOCs in many societal areas (health policy, evaluation of IAQ data, regulatory compliance, and building design) and are listed in Table 1 ^[19]. Additionally, other countries have estimated costs of poor IAQ. In 2014, the Indoor Air Quality Observatory (OQAI) in France conducted such a study and estimated that approximately 28,000 new cases of illness and more than 20,000 deaths per year were linked to only six frequently encountered indoor air pollutants, namely benzene, trichloroethylene, radon, carbon monoxide, particles and environmental tobacco smoke ^[20]. This resulted in a cost of approximately 19 billion euros, which can be considered a great impact ^[21]. The economic impact attributed to benzene as single VOC was 851 million euros a year ^[20]. Agencies like the WHO and EPA emphasize minimizing exposure to these pollutants due to their potential health risks ^[8,18]. In the case of the WHO this is done by calculating risk metrics and reference values and by providing general principles for maintaining IAQ ^[8,18]. While the WHO does not provide specific advised limits for individual indoor VOCs, the agency stresses that for precise numerical limits, it is often necessary to refer to national or regional guidelines based on local health assessments and regulations ^[8]. In the case of Belgium, the Superior Health Council has determined its thresholds for BTEX based on reference values found in publications from different agencies, including the WHO, ATSDR and OEHA ^[18]. These often-used threshold values and their corresponding agencies can be found in Table 1.

vi The questionable safety of exposure thresholds

Amongst BTEXF several compounds are categorized as carcinogens, indicating their ability to induce cancer in humans ^[8]. The International Agency for Research on Cancer (IARC) classifies Benzene and Formaldehyde as carcinogenic to humans (Group 1), Ethylbenzene and Acetaldehyde as possibly carcinogenic to humans (Group 2B), and Toluene and Xylene as not classifiable regarding their

carcinogenicity to humans (Group 3) ^[18,22]. A relevant metric that the WHO publishes as a guideline for carcinogenic risk is the cancer potency factor for inhaled compounds, which can be expressed as the Inhalation Unit Risk (IUR) ^[18]. IUR is the upper-bound excess lifetime cancer risk estimated to result from continuous exposure to an agent at a concentration of 1 $\mu\text{g m}^{-3}$ in air ^[18]. It is crucial to note that while agencies and governments set thresholds and limits for pollutants, this is not translated into zero risk and health effects. As an example, genotoxic effects are non-threshold effects and compounds provoking them have no limit below which no effects are likely ^[18]. As a result, it can be implied that the carcinogenic compounds amongst BTEXF like benzene, do not have a safe exposure threshold, indicating that any level of exposure could pose health risks ^[8]. (Table 1)

vii Current technologies and market

Improving indoor air quality requires reducing the VOC levels in the indoor air, which can be accomplished by several approaches. It is suggested that the first step is decreasing indoor pollution sources, encompassing avoiding the use of emission sources and reducing emitting behaviours such as natural and human activities (e.g., industrial activities) ^[5].

Source substitution emerges as a pivotal approach in addressing this first step in manufacturing processes. Particularly within the furniture industry, VOCs are often emitted from raw materials like coatings, which can lead to indoor emissions during and after the production process ^[15]. The strategic replacement of VOC-emitting materials with alternatives that emit lower or no VOCs plays a critical role in mitigating these emissions. For instance, the substitution of solvent-based coatings with water-based counterparts has shown substantial promise. As evidenced in the study conducted by Liu et al. (2023) in the Pearl River Delta, China, the furniture manufacturing sector is a considerable source of VOCs due to its reliance on traditional, high-emission coatings. This study discusses source substitution as the most effective way to reduce VOC emissions in industries like furniture manufacturing ^[15].

The final step involves using effective air purification methods to capture, eliminate or neutralize the compounds. This can be accomplished by two main approaches: improving ventilation and removing the pollutants ^[5]. The first approach relies on reducing pollutant concentrations through ventilation, while the latter leverages various technologies to mitigate air pollutants ^[23]. The basic principle behind ventilation is diluting indoor air pollutants with fresh outdoor air, which can be achieved naturally, e.g., by opening up a window, or through mechanical systems. Some mechanical systems include heat recovery ventilation (HRV) and energy recovery ventilation (ERV) to exchange stale indoor air with fresh outdoor air constantly ^[23]. While ventilation is important, it is not always sufficient. There are situations where ventilation is not possible or is restricted, e.g., due to the outdoor air itself being highly polluted, or a high temperature differential. Therefore, there is a need for cleaning/purification technologies. These come with many options but can broadly be categorized into physicochemical and biological technologies. In the former, physical or chemical processes are used to remove pollutants from the indoor air. (e.g., filtration, adsorption, ionization, UV-photocatalytic oxidation) ^[23]. Biological technologies encompass a wide range of innovations including, Microbial Fuel Cells (MFCs), Microalgae-Based Air

Purification Systems, Plant Purification Methods, and most importantly in the scope of this study, Botanical Biofiltration (BB) ^[23,24].

Conventional physicochemical technologies which are believed to remove indoor air pollutants are not all fit for the removal of VOCs ^[23,25]. For example, HEPA filters use mechanical filtration to trap particles such as PM_{2.5} effectively, but they are not capable of removing gaseous pollutants such as VOCs. New nanofiber materials that can adsorb VOCs are being developed, but mechanical filtration brings additional drawbacks. The longer these filters operate, the higher the chance of potential pollution by re-emission of VOCs (if not regularly replaced or maintained) ^[23,25].

The most widespread technique for retaining VOCs is the use of activated carbon, which is considered highly efficient ^[23,25]. Given its high adsorption capacity, it captures air pollutants like VOCs on its surface. Similar to PM-removing filters, adsorbents used in active carbon filters suffer from VOC saturation and require regeneration or replacement to maintain their capture efficiency ^[23,25]. Otherwise, VOCs may desorb again ^[25]. Regeneration of activated carbon involves adsorbent loss and is a cost intensive process ^[23,24]. Its disposal creates hazardous solid waste that must be further treated and/or disposed of correctly. Due to the constant need for new materials and the associated high energy cost of the before-mentioned processes activated carbon adsorption is considered not economically feasible ^[23,24].

Another interesting physicochemical air cleaning technology is UV-Photocatalytic Oxidation (PCO) ^[23]. PCO combines UV-light and a photocatalyst (e.g., TiO₂) to break down VOCs (amongst other indoor air pollutants) at a molecular level. Though multiple studies have achieved up to 72% VOC removal efficiencies with different configurations of the technology, some downsides are also present. Firstly, the oxidizing process can be incomplete, resulting in the creation of harmful by-products like formaldehyde and acetaldehyde. Also, some UV light sources (e.g., UV-V lamps ~185 nm) produce ozone ^[23]. Secondly, it is important to note that PCO is mostly efficient under UV light rather than visible light, which limits its application in indoor environments. Given that indoor air environments often suffer from limited (and changing) lighting conditions. This creates further challenges for effective VOC reduction ^[23]. As a result, researchers are exploring plasmonics to enhance the efficiency of PCO in achieving better degradation rates under available lighting conditions ^[26].

A last physicochemical technology that can aid removing VOCs is Ionization. Air ionization-based devices integrating this technology (e.g. Corona Discharge and Needlepoint (NBPI)), make use of ionizers that generate negative and sometimes positive, ions that react with pollutants ^[23]. Though the associated mechanisms have not yet clearly been established, the ions attach to particles, clumping them together, making it easier to neutralize and remove pollutants from the air. This way the weight of VOC particles is increased, making them easier to remove from the air. However, this does not destroy VOCs. Ionizers are generally not as effective at removing gases, odours, or VOCs compared to other purification methods, such as activated carbon filters. Additionally, similar to UV-based systems, they can, in some cases, produce high levels of ozone and other organic compounds. ^[23,27]. Thus, in real-life applications, air ionisation modules are often combined with HVAC and activated carbon systems ^[23].

Table 2 shows that conventional physicochemical technologies exhibit disadvantages in the long term [23]. The high energy costs and waste (e.g., saturated filters, bulbs, ...) associated with these technologies are hard to avoid, since continuous operation is necessary to avoid emission build-up. In addition, the high capital and operating costs associated with them, render them inaccessible for many consumers [23]. Thus, there is a need to transition to a more environmentally and economically sustainable technology in terms of VOC removal indoors.

Table 2: Indoor air pollution technologies conventional physicochemical technologies compared to Botanical Biofiltration. Adapted from Alvarado-Alvarado et al. (2024) and from various sources.

Indoor air purification technology	conventional physicochemical technologies				Biological technologies
	HEPA Filter	Active carbon filtration	UV-Photocatalytic oxidation (PCO)	Ionization	Botanical biofiltration
					
Type	Mechanical filtration	Physicochemical Adsorption	Physicochemical Oxidation	Physicochemical Ionization	Biological
Main mechanism	Filtration				
VOC removal	No (primarily designed for particle removal)	≈ 90%	≈ 72%	Low	Moderate to high depending on configuration of components. Removal range: 50 – 90%
VOC mineralisation	No	No	Yes, but incomplete	No	Yes, due to multiple pathways
Hazardous by-products	Resuspension of VOCs	VOCs might desorb	reaction byproducts that are more toxic or harmful than the original constituents	Ozone and other organic compounds	Intermediate compounds can be metabolized
Waste generation	Spent filters	Spent adsorbent	Catalyst, UV source	-	Organic waste
Energy Consumption	Moderate	Moderate	Moderate to high	Low	Low
Additional downsides	regular filter replacement [23]	regular filter replacement [23] require regular and expensive maintenance	Ozone generation Need for perfect precise lighting conditions	- - -	not widely commercially available - -
Additional benefits	-	-	actual breakdown of VOCs	easily combined with AC and HVAC [27]	Enhanced productivity, esthetics, thermal comfort, noise reduction.

It is argued that there is no singular effective method for removing VOCs from the indoor air due to challenges associated with their very low concentration range (in the $\mu\text{g}/\text{m}^3$ range), diversity of chemical characteristics, and variability of composition commonly observed in indoor environments [28]. Nevertheless, biological methods have shown a certain potential for tackling some of the aforementioned disadvantages associated with the conventional technologies (illustrated in Table 2). This research field is mostly dominated by botanical purifiers which leverage plants, the soil (or substrate) and their associated microorganisms and enzymes to remove and break down contaminants through various mechanisms [28]. Botanical (or plant-) purification methods include passive botanical biofiltration systems, biotrickling filters (including botanical bioscrubbers), dynamic botanical filtration (DBAF) and active botanical biofiltration systems [23,29,30]. Other biological methods like, microalgae-based methods do exist, but currently (2025) see little further development in terms of real indoor scenario applications [23].

viii Botanical Biofiltration: Definition and Description

Botanical biofiltration or plant-assisted biofiltration is considered a sustainable, biological-based treatment method suitable to remove hazardous VOCs and other air pollutants (e.g., PM, NO_x , O_3 , CO_2) using plants and their associated microorganisms through phytoremediation, biofiltration, and

bioremediation ^[25]. It leverages complex, symbiotic processes where plants and microorganisms collaborate to remediate airborne contaminants ^[25,31]. Unlike most of the conventional air filtration methods that merely trap pollutants or transfer them into another phase, botanical biofilters actively break down a wide range of harmful compounds through biological processes, transforming them into less toxic or nontoxic substances ^[25]. Thus, they represent a more sustainable approach to air purification that addresses the root of the problem rather than simply relocating it.

The concept of botanical biofilters represents an intersection between natural biological processes and engineered systems designed to improve IAQ. This approach to air purification originated in NASA research conducted by Wolverton et al., (1989) in the late 1980s. Motivated by the emerging SBS in the late 1970s (when energy-efficient buildings were designed with superinsulation and reduced fresh air exchange), they pioneered the search for solutions aiding indoor air pollution abatement. NASA's work demonstrated that low-light-requiring houseplants could effectively remove trace organic pollutants from indoor air ^[31]. They also concluded that the plant root-soil zone was the most effective area for removing VOCs, with soil microorganisms playing a crucial role in breaking down toxic chemicals ^[31]. Although the experiments were merely based on single potted plants rather than a biofilter, this research laid the foundation for the development of botanical biofilters as we understand them today.

ix Botanical Biofiltration: Component Overview

Botanical biofilters consist of several integrated components and mechanisms working jointly. The main components are a botanical, a microbial, a substrate, and an optional airflow-enhancing component (Figure 1).

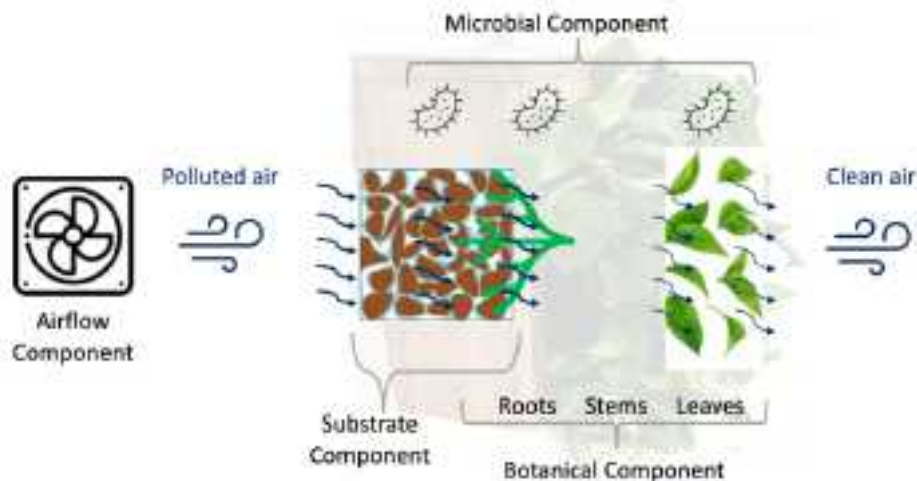


Figure 1: The components of an Active Botanical Biofilter.

The botanical (plant) component, we defined in this thesis as the sum of the foliage and leaf surfaces, stomata (leaf pores), plant stems (above-ground organs), root systems (below-ground organs), and the rhizosphere ^[25,32]. Different plant species have shown varying effectiveness for different pollutants, with some of the most effective species for VOC removal including *Hemigraphis alternata* (Red Ivy), *Hedera helix* (Ivy), *Hoya carnosa*, *Asparagus densiflorus*, and *Spathiphyllum wallisii* (Peace Lily) ^[33]. (Removal was tested for benzene, toluene and TVOC concentrations amongst others.)

The microbial component encompasses microbiomes located on both the botanical component and in the substrate. The microbiomes, in turn, consist of a diverse array of microorganisms (including bacteria, fungi, rhizosphere microbes amongst others) and are also present in the form of biofilms ^[5,23,29]. These microorganisms play a crucial role in breaking down toxic chemicals and VOCs in particular ^[5,24]. In fact, just like the plants themselves, different bacterial strains can remediate higher concentrations of different pollutants ^[29]. NASA research identified several bacteria in the root zones including *Alcaligenes*, *Bacillus*, *Flavobacterium*, *Micrococcus*, and *Pseudomonas* ^[31]. These are common soil microorganisms, and most are known to be capable of biodegrading toxic chemicals when activated by plant root growth.

The substrate includes growing media like soil, compost, coconut husk, pine bark or expanded clay ^[23,34,35]. These materials provide porosity for microbial colonization, and a support structure for the plants. Additionally, activated carbon is sometimes added for increased adsorption capabilities, which has been criticized because of its high energy cost for regeneration ^[23,34,35]. Other growing media such as polyethylene are not uncommon, but it can also consist of a multitude of other material, and furthermore, it may be a combination thereof ^[36]. Substrate compositions used in the state of the art can be consulted in Table 3.

Other components that are often added to botanical biofiltration systems are air-circulation mechanisms, ventilation components (e.g., fans), and distribution systems for uniform air contact ^[37]. In this fashion, the contaminated air is circulated through the root zone and the growing medium for maximum effect. Systems incorporating these elements are called active botanical biofilters (ABBs) ^[37]. These systems enhance the performance of botanical biofilters by ensuring that contaminated air comes into contact with the biological components responsible for pollutant degradation ^[29].

x Botanical Biofiltration: VOC Removal Mechanisms per Component

The removal of VOCs by botanical biofilters involves multiple mechanisms across different components of the system that fall under the umbrella term of bioremediation. This is any process that uses microorganisms, fungi, or plants to remove environmental contaminants from soil, water, or other substrates ^[24]. In the context of this study, the term bioremediation will be solely used to refer to bacterial degradation ^[25]. Another mechanism in botanical biofilters is phytoremediation, a biological technique that uses plants to remove, degrade, or stabilize contaminants ^[24]. This method leverages the natural abilities of the plant to tolerate, absorb, accumulate, and sometimes detoxify pollutants ^[24]. The last mechanism is substrate remediation ^[25]. This process involves the use of substrates to facilitate the transformation, capture, or biodegradation of indoor air pollutants, particularly VOCs ^[25]. In the upcoming sections the mechanisms per component highlighted in Figure 1, will be explored.

1.10.1 Plant Organ-Attributed Mechanisms

The botanical component of a plant-assisted biofilter provides mechanisms that occur jointly in the above-ground and below-ground organs. In this section only plant cell degradation is discussed.

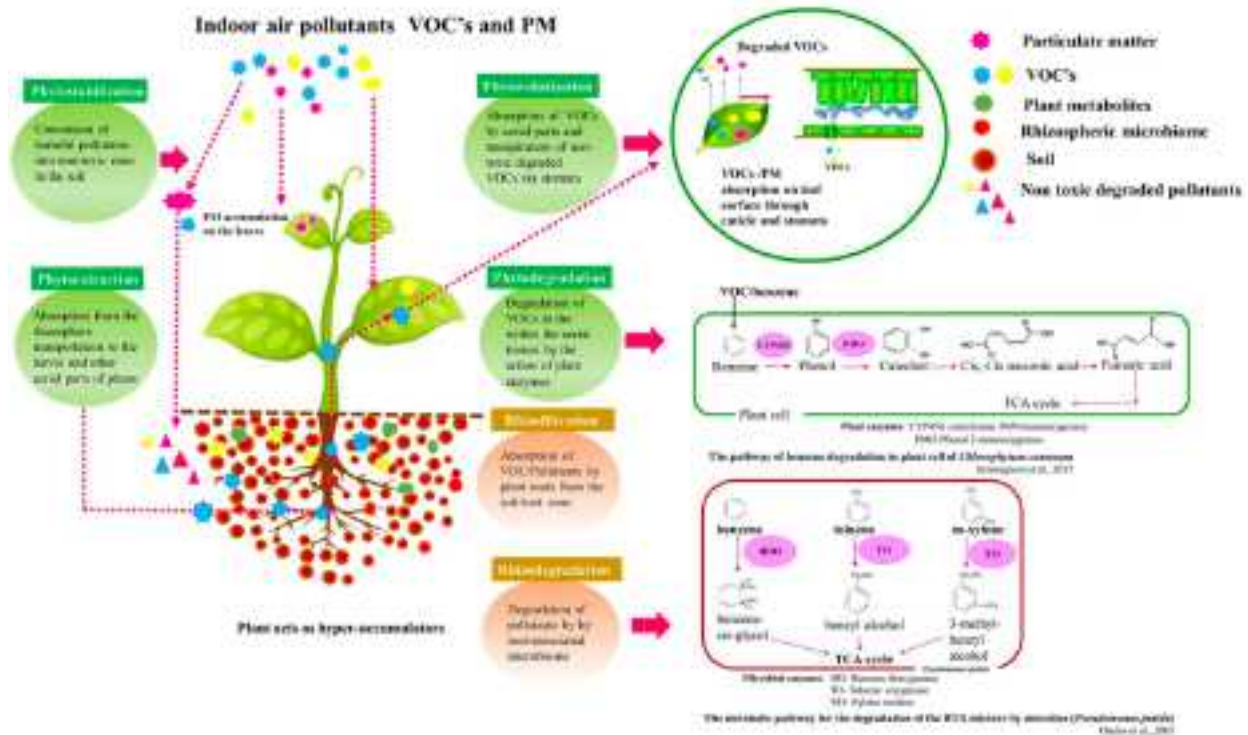


Figure 2: Mechanisms of phytoremediation/plant-based approach for mitigation of indoor air pollution and metabolic pathways by Raghawendra et al. (2023)

The leaves and plant tissue take part in the phytoremediation role. Firstly, VOCs can diffuse through the waxy cuticle according to the VOCs' chemical properties [5,24]. More importantly, through gas exchange or evapotranspiration, VOCs can enter the mesophyll region through stomata and be phytodegraded or metabolically transformed (using plant enzymes) into less harmful substances [5,24].

For instance, formaldehyde is known to be metabolised by a two-step oxidation into CO_2 , governed by (the enzymes) formaldehyde dehydrogenase (FDH) and formate dehydrogenase (FTDH) [38]. The formaldehyde-derived CO_2 can thereafter enter the Calvin cycle and be assimilated in intermediary metabolites (like sucrose). These VOC-derived metabolites can also be translocated to the stems and roots. Thus, in leaves formaldehyde behaves very much like photoassimilated CO_2 [38].

Aromatic hydrocarbons (lipophylic molecules) like BTEX, are easily absorbed by the cuticle's waxy surface and accumulate (before penetrating the epidermis) [39]. Though, for benzene and toluene the primary mode of leaf penetration has been found to be through the stomata (when open). The bulk of the absorbed benzene and toluene is then transformed in the plant cells. A first transformation by chloroplasts, catalyzed by phenolases (CYP450 and PMO) results in phenol and pyrocatechol (hydroxylation of the aromatic ring). This is followed by oxidation leading to aromatic ring cleavage into muconic acid and further conversion into fumaric acid [39]. After this benzene-carbon-skeleton-conversion the VOC-derived carbon gets used in further organic acid metabolism (TCA cycle) (Figure 2) [5,39]. Benzene and toluene derived carbon has been found in non-volatile organic acids, emitted CO_2 and biopolymers, but not in sugars. [39]

It has been concluded that VOCs are a carbon source for plants and are converted into metabolites, lignins and even amino acids [5,38,39]. This aerobic oxidation process also releases CO_2 . Since the

beforementioned processes heavily depend on chloroplast and stomatal activity, there is a pronounced light dependence for VOC assimilation (reported for benzene toluene and formaldehyde) [38,39].

Comparable to the aerial plant part, plant roots can adsorb VOCs from the soil/root zone through rhizofiltration [5]. In some cases, the roots can metabolize VOCs, converting them into less harmful or non-toxic forms through various biochemical pathways [5,29]. In other cases, VOCs can be phytoextracted from the root zone and be transported to the aerial biomass (phytoextraction), where further degradation can occur [5,24]. Another possible mechanism is the immobilization of VOCs (by adsorption, reduction, and precipitation) around the roots, i.e. phytostabilization [5,24]. Additionally, certain plants have specialized root structures, such as root hairs, that increase the surface area for adsorption and absorption, possibly increasing VOC uptake capabilities [35]. The region surrounding root surfaces contains complex microbial communities that are stimulated by compounds exuded from the roots [5,24]. The exudates increase the microbial diversity in the root zone possibly leading to enhanced purification [5,24]. This indicates that specific microbes need these plants in BB systems. Without the living plants BB systems (then acting as MB (microbial biofilter)) can have major disadvantages in terms of VOC removal [36].

A study by Kim et al., (2008) examined the contribution of aerial plant parts versus the root zone of *F. japonica* and *F. benjamina* to VOC (formaldehyde) removal under day and night conditions. Both were evaluated as potted plant (passive BB-) systems in a closed climate chamber where formaldehyde was added, and the concentration decay was monitored. It was demonstrated that the aerial part is active under daylight and can be of the same extent of the root zone. For *F. japonica* 39% of the daytime removal happened in the root zone compared to 98% at night. Obviously, most of the removal at night occurred at the root zone, but the aerial part still exhibited some removal, likely due to cuticular absorption. The root zone was then sterilized and exhibited little removal due to root adsorption which implies that the previous removal in this zone was due to the microorganisms [40]. This indicates that (at least in passive BB systems) root zone and/or rhizosphere mechanisms are the primary source of VOC removal [29,40].

Yet, some research suggest that the use of plants is unlikely to be of value for indoor air purification, due to their low metabolic rate [38]. Nevertheless, root systems provide surface area for microbial colonisation and help convert toxic chemicals into nutrient sources for plants and microbes (with much higher metabolic rates) [5,32].

1.10.2 Microbe-Attributed Mechanisms

VOC biodegradation can occur in almost all parts of the BB system [5]. Most notably there are bacterial communities supporting VOC removal on the phyllosphere (leaves), the rhizosphere (roots) and in the substrate itself.

1.10.2.1 *Phyllosphere associated effects*

On the phyllosphere, most microorganisms are bacteria, non-pathogenic, and usually from a few predominant phylogenetic groups [32]. Some classes include *Alphaproteobacteria* and *Gammaproteobacteria*, and the phyla *Bacteroidetes* and *Actinobacteria*. Despite the presence of a few

dominant phyla, diverse microbial communities are found in the phyllosphere. Their community structure depends on plant species, environmental conditions, and numerous other biotic and abiotic factors [32]. Leaf-associated microbes can metabolize VOCs that adsorb onto the leaf surface or are taken up through stomatal openings [33,41]. Thus, the aforementioned phytodegradation (by plant tissue) can be assisted by bacterial biodegradation of VOCs, which employs enzymatic pathways that break down aromatic compounds like benzene and toluene [5,29,42]. Though information regarding phyllosphere microbes for the remediation of air pollutants is scarce, with most of the research focussing on just the plants themselves [43].

Research suggests that significant removal of VOCs is largely facilitated by the rhizosphere microorganisms and the stomatal uptake during the day [40]. Additionally, it is suggested that the phyllosphere is a relatively harsh environment compared to other plant parts for microbial growth [43]. This is demonstrated by the total bacterial numbers found on the leaves (10^6 - 10^7 bacterial cells per cm^2) relative to those commonly found in soil (10^8 - 10^9 cells g^{-1} dry soil) and the rhizosphere (100–1000 times higher than bulk soil) [32,44,45]. The majority of recent research recognizes that the mechanisms of removal are predominantly facilitated by the microflora associated with the growth substrate (rhizosphere included), rather than the plant itself [43]. This implies that the contribution of phyllosphere bacteria may be very low to almost negligible [25,40]. Therefore, additional strategies like acclimatization or bioaugmentation have been proposed to optimize its effect [25].

1.10.2.2 Rhizosphere associated effects

Microbial mechanisms in the rhizosphere play a crucial role in removing VOCs through diverse metabolic processes. Microbes associated with plant roots, including bacteria and fungi, can utilize VOCs as carbon and energy sources [42]. As mentioned for the botanical component (Figure1), VOCs can be immobilized by Phytostabilization (e.g., by adsorption, precipitation, and accumulation) near the roots [24]. Subsequently, through bacterial biodegradation VOCs (among other complex organic compounds) break down into less harmful substances, biomass, carbon dioxide (CO_2) and water [5,35]. This degradation of pollutants by the root-associated microbiome is also known as rhizodegradation (Figure 2) [5].

Research suggests that depending on the VOC tested there is a positive correlation between removal efficiency and root surface area, mass and diameter [46]. The root-associated microbial community can also engage in synergistic relationships with the plant, enhancing the overall degradation of contaminants. The rhizosphere microorganisms produce extracellular polymeric substances (EPS), which can enhance adhesion to root surfaces and facilitate the encapsulation of VOCs, making them more bioavailable for microbial uptake and degradation.

1.10.2.3 Substrate associated effects

The substrate also plays a significant role in VOC removal, facilitated by microbial mechanisms. Typically composed of a mix of organic and inorganic materials, it provides an ideal environment for microbial colonisation [35]. Various microorganisms in the substrate, including bacteria and fungi, are capable of degrading VOCs through biodegradation in both aerobic and anaerobic conditions [5,24,35,47].

For example, bacteria, such as *Pseudomonas* species, are known to degrade BTEX due to their unique enzymatic capabilities [24]. Additionally, microbial biofilm formation on substrate particles can enhance the adsorption capacity for VOCs, effectively increasing the contact time between the contaminants and microbes, thereby improving removal efficiency [7]. Biofilms form a thin liquid layer covering porous surfaces, facilitating gas-liquid transfer of pollutants and enabling bacterial cell contact with VOCs [7,25,29]. This biofilm distributes biodegradation functions across the biofilter [7,25,29]. Multiple studies suggest that the substrate microbial community's VOC removal efficiency improves with repeated exposure over time, indicating these communities can be augmented in favour of the VOC degrading species [29,34]. The substrate can also influence microbial community dynamics, with changes in moisture, pH, and nutrient availability directly impacting the degradation rates of VOCs [7,35,42]. In turn, it is suggested that the botanical part can modify abiotic chemical or physical properties of the substrate (e.g. hydrophobicity), influencing VOC binding sites [46].

1.10.3 Substrate-Attributed (physicochemical) Mechanisms

In traditional biofilters the packing media or substrate provides a surface for microorganism's attachment and growth [7,25]. The same principle is thought to occur in the substrate compartment of a botanical biofilter, besides serving as support for plants and root system to develop. However, it is thought that prior to be degraded in the substrate, the VOC must undergo absorption or the transfer of the VOC from the gas to the liquid phase must occur first [7,25]. A biofilm can also develop in the substrate compartment (Figure 3). Thus, the mass transfer from the air to the aqueous phase is the rate limiting step to some VOC's degradation process [7]. The adsorption of the pollutants is possible after diffusion through the whole thickness of the biofilm, or directly occurs on the pore water or packing material (Figure 3).

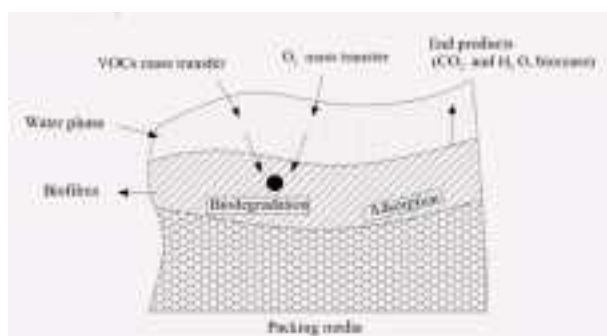


Figure 3: Phenomena involved in the operation of bioreactors. By Y Cheng et al. (2016).

A way to increase the transfer of the VOC into the liquid phase is by creating additional pressure drop by an active flow [48]. Also, other studies have increased the removal rate of VOCs by adding activated carbon. Yet it is unclear if biofilms and the associated microbes can attach and perform on activated carbon used in BB-systems. Nevertheless, in research applications like bioreactors for dark fermentation (which includes totally different microorganism), biofilms are known to attach to granular activated carbon (GAC) [48].

Activated carbon (AC), a highly efficient adsorbent, traps VOC molecules within its porous structure, providing sites for VOC adsorption [43]. The combination of inorganic growing media and activated carbon

shows promising results, with removal efficiencies ranging from 47.05 up to 99.9%VOC for formaldehyde (depending on inlet concentrations) ^[35]. (See Table 3 for operational details).

However, similar to the previously discussed active carbon filters, some drawbacks are presented. Decrease in removal efficiency with increasing relative humidity can occur due to the capillary condensation of water vapour inside the AC, blocking adsorption sites ^[23]. Additionally, it is reported that high temperatures are needed for regeneration (300 °C), implying high energy costs down stream. Adsorbents need to be regularly replaced as well, (to avoid re-emission) resulting in waste ^[23]. Additionally, it is suggested that acetaldehyde and formaldehyde are not effectively removed by activated carbon filters due to being light and highly volatile ^[25].

Activated carbon's potential impact in the substrate is often overlooked when considering the components ^[43]. The ratio of plant matter and substrate to AC mass is not always fully disclosed. In fact, substrate composition (like AC content) details are sometimes de-emphasized in commercial green wall products, raising questions about sustainability claims ^[43]. Therefore, it was decided that in the upcoming study the biofilter systems used contain no activated carbon and it should not be used.

xi Recent studies on BTEXFA removal and ABB

Many studies and reviews have demonstrated the potential of botanical biofiltration to remove indoor VOCs ^[28,29,37,43,49]. Since the scope of this work is focussed on ABBs and the removal of BTEXFA, a summary of fitting recent academic research is required to identify the current knowledge gaps (to which this dissertation can contribute). Table 3 shows a summary of the most recent findings concerning active BB and BTEXFA removal. Recent studies were selected prioritizing those targeting the VOCs of interest (BTEXFA) and excluding GAC in the substrate.

When analysing the current state of the art shown in Table 3, gaps became apparent. To begin, no studies were found reporting or testing the removal of acetaldehyde. This may come as a surprise, as in recent indoor air studies acetaldehyde is often measured as a relevant VOC ^[5,8,50]. The fact that this very volatile organic compound (VVO) is not yet tested in the novel research field of ABB, can be explained by the fact that interest in VVOs is historically dominated by formaldehyde and higher aldehydes ^[50]. The European Union took until 2013 to derive and set an LCI (lowest concentration of interest) for acetaldehyde ^[50]. In the upcoming study acetaldehyde is included, expecting to set precedent for future research.

Furthermore, it was observed that currently the testing of single VOCs is dominating the field ^[34,51]. Studies in which a mix of different VOCs were tested often do not report on the individual VOC behaviour within the mix ^[34,51]. Also, the initial concentrations of the individual VOCs in the mix were not explicitly reported ^[34,46,52]. This is important, as in real life conditions exposure will most definitely be to a mix of different VOCs (Table 1).

In the same way, the composition of the substrate was either not disclosed, reported, or left unclear ^[5,34,46,47]. Clear reporting of substrate characteristics is crucial as a great percentage of VOC removal is

attributed to this part ^[40]. For example, if the presence of AC is not reported, it can lead to biased conclusions on BB mechanisms and decisions for improvement of the technology.

Recent studies also reveal that already many beneficial insights have been gathered concerning the active BB of BTEXFA. For instance, it was found that formaldehyde removal efficiency (SPRE at single VOC tests) by the ABB's substrate is highest, when lowering inlet air flow rates and inlet concentrations (independently and simultaneously) ^[35].

Only two studies were found testing the effect of varying airflow ^[35,36]. Out of these works, it can be concluded that inlet air flow rate greatly influences the operational efficiency and performance of the biofilter. Though the effect of changing this operational parameter appears to be different for each individual VOC. For example, formaldehyde and toluene SPRE increased when lowering the airflow whilst the removal of acetone seemed unaffected by the change in airflow ^[35,36].

Other studies show that there is an added value to adding plants (and their associated root microbiome) to the substrate of an ABB system, in terms of SPRE for BTEXF and TVOC removal ^[35,36,52]

Table 3: Overview of the state of the art on active botanical biofiltration and BTEXFA removal including; design, experimental conditions, operational parameters, and tested performance metrics. ABB: Active botanical biofilter ; AGW: Active green wall ; GAC: Granulated active carbon.

N	Study	Year	Botanical biofilter type/morphology	Dimentions (chamber/testing volume + filter)	Substrate composition	Substrate volume	Plant species	Experimental conditions	Pollutant starting/inlet concentrations	Filter inlet airflow [m ³ /h]	Resulting removal metrics	Contains activated carbon?	Combined with modelling approach?
1	Lee et al.	2015	Flat-type biofilter with moisture supply device	Test room: 210 m ³ Filter enclosure: 0.5 × 0.5 × 0.5 m Substrate surface area: 0.25 m ²	flowering soil: Pit Moss: Pit Moss: Bermi Kulite = 2: 1: 1, V/V/V	/	<i>Dieffenbachia amoena</i>	Average room temperature: 26.6 ± 3.0 °C Average relative humidity: 62 ± 3.0%	Mixed VOCs TVOC: 1000ppb Formaldehyde: 2.0 ppm	0.45 m ³ min ⁻¹	Mixed VOCs TVOC, RE: ~ 78.3 % Benzene, RE: 38.9 % Toluene, RE: ~ 78.3 % Ethylbenzene, RE: ~ 72.8 % m-Xylene, RE: ~ 72.8 % Formaldehyde, RE: 42.8 %	no	no
2	Siswanto et al.	2019	Horizontal system, reversed flow	Chamber: 0.9 m × 1.5 m × 0.8 m, volume = 1 m ³ Filter: 0.40 × 0.15 × 0.25 m	1:1 mix - cocnut coir : soil (40:50% clay, 25–30% silt and 25–30% sand)	40 × 25 × 15 cm (10 kg)	<i>Sansevieria trifasciata</i> , <i>Chlorophytum comosum</i>	Temperature range: 30–32 °C	Mixed VOCs (sigarette smoke, 1 sigarette) TVOC: / Benzene: 15–35 ppb Xylene: 30–70 ppb Formaldehyde: 120–150 ppm Acetone: 127–145 ppm	2 m ³ / min	Mixed VOCs (sigarette smoke, 1 sigarette) TVOC, RE after 8, 24h: ~ 50, ~ 70 % Benzene removal after 8, 24h: ~ 100, ~ 120 µg Xylene removal after 8, 24h: ~ 70 µg Formaldehyde removal after 8, 24h: ~ 70, ~ 90 mg Acetone removal after 8, 24h: ~ 130, ~ 200 mg (plant composition varied, max. value for removal was selected)	no	no
2	Siswanto et al.	2019	Horizontal system, reversed flow	Chamber: 3.70 × 2.40 × 2.70 m, volume = 24 m ³ Filter: 0.40 × 0.15 × 0.25 m	1:1 mix - cocnut coir : soil (40:50% clay, 25–30% silt and 25–30% sand)	40 × 25 × 15 cm (10 kg)	<i>Sansevieria trifasciata</i> , <i>Chlorophytum comosum</i>	Temperature range: 30–32 °C	Mixed VOCs (sigarette smoke, 20 sigarettes) TVOC: / Benzene: / Xylene: / Formaldehyde: / Acetone: /	2 m ³ / min	Mixed VOCs (sigarette smoke, 1 sigarette) TVOC, RE after 24h: ~ 80 % Removal per substrate surface area [µg/cm ²] after 24h. (max.) Benzene removal: ~ 6 Xylene removal: ~ 8 Formaldehyde removal: ~ 5000 Acetone removal: ~ 290	no	no
3	Montaluisa -Mantilla et al.	2025	AGW	Chamber: 1 × 0.80 × 0.65 m	Polyurethane foam + mineral salt medium	0.60 m × 0.60 m × 0.11 m	<i>Epipremnum aureum</i>	Average temperature inside the chamber: 23.7 ± 1.4 °C Average humidity inside the chamber: 98.3 ± 2.4%	Toluene: 3.5 ± 0.6 mg / m ³ Acetone: 2.2 ± 0.5 mg / m ³	Chamber: 2.8 L min ⁻¹ (of contaminated air) Filter: a) 36 L min ⁻¹ b) 20 L min ⁻¹ c) 0 L min ⁻¹	Toluene, RE: a) 71.1 ± 5.2 % b) 73.5 ± 4.1 % c) 74.1 ± 4.3 % Acetone, RE: a) 99.8 ± 0.8 % b) 99.3 ± 1.0 % c) 99.0 ± 0.3 %	no	no
4	Pettit et al.	2018	Full-scale AGW module	Chamber: 0.6 × 0.6 × 0.6 m (216 L)	a) Coarse coconut husk b) Coarse coconut husk : GAC - 50:50	/	<i>Nephrolepis exaltata bostoniensis</i>	Contact time between pollutant and filtration materials ranged between 11.2 and 11.3 minutes. Trials for each pollutant were run independently.	Bensene: 1.275 × 10 ⁻⁵ mol	/	SPRE: a) ~ 28.7 - 36% b) 60.24%	a) no b) yes	no
5	Abedi et al.	2022	AGW module	Chamber: 0.51 × 0.51 × 0.70 m Filter module: 0.5 × 0.5 × 0.13 m (with 0.5 cm wall thickness)	GAC, leca, and commercial pot soil (contains coco-peat, perlite, leaf soil, clay, vermicompost, and minerals)	/	Mixed: <i>Epipremnum aureum</i> (4 per modules), <i>Syngonium podophyllum</i> , <i>Chlorophytum comosum</i> , <i>Peperomia obtusifolia</i> , <i>Pilea cadieriei</i> , and <i>Aglaonema treubii</i>	Mean light intensity: 248 ± 11 lux Average temperature: 24.6 ± 0.9 °C Air pressure: 636.6 mmHg Relative humidity: 55 ± 10%	Formaldehyde: I.) 0.3 ppm or 0.30 mg / m ³ II.) 0.5 ppm or 0.50 mg / m ³ III.) 1.0 ppm or 1.03 mg / m ³ IV.) 2.0 ppm or 2.06 mg / m ³	a) 0.8 L/s (2.88 m ³ /h) b) 2.3 L/s (8.28 m ³ /h) c) 3.9 L/s (14.04 m ³ /h) d) 5.5 L/s (19.8 m ³ /h)	Formaldehyde, SPRE: (for I, II, III, IV) a) 99.99%, d) ..., ..., ..., 88.16 ± 0.56%	yes	no
6	Wang et al.	2011	Horizontal filter bed, reversed airflow	/	activated carbon, porous shale pebbles	/	<i>Epipremnum aureum</i>	Inlet air temperature: 20 °C Relative humidity: 30%	/	/	Formaldehyde, SPRE: 60% Toluene, SPRE: 20%	yes	Yes, numerical simulation model (CHAMPS-BES)
6	Wang et al.	2011	Horizontal filter bed, reversed airflow	/	activated carbon, porous shale pebbles	1.8 m x 0.6 m x 0.2 m	<i>Epipremnum aureum</i>	Inlet air temperature: 20 °C Inlet relative humidity: a) 55% b) 75% c) 92%	Formaldehyde: a) 0.11 mg / m ³ b) 0.085 mg / m ³ c) 0.018 mg / m ³	0.229 m ³ /s	Formaldehyde, SPRE: a) 20% b) 24% c) 34%	yes	Yes, numerical simulation model (CHAMPS-BES)
7	Pettit et al.	2019	AGW system	Test room: Floor area = 40.07 m ² , volume = 120.2 m ³ Filter: surface area = 9 m ² (36 modules, 0.25 m ² each)	Coconut husk-based substrate	150 L total substrate volume	Mixed: <i>Epipremnum aureum</i> , <i>Nephrolepis exaltata</i> , <i>Peperomia</i>	The room was ventilated by a compartmentalized HVAC system, and a pedestal fan was used to ensure air mixing.	TVOC: 300 ± 3.04 ppbv	283.53 m ³ h ⁻¹	TVOCs was reduced to 217 ± 2.00 ppbv over the 20-min trial (~ 28% reduction)	not disclosed	no, model was created later by [56]
7	Pettit et al.	2019	AGW system	Test room: Floor area = 8.75 m ² , volume = 22.70 m ³ Filter: surface area = 1.5 m ² (6 modules, 0.25 m ² each)	Coconut husk-based substrate	25 L total substrate volume	Mixed: 8 plant species in varying proportions	Room's ambient temperature: 20 - 24 °C	TVOC: 120 ppb (Incl. toluene and o-xylene)	2 x 320 m ³ h ⁻¹	The average time-weighted TVOC concentration was 72.5% lower than t in the empty controll room.	not disclosed	no
8	Paull et al.	2019	AGW module	Chamber: 0.6 × 0.6 × 0.6 m (216 L) Filter module: 0.5 × 0.5 × 0.13 m Front surface area: 0.25 m ²	Coconut coir-based substrate	25 L total substrate volume	a) <i>Dianella caerulea</i> , b) <i>Lomandra longifolia</i> , <i>Blechnum gibbum</i> , ...	/	Benzene: 4.170 ± 0.144 ppm	14.90 L/s	Bensene, SPRE: a) 59.04% (highest) b) 39.96% (lowest)	not disclosed	no
9	Irga et al.	2019	AGW module	Chamber: 0.6 × 0.6 × 0.6 m (216 L) Filter module: 0.5 × 0.5 × 0.13 m Front surface area: 0.25 m ²	Coconut coir-based substrate	25 L total substrate volume	a) <i>Chlorophytum orchidastrum</i> (Fire flash) b) <i>Nematanthus glabra</i> (Goldfish plant) c) <i>Nephrolepis cordifolia</i> (Lemon button fern) d) <i>Schefflera arboricola</i> (Dwarf umbrella tree)	Glasshouse conditions with average temperature of 23.7 ± 3.6 °C Relative humidity of 68.1 ± 16.0% Maximum mid-day light level of 90 ± 10 µmol / m ² s	Bensene: 4.170 ± 0.144 ppm Ethyl acetate: 3.997 ± 0.074 ppm TVOC: 35 ppb	14.90 L/s	Bensene, SPRE: a) 47.65 ± 1.46% b) 58.78 ± 1.07% c) 48.00 ± 2.19% d) 51.01 ± 3.03% Ethyl acetate, SPRE: a) 82.61 ± 5.97% b) 39.97 ± 5.17% c) 64.02 ± 1.06% d) 80.69 ± 5.97% TVOC: SPRE: ~ 65%	No details on the biofilter packing medium but mentioned in [34]	no

xii VOC mass transfer in BB

1.12.1 VOC's Chemical Properties

The removal performance of VOCs in biofiltration systems highly depends on the specific VOC or combination of VOCs being tested ^[36]. Each VOC possesses distinct physicochemical properties and microbial interactions that influence its biodegradation ^[36]. The VOC removal in a biofiltration system is notably influenced by various physicochemical factors, including: water solubility, Henry's law constant, molecular structure, gas-liquid mass transfer coefficient, airflow rate, microbial activity, and moisture levels ^[7,36]. The physicochemical properties of BTEXFA are listed in Table 4.

Table 4: Physicochemical Properties of BTEXFA. Adapted from Mackay et al. (2006).

Name and formula	Chemical structure	Molecular weight [g/mol]	Water solubility at 25°C [mg/L]	Henry's law constant Hb [Pa m ³ /mol]	Vapour pressure [Pa]	LogK _{ow}
Benzene C ₆ H ₆		78.112	1740 (21°C) 1796 (25°C)	466 (20°C) 488 (23°C) 564 (25°C)	9960 (20°C) 12654 (25°C)	2.13
Toluene C ₇ H ₈		92.139	479 (21°C) 526 (15–45°C)	541 (20°C) 625 (23.0°C) 652 (25°C)	3790 (25°C) 2666 (18.4°C)	2.73
Ethylbenzene C ₈ H ₁₀		106.165	169 (21°C) 170 (25°C)	602 (20°C) 895 (25°C)	1300 (25°C)	3.15
m-Xylene C ₈ H ₁₀		106.165	170 (20°C) 160 (25°C)	590 (20°C) 675 (25°C)	833 (20°C) 1113 (25°C)	3.20
Formaldehyde CH ₂ O		30.026	1220000 (25°C) very soluble, up to 55%	0.0331 (20°C) 0.0169 (25°C)	517690 (25°C) (1 atm, Howard 1989)	0.35
Acetaldehyde C ₂ H ₄ O		44.052	miscible	5.39 (20°C) 6.69 (25°C)	120230 (25°C)	0.45

The Henry's law constant represents the gas solubility in a liquid at a given temperature, with lower values indicating a greater solubility of the compound in the aqueous phase ^[36]. This constant considers the partial pressure of the target contaminant in the gas phase and the concentration in the aqueous phase at specific temperature and pressure conditions, expressed in the units of [Pa · m³/mol] ^[28]. If BTEXFA must first transfer into an aqueous phase before biodegradation, the maximum aqueous concentration (to which most microorganisms will be exposed) integrally depends on this number (Figure 4) ^[28]. Understanding the relationship between Henry's law constant and hydrophobicity is vital for predicting the behaviour of VOCs in aqueous environments—such as in active botanical biofiltration (ABB) systems—where solubility affects their availability for microbial degradation ^[28,36].

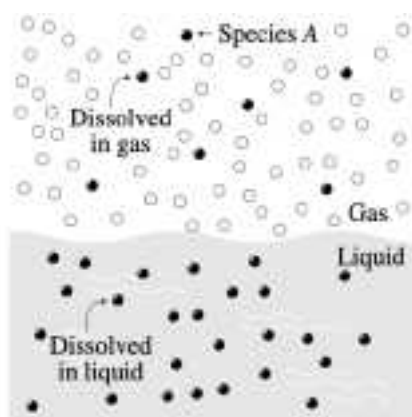


Figure 4: Schematic of equilibrium between a gas and a liquid phase by Datta et al. (2002).

1.12.2 Removal of BTEX and AF

BTEX refers to aromatic hydrocarbons that are monoaromatic in nature, which increases their solubility in water ^[24]. On the other hand, formaldehyde and acetaldehyde (FA) are classified as hydrophilic VOCs, exhibiting a much lower Henry's law constant compared to BTEX. This contrast indicates even greater hydrophilicity for FA, which enhances its solubility in water relative to BTEX.

1.12.3 Liquid Phase in Biofiltration

The use of polar, water-soluble VOCs for validation experiments may not accurately reflect their ability to remove all VOCs from indoor air. Biofiltration systems with high water content in substrates may demonstrate a higher removal rate for highly polar VOCs, complicating the determination of whether removal is due to plants, bacteria, or adsorption to the growth media ^[43]. The transfer of volatile organic compounds from the gas phase to the liquid phase, and subsequently to the biofilm phase, is crucial for establishing contact between microbes and these organic compounds ^[7]. Bioavailability plays a significant role in the biodegradation of VOCs in biofilters. Therefore, the mass transfer of VOCs is critical in determining the fate of a VOC molecule and is a key variable impacting the effectiveness of gas biofiltration within these systems ^[7]. A limited mass transfer of hydrophobic VOCs, such as those in the BTEX group, from the gas phase to the biofilm phase restricts the substrate supply to microorganisms, resulting in reduced bioavailability and slower biodegradation of these compounds ^[7].

xiii Acclimation, Acclimatization and Reactor Start-Up

In the context of biofiltration, acclimation is referred to as the period required for the development of the optimum populations of substrate microorganisms before they start vigorous biodegradation ^[53]. Acclimatization is described as a factor that is affecting bioremediation processes in the natural environment ^[24]. This involves acclimatisation of the microbes to the compounds that these microbes are meant to break down and to other environmental factors ^[24]. In literature both acclimatization and acclimation are sometimes used interchangeably depending on the context.

The concept of acclimatisation is well known in the applications of breaking down pharmaceuticals and dyes in the natural environment ^[24]. However, in the context of biofilters, acclimatization of the micro-community to target VOCs is a scarcely discussed topic ^[53,54]. Following the inoculation of the filter with some sort of microbial suspension, preliminary acclimation of the biomass to the target pollutants is a strategic approach that can effectively shorten the start-up period of biofilters and enhance their long-term operational success ^[53].

Beyond adapting to target pollutant concentrations, factors such as nutrient status and the mode of reactor operation (continuous or batch) also play significant roles in the acclimatization process^[5,54]. In the field of BB it is known that the VOC removal rate of plants by themselves (in hydroponic medium), can be increased by allowing a 2-day or more resting period (after transplantation) prior to exposure to VOCs ^[5]. This can be attributed to an enhanced proliferation of microorganisms in the surrounding water, underscoring the significance of allowing microbial communities to rest for optimal operation and exposure.

Despite being mentioned in the past, many of the recent studies on indoor biofilters (e.g., those referenced in Table 10) fail to report on the start-up periods and acclimatisation strategies or conditions used ^[53]. Since Darlington et al. (2002) reported on the notable effects of acclimation to toluene in their indoor biofilter, no in-depth research was done for the newer (and very different) reactor types that dominate the field of botanical biofiltration today. This represents a research gap of massive proportions. As microbial communities change over time and adapt according to the resources present, the importance of acclimatization of the microorganisms cannot be underestimated ^[53,54]. Consequently, in the upcoming study proper attention shall be given to the acclimatization of the microbes involved in the ABB-process.

II Research Objectives and Outline of The Study

i General Goal

The general goal of this study was to evaluate the performance of an active botanical biofilter (ABB) and a microbial biofilter (MB) removing a mixture of priority indoor VOCs (benzene, toluene, ethylbenzene, xylene, formaldehyde, and acetaldehyde or BTEXFA), by combining an experimental and modelling approach. The insights gained from both approaches are ultimately aimed at improving ABB-technology in different contexts. The experimental phase of this master's thesis covered the acclimatization period and the analysis of operational boundary conditions (airflow rate) and of environmental variables. Experimental findings were integrated into a preliminary 3D Multiphysics model of the substrate compartment of an ABB system, i.e., MB comprising airflow analysis and VOC removal. This integration is considered as the first step towards a fully developed model to optimize ABB performance and design.

ii Specific objectives

The general goal is translated into three specific objectives covering the acclimatisation and airflow variation studies (experimental approach), and the modelling approach, as follows:

1. Acclimatisation Process and Environmental Parameters: The first objective is to document the acclimatization process of the ABB and MB units and the resultant dynamics in the removal of the VOC mixture (BTEXFA). This includes assessing how each unit adapts to the presence of VOCs with different physicochemical characteristics over time. The impact of environmental parameters (i.e., temperature, CO₂ concentration) was likewise investigated. The following research question was explored.

- What impact does acclimatization exert on VOC removal, and how do other parameters affect it reaching stationary state, such as time of VOC dose application, VOC dose count, mass changes of the ABB, net CO₂ production and temperature variations?

2. Impact of Operational Parameters: The second objective entails evaluating how variations in operational boundary parameters influence the VOC removal performance of the ABB system. Key parameters analysed were: airflow rate, resting time after exposure, testing order, and number of VOC (BTEXFA) doses received. The following research questions were investigated.

- What is the optimal airflow rate that achieves maximum VOC removal in the shortest time?
- How does the removal of individual VOCs when tested in isolation compare to being mixed with other BTEXFA compounds?
- Are there any interactions or antagonisms amongst VOCs?

3. Modelling Approach: The last objective involved developing a preliminary model for the substrate compartment of an ABB excluding the above-ground organs (foliage), integrating the aerodynamics and the transport and removal of a single VOC as model compound. Firstly, the substrate aerodynamics was modeled including pressure drop, permeability and inertial effects. Then, the study was coupled with the

transport and removal of a VOC. Both submodels were validated against experimental data. The research questions set for this modelling section are as follows:

- Can the aerodynamic characteristics of the substrate compartment of an ABB be represented and validated via CFD analysis?
- Can the aerodynamics of an ABB be coupled with the VOC transport and removal to be successfully validated by experimental findings?

iii Outline of the study

The outline of this study is illustrated in Figure 5, providing a schematic representation of the research flow and structure. Different boundary conditions such as varying airflow rates and the presence of other VOC species (VOCs in mixture vs alone), were tested in batch chamber experiment on multiple biofilter units. Simultaneously a model was built, using experimental results from these same units for substrate and removal characterisation. Both the model and the chamber experiments yielded biofiltration metrics (SPRE and CADR), which were compared for the purpose of model validation (objective 3). The removal metrics resulting from experimentation were separately analysed to make an assessment on the biofilters themselves (objective 1 and 2).

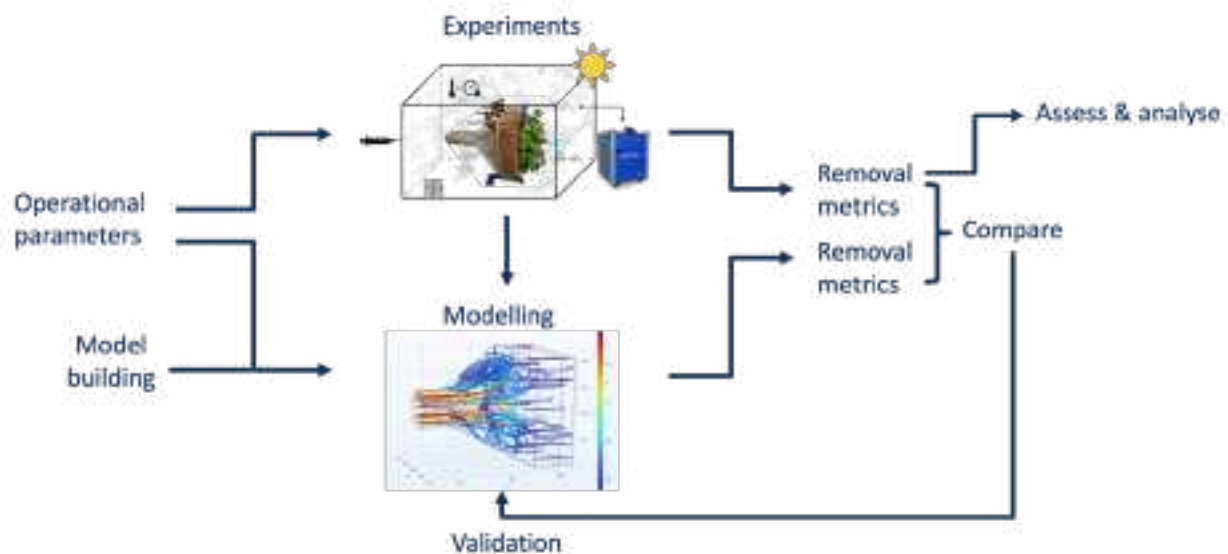


Figure 5: Schematic representation of the research flow and structure of this master's thesis.

III Materials and Methods

Three biofilters were constructed and tested in this dissertation. One active botanical biofilter ABB and one microbial biofilter without plants (MB). The ABB and MB were used in the experimental approach of this work as they were operated under similar operational conditions. A second microbial biofilter, MB2 was used solely for the modelling approach. However, MB2 underwent the same schedule and treatment as the ABB and MB. In summary, results and conclusions concerning the first two research objectives strictly stem from data collected from the ABB and MB.

i Experimental Approach: VOC removal

3.1.1 Active Botanical Biofiltration System Design and Assembly

The in-house available active (botanical) biofilter modules were constructed according to Figure 6 by combining a grid basket and a detachable wooden frame. Each basket (volume: 15.27 L) was made of galvanised metal (460 mm (L) x 80 mm (W) x 415 mm (H)) to contain the substrate medium and plants. Stainless steel mesh layers (0.56 mm thick) were attached to the to the front and rear grids to prevent substrate loss. Each basket was introduced into a detachable wooden frame (Iroko wood: measuring 503 mm (L) x 159 mm (W) x 491 mm (H)). The mass of the ABB module was 7.75 kg. The frontal area (0.18 m²) was perforated with nine holes (diameter: 30 mm) for plant insertion. Polyethylene foam was used at the bottom to prevent loses and tiny holes were perforated to allow drainage. The rear side of the module was connected to an air duct (using a round-to-square transition) containing a variable speed fan (Wathai, 110-240V, 120 mm dia.), for drawing the VOC contaminated air into the substrate compartment and further to the botanical part. (Figure 6)

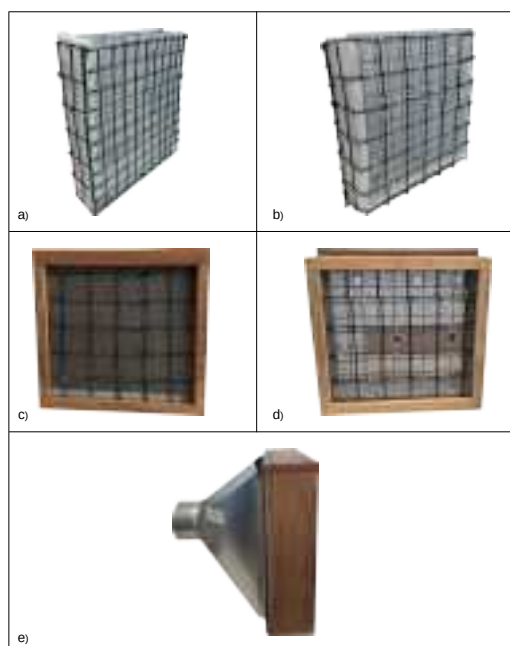


Figure 6: Biofilter module housing and internal structure. a) rear face galvanised plant box, b) front face galvanised plant box, c) front face frame, d) rear face frame, e) side view; duct fitting on rear face. Cabinetry by prof. dr. ir. Siegfried Denys.

3.1.2 The substrate mixture

The substrate medium used in the biofilters consisted (in %v/v) of 40% expanded clay, 40% pine bark and 20 % potting soil. The first two components accounting for 80% are considered the coarse fraction that provides most porosity whereas potting soil is responsible for the main source of microorganisms and water holding capacity. Physical properties were: dry density of 293 kg m^{-3} , wet density of 363 kg m^{-3} , total air-filled porosity of 0.52, porosity after field capacity of 0.48 and water holding capacity of 10%. In ABBs, designed with these substrate combinations, a pressure drop across the medium is inevitable. Although a moderate pressure drop can enhance the mass transfer of pollutants from the gas to the liquid phase or bioactive phase—potentially increasing removal efficiency—an excessive pressure loss remains undesirable. This underscores the need to balance substrate composition and structure to optimize both microbial activity and gas flow dynamics within these systems.

3.1.3 Plant species selection

The plant species, *Epipremnum pinnatum* (Plant Passport A: *Epipremnum pinnatum*; B: NL-791163156; C: 4SCAUHA05 533583; D: NL)), was chosen for this study based on extensive scientific literature recording its VOC removal capacity and economic relevance in the indoor greenery sector^[55]. It exhibits desirable characteristics indoors such as low maintenance requirements, shade-tolerance, and drought resistance. Furthermore, its ease of propagation makes it an economical, easily accessible option^[55]. *Epipremnum sp.* has demonstrated tolerance to, and removal of formaldehyde and acetaldehyde (FA) levels, unlike many other indoor plants^[25]. Likewise other VOCs such as acetone, benzene, toluene, xylene and α -pinene are known to be removed by the plant species^[31,33]. Plants were carefully inserted into the ABB module previously filled with the substrate mixture, in such a way that their roots spread throughout the whole substrate volume. The assembled ABB unit and MBs (without plants) were exposed to natural outdoor conditions in a forested area outside the laboratory (T: 19.5 °C, RH: 62%) for 9 weeks to gain airborne bacteria and increase its microbial diversity. During this inoculation period 1L of tap water added weekly.

3.1.4 VOC removal capacity set-up

To determine the VOC removal capacity of both the active (ABB) and microbial biofilter (MB), a 1.2 m^3 airtight clear acrylic test chamber was used (internal dimensions, 1.5m (L)× 0.8m (W)× 1.0m (H)). This climate chamber set-up follows the commonly used configuration in Figure 7 mentioned by Alvarado et al. (2024). Alike set-ups have been widely used for determination of VOC removal capacity of potted

plants, though some more distinguishable elements for this study, are the use of a natural light source (ambient indoor sunlight) and more robust analytical equipment used (Syft MS) [36,49,52].

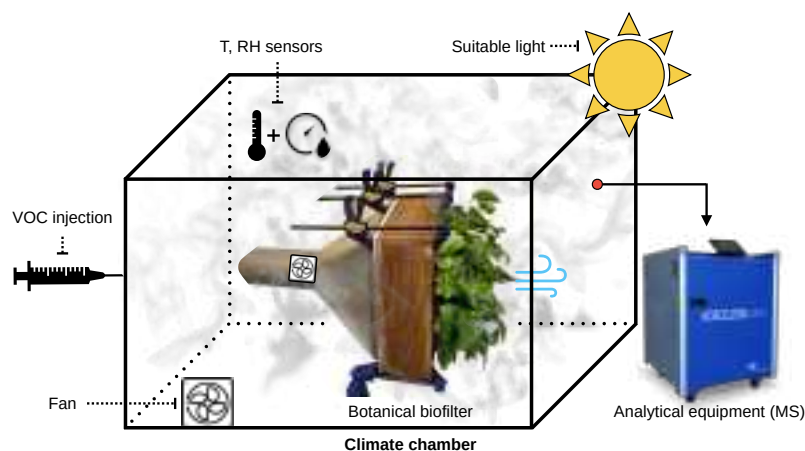


Figure 7: A batch-like climate chamber configuration commonly used in assessing the drawdown capacity of botanical biofilters where a VOC is injected, and the removal is quantified over time. Adapted for this study from Alvarado et al. (2024).

Inside the chamber, a temperature hygrometer (SUPOELE model HTC-1; temperature range: $-10\text{ }^{\circ}\text{C} \pm 50\text{ }^{\circ}\text{C}$; humidity range: 10% - 99%; resolution: $\pm 0.1\text{ }^{\circ}\text{C}$; 1%) and a CO_2 probe (VAISALA GMP222, Vanta, Finland, range 0 – 3000 ppmv; accuracy $\pm 2\%$) were placed to monitor environmental temperature, relative humidity and CO_2 concentration within the chamber, as such parameters may indicate biodegradation or impact VOC removal. Two 12-V DC brushless homogenisation fans (Panasonic SF10, 126-mm dia., 160mA) were placed at a height of 0.63m at the chamber's centre to circulate the air inside the chamber and homogenise the pollutant concentration.

Each test lasted 8 hours during the first five days of the acclimatisation period, aligned with the plant's diurnal cycle (10:00 - 18:00 h). As VOC removal progressively increased, exposure shortened. Between the trials, the climate chamber was ventilated, and the biofilter units were stored in indoor conditions. Prior to testing, the ABB or MB was irrigated with 1 L of tap water until field capacity, reaching approximately $17.9 \pm 0.55\text{ kg}$. In each test, 0.1 L was lost due to evaporation. The unit was placed in the chamber's centre as, with foliage oriented toward the incoming ambient light (Figure 8). The interior fan in the air duct was activated on the selected setting, and the climate chamber was closed. A sharp increase in RH was recorded.

VOCs were individually added into the chamber (order: BTEXAF) by injecting a calculated volume of saturated headspace from a bottle containing 30 mL of liquid VOC at equilibrium at room temperature. The aim was to produce an initial concentration equal to five times the maximum indoor exposure limit defined by the Superior health Council of Belgium (benzene: $50\text{ }\mu\text{g m}^{-3}$, toluene: $1300\text{ }\mu\text{g m}^{-3}$, ethylbenzene: $1300\text{ }\mu\text{g m}^{-3}$, xylene: $1000\text{ }\mu\text{g m}^{-3}$, formaldehyde: $500\text{ }\mu\text{g m}^{-3}$, acetaldehyde: $700\text{ }\mu\text{g m}^{-3}$). (Figure 8)

VOC concentrations were continuously monitored employing a Selected-Ion Flow-Tube Mass Spectrometry (Syft VOICE200 ultra, New Zealand), a technique that enables real-time quantitation of VOCs employing soft chemical ionization. This method is highly relevant for indoor air purification

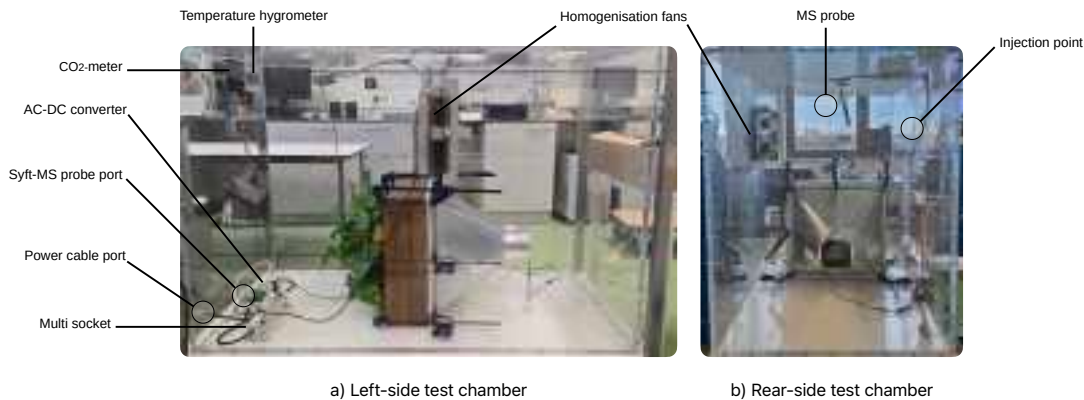


Figure 8: Experimental batch removal chamber set-up with biofilter unit (duct attached) inside.

studies where pollutants are found in low concentration and often in mixtures. Each test produced a .csv file with time-resolved VOC concentration data, as well as a .xml file for visualization with LabSyft Pro version 1.8.1. VOC decay rates and removal metrics were extracted and analysed, as explained in section 3.1.6.

3.1.5 Experiment Phases

The phases in Table 5 divided the tests conducted for the experimental approach into three parts.

For this dissertation's inquiry on the acclimatisation process (Phase I), the ABB and both MB units underwent an acclimatisation regime of 10 exposures in a period of 13 to 14 days, with roughly the same resting period between doses. The main aim of this phase was to start up the VOC removal process, by activation of plant and bacterial enzymes, and by promoting microbial growth. During Phase I, both units were operated at almost the same base airflow rate of $60 \text{ m}^3\text{h}^{-1}$ (Table 5).

Table 5: Phases of biofilter testing concerning the experimental approach of this dissertation.

Phase I: Acclimatisation to BTEXFA mixture					
Unit	VOCs tested	Fan Settings	Airflow Rates [m ³ h ⁻¹]	Average Operating Temperature range [°C]	Daily RH [%]
ABB	BTEXFA	1x	59.80	18.57 , 19.62	87.88
MB	BTEXFA	1x	59.93	20.51 , 21.44	90.67
Phase II: Airflow variation of VOC mixture					
Unit	VOCs tested	Fan Settings	Airflow Rates [m ³ h ⁻¹]	Average Operating Temperature per trial [°C]	Daily RH [%]
ABB	BTEXFA	2x + 3x + 1x	108.01 + 170.34 + 59.80	20.60	92.19
ABB	BTEXFA	1x + 2x + 3x	59.80 + 108.01 + 170.34	19.97	
ABB	BTEXFA	1x + 3x + 2x	59.80 + 170.34 + 108.01	20.34	
Phase III: Airflow variation of singularly tested VOC					
Unit	VOCs tested	Fan Settings	Airflow Rates [m ³ h ⁻¹]	Average Operating Temperature [°C]	Daily RH [%]
ABB	B	1x + 2x + 3x	59.80 + 108.01 + 170.34	21.13	84.00
ABB	T	1x + 2x + 3x	59.80 + 108.01 + 170.34	21.8	84.12

Afterwards, each unit was altered in its operational flow rate from roughly 1, to 2, to 3 times a base airflow in a non-sequential randomised manner to assess the impact on the VOC removal (Phase II). This was achieved through a comprehensive airflow variation study in which the airflow impact was,

investigated with an extensive statistical data analysis (see section 3.1.7). Each of the three airflow rates was triplicated (ABB) and their testing was in close succession although not always sequential.

The effect of singular VOC removal versus removal of that same VOC in a mixture is tested in Phase III. Aside from the airflow variation trials of the ABB with exposure to a BTEXFA mixture conducted in Phase II, this third phase contains two extra trials. Phase III in Table 5 was conducted with the ABB only being subjected to one singular VOC. These tests were performed only once due to time and resource constraints. Both benzene and toluene removal were tested.

3.1.6 Data Analysis

To obtain the VOC decay dynamics and calculate the biofilter performance, three kinetic decay models with different reaction orders were fitted to the VOC-concentration-over-time data generated by the SIFT-MS: zero order, single first-order and multiple first-order reaction (Table 6). The fit was evaluated based on the coefficient of determination (R^2), as it was observed that not all VOCs followed the same decay order.

The decay behaviours for BTEX changed from exponential to linear after 13 days of acclimatisation, while they remained single and multiple exponential in case of acetaldehyde and formaldehyde. Consequently, from the fitted Equations (1-3) in Table 6, a decay constant (k) was obtained and normalized (4-6) to be comparable. Finally, three main metrics widely used in the field of biofiltration were calculated by Equations (7-9), namely the Clean Air Delivery Rate (CADR), the single-pass removal efficiency (SPRE), and the net CO_2 production. (Table 6)

Table 6: Equations used for biofiltration metric calculation.

Reaction order models	Order	Equation	Normalised decay constant [h^{-1}]	
	Zero-order	$C(t) = C_{0,\text{chamber}} - k_{\text{linear}} \cdot t$	(1)	$k_n = \frac{k_{\text{linear}}}{C}$ (4)
	Single first-order	$C(t) = C_{0,\text{chamber}} e^{-k_{\text{exp}} \cdot t}$	(2)	$k_n = k_{\text{exp}}$ (5)
	Multiple first-order	$C(t) = C_{0,\text{chamber}} [p e^{-k_{\text{exp},1} \cdot t} + (1-p) e^{-k_{\text{exp},2} \cdot t}]$	(3)	$k_n = k_{\text{exp},1} p + k_{\text{exp},2} (1-p)$ (6)
Biofiltration metrics	Metric	Equation	Unit	
	Clean air delivery rate (CADR)	$\text{CADR} = V_{\text{chamber}} (k_n - k_{\text{leak}})$	(7)	$\text{m}^3 \text{h}^{-1}$
	Single-pass removal efficiency (SPRE)	$\text{SPRE} = \frac{\text{CADR}}{Q} \cdot 100$	(8)	%
	Net CO_2 production	$C_{\text{CO}_2}^{\text{net}} = C_{\text{CO}_2}^{\text{in}} - C_{\text{CO}_2}^{\text{out}}$	(9)	ppm

For the reaction order models; $C(t)$ is the individual VOC concentration in the chamber as a function of time, $C_{0,\text{chamber}}$ is the initial VOC concentration in the chamber, and t is time.

The Clean Air Delivery Rate (CADR) or the clean airflow rate produced by the system, was based solely based on the individual removal of each VOC (BTEXFA). As the current work was based in a batch-like climate chamber, where a VOC decays over time, the CADR was calculated according to Equation (7) with: $(k_n - k_{\text{blank}})$ as corrected decay constant and V_{chamber} the volume of the climate chamber. Any further mention of k in this work refers to the corrected decay constant [h^{-1}], which is the normalized decay constant (k_n) corrected according to Equation (10), accounting for the blank decay constant k_{blank} . The blank decay constant represents the results obtained from a blank batch removal test, where the ABB unit was tested without botanical, substrate, or microbial components.

$$k = k_n - k_{\text{blank}} \quad (10)$$

SPRE was calculated by Equation (8) with, Q the experimentally determined airflow rates [m^3h^{-1}] for the relevant fan setting. The net CO_2 production $C_{\text{CO}_2}^{\text{net}}$ in Equation (9), was defined as the difference between, $C_{\text{CO}_2}^{\text{end}}$ the CO_2 concentration [ppm] measured at the end of the removal test, and $C_{\text{CO}_2}^{\text{start}}$ the CO_2 concentration [ppm] measured when starting the batch removal test.

3.1.7 Statistical Analysis

3.1.7.1 Acclimatisation process and environmental variables

To assess the overall impact of the acclimatization process on removal efficiency, the VOC removal data of ABB and MB were analysed in R Studio. Single factor linear models were applied in which SPRE was response variable and time was the explanatory variable. This was to assess overall trends (i.e., expected efficiency increase associated with bioreactor acclimation).

Independently, multifactor linear models were applied in which SPRE was response variable, with the number of VOC doses (independent variable) and/or time as explanatory variable. Covariates like initial temperature and initial mass were included as well to account for their potential effects on SPRE. ANCOVAs were performed on each test unit-VOC combination (ABB/MB - BTEXFA) to examine the influence of various contributing variables (environmental and operational) on the response variable, which is removal. The explanatory variables, characterizing the acclimatization period, included VOC cumulative dose count, initial temperature in the chamber, net CO_2 production, time of VOC dose administration (since the start of the acclimatization process), and the initial mass of the unit before the test. Ultimately, linear models were optimised by only including predominantly significant contributing variables and interactions. The selection of variables was based on their significance and relative contribution to variation.

ANCOVAs usually require multiple replicate measurements. Due to the timely nature of the acclimatisation regime, and the resource intensive process of the measurements, this was not possible in the context of this master's dissertation. Yet, the ANCOVAs were consulted as a preliminary way to assess what environmental factors could influence acclimatisation results. Consequently, more intentional choices can be made on what environmental factors to test or in future sensitivity analyses.

Nevertheless, the robustness of the environmental effects must stay a point of caution. Due to the small sample size a higher likelihood of Type II errors (failing to detect effects when they exist), have to be

considered when interpreting the results. Additionally, due to the lack of replicate measurements, any variability in the results might stem from the environmental factors posing as covariates.

3.1.7.2 Airflow variation study

The trials were randomized by conducting tests in a random varying order within each trial. Linear mixed models (LMM) were applied (using the lmerTest package in R-studio) on the data to assess the impact of increasing airflow rate on VOC removal. Six models (one for every VOC) we made with SPRE as response variable, and likewise six more with SPRE as response variable. The LMMs took both variations due to the trial, and due to the day the test was conducted on into account as random effects. The explanatory variables tested were airflow rate, the order in which the airflow rates were tested in each trial, and the interaction between these two. An ANOVA was conducted on the 12 models. The selection of the explanatory variables too keep in the LMM was based upon significance.

ii Modeling approach: aerodynamics and VOC removal

Before building the multiphysics model of the botanical biofilter, aerodynamic characteristics of the biofilters (ABB, MB and MB2) were experimentally determined, namely permeability and Forchheimer drag. These were translated into the model later on, by calculation of a dimensionless Darcy-Forchheimer coefficient. (Figure 9)

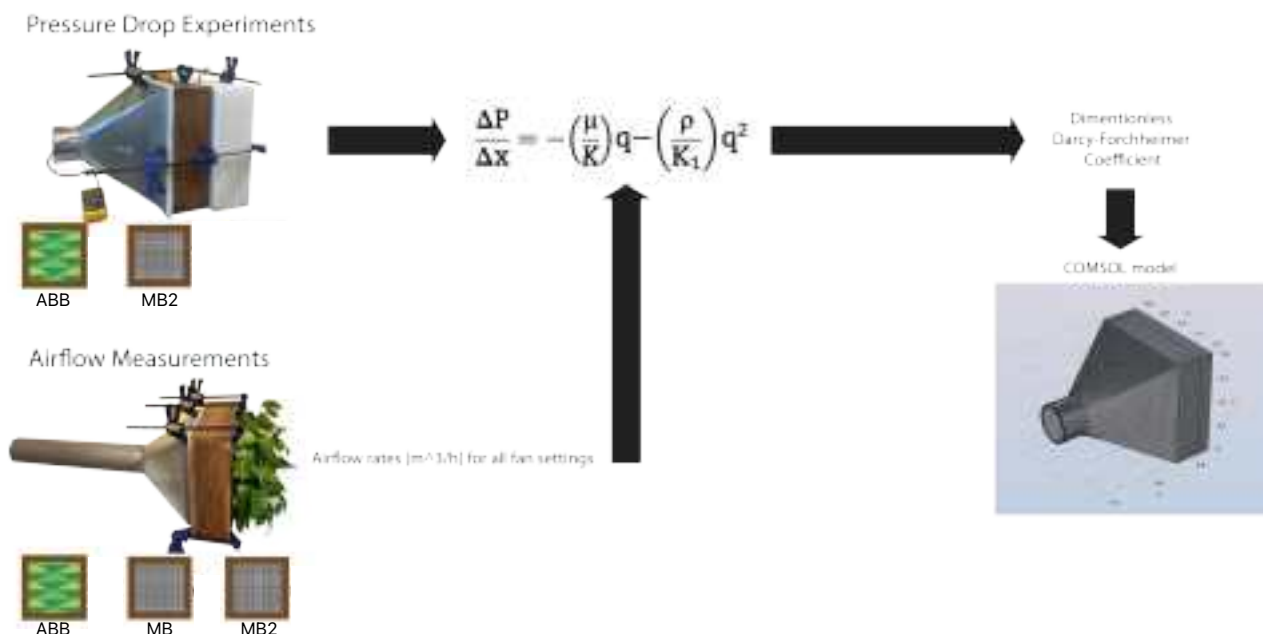


Figure 9: Flow of experiments, characterizing filter aerodynamics and supporting the model.

3.2.1 Airflow and pressure drop measurements

Firstly, airflow measurements were conducted to estimate the airflow rate corresponding to different fan settings in each biofilter. Before measuring the airflow rate, the biofilters were weighed and watered to field capacity. A plastic 6-inch internal diameter pipe was connected to the round section of the air duct and a hole was perforated to insert an anemometer (KIMO CTV110) at different heights sampling the entire pipe (Figure 10). Every fan setting and their corresponding velocity measurement was triplicated.

The resulting velocities over the pipe height were fitted to a 5th order function to generate a velocity profile that by integration allowed estimating the airflow rate.

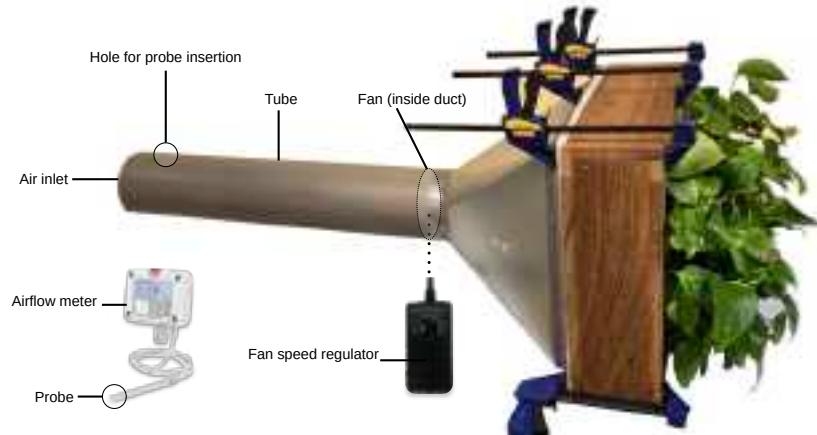


Figure 10: Experimental set-up for Airflow measurement.

Simultaneously, the pressure drop corresponded to each airflow rate was recorded using a pressure calibrator (Fluke 717 30G) and a pressure module (Fluke). The differential was measured between point 1 (in air duct, behind the substrate) and point 2 (atmospheric pressure), depicted red in Figure 11. In the same manner, three values of pressure drop were averaged for every fan setting. It is important to highlight that 15-min breaks were taken between each trial to reduce confounding effects of previously applied airflow rates.

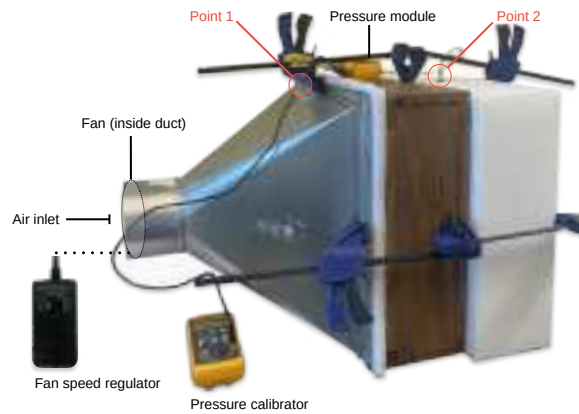


Figure 11: Experimental set-up for pressure drop measurement.

Table 7 (section 4.3.1) was generated showing the airflow rate generated by each fan setting and the corresponding pressure drop. In addition, Re numbers were likewise calculated.

The airflow rates and their corresponding pressure drop over the 0.09 m- thickness substrate were fitted to the Darcy-Forchheimer equation (Eq. 11), which allowed characterization of the airflow through a porous medium in the model:

$$\frac{\Delta P}{\Delta x} = -\left(\frac{\mu}{K}\right)q - \left(\frac{\rho}{K_1}\right)q^2 \quad (11)$$

Where q is the Darcy velocity or Darcy flux [m s^{-1}], also known as volumetric flux over the entire area of the porous medium including the solid and void phases. ΔP is the pressure drop [Pa] across the porous medium that has a length Δx [m]. μ is the dynamic viscosity of air [Pa s] and K represents the permeability [m^2] of the porous medium. The coefficient ρK_1^{-1} is called the Forchheimer-drag with ρ the air density [kg m^{-3}] and K_1 the inertial permeability [m]. In addition, a dimensionless Forchheimer drag coefficient C_F was calculated that relates the Darcy and inertial permeability.

From the pressure drop measurements both ΔP and Δx are known, resulting in the first defined term of the Darcy-Forchheimer equation ($\frac{\Delta P}{\Delta x}$). The fluid flux (q), was calculated using the previously obtained airflows, in Equation (12).

$$q = Q/A \quad (12)$$

With Q , the airflow [m^3s^{-1}], and A the substrate area perpendicular to the flux [m^2]. By applying second order polynomial regression, the coefficients c_a and c_b in Equation (13) can be obtained.

Through Equation (14-15) the Darcy Permeability (K) and non-Darcy Permeability (K_1) are calculated. Finally, K and K_1 result in the dimensionless Forchheimer C_F coefficient through Equation (16).

$$\frac{\Delta P}{\Delta x} = -\left(\frac{\mu}{K}\right)q - \left(\frac{\rho}{K_1}\right)q^2 = c_a q + c_b q^2 \quad (13)$$

$$\text{with} \quad K = \frac{-\mu}{c_a} \quad (14) \quad \text{and} \quad K_1 = \frac{-\rho}{c_b} \quad (15)$$

$$C_F = \frac{\sqrt{K}}{K_1} \quad (16)$$

3.2.2 Airflow CFD simulation

The software package COMSOL Multiphysics was chosen given its versatility to couple computational fluid dynamics (CFD) with mass transport phenomena. This is added value in this master's thesis since previous work on botanical biofiltration has mostly focussed on biological aspects and overlooked the fluid dynamics part [30,56]. Firstly, the geometry of the MB and the air duct section was built identically to the experimental set-up. Using this foundation, experimentally determined values for porosity, water holding capacity and permeability were used in a first submodel for the airflow simulation. The second submodel involved the mass transport and removal of the VOC, by considering the previously generated airflow field as an input. Each submodule and their boundary conditions are discussed below.

The CFD module was chosen for the airflow study and the standard $k-\omega$ model with no-slip wall boundary condition was used. The inlet airflow rates were experimentally defined (section 3.2.1). Out of the selected rates in Table 7 near all values correspond to Re values > 10000 (free flow) and > 10 (porous flow), supporting the use of turbulent airflow kinetics. Additionally, a low-Reynolds-number wall treatment was opted-in to enforce resolution down to the wall. The contaminated VOC airflow through the MB was considered stationary, incompressible, and turbulent. A free airflow model was used for the

air duct and the air layer after the substrate whereas a porous medium was enabled for the substrate section.

3.2.2.1 Duct and Rear Air Layer: Free Airflow Model

A free airflow model was used in the duct and the air layer after the substrate (blue in Figure 12). Turbulent flow was solved using 3D Reynolds-averaged Navier-Stokes (RANS) equations in combination with the k- ω turbulence model.

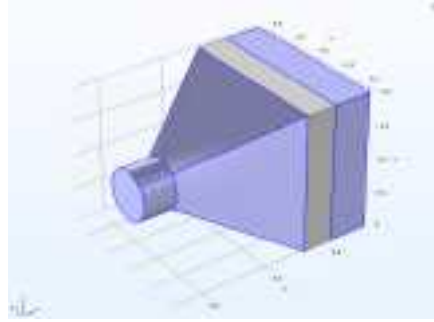


Figure 12: Model of microbial biofilter (MB), duct and air layer: parts where free flow is applied.

In COMSOL this translates to using the Turbulent Flow, Low Re k- ω interface to solve RANS equations (Eq. 17) for conservation of momentum and the continuity equation (Eq. 18) for conservation of mass.

$$\rho \nabla \cdot \mathbf{u} = 0 \quad (17)$$

$$\rho(\mathbf{u} \cdot \nabla) \mathbf{u} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] \quad (18)$$

Equations for the viscous stress tensor $\mathbf{K}$ [Pa], the Turbulent Kinetic Energy (TKE) k [$\text{m}^2 \text{s}^{-2}$], Specific Dissipation Rate (SDR) ω [s^{-1}], and turbulent viscosity μ_T [$\text{kg m}^{-1} \text{s}^{-1}$] are represented by the model by Equations (19-22) respectively.

$$\mathbf{K} = (\mu + \mu_T)(\nabla \mathbf{u} + (\nabla \mathbf{u})^T) \quad (19)$$

$$\rho(\mathbf{u} \cdot \nabla k) = \nabla \cdot [(\mu + \mu_T \sigma_k^*) \nabla k] + P_k - \beta^* \rho \omega k \quad (20)$$

$$\rho(\mathbf{u} \cdot \nabla \omega) = \nabla \cdot [(\mu + \mu_T \sigma_\omega) \nabla \omega] + \alpha \frac{\omega}{k} P_k - \beta \rho \omega^2 \quad (21)$$

$$\mu_T = \rho \frac{k}{\omega} \quad (22)$$

With 3D velocity field $\mathbf{u}$ [m/s], the identity matrix $\mathbf{I}$, pressure p [Pa], the dynamic viscosity of air (the fluid in this model) μ [$\text{kg m}^{-1} \text{s}^{-1}$] and the fluid (air) density ρ [kg m^{-3}].

3.2.2.2 Substrate: Porous Medium Airflow Model

To solve the airflow through the substrate compartment (blue in Figure 13), an unsaturated porous medium was enabled. The porous medium is characterised in terms of porosity, permeability and Forchheimer drag which were obtained experimentally (section 3.2.1).

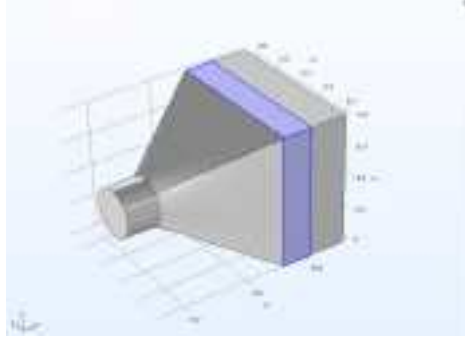


Figure 13: Model of microbial biofilter (MB) substrate section, where porous media flow is applied.

To achieve this in COMSOL, within the CFD module, the Porous Media Flow Interface was used. Here Darcy's law (adjusted for higher velocities) is used together with the RANS and continuity equations [57,58]. Darcy's law describes the movement of a liquid in porous media, and can be described as:

$$K = \frac{v A \mu \Delta x}{\Delta P} \quad (23)$$

with

- K : the (Darcy) permeability of a porous material
- v : the bulk fluid speed [$\text{m}\cdot\text{s}^{-1}$] (the mean speed within the pores of the porous media)
- μ : the viscosity of the fluid [$\text{Pa}\cdot\text{s}$]
- Δx : the length of the porous medium [m]
- A : the cross-section area of the flow [m^2]
- ΔP : the pressure loss [Pa]

[57,58]. This equation assumes a linear relation between the pressure drop over the porous medium, and the fluid flow rate (in this case airflow rate), and a unique value (K) for the permeability [57]. Sometimes also called the Darcy permeability, K represents the ease with which fluid can be transported through a porous matrix [57]. Its use is considered ideal for modelling low velocity flows where the pressure gradient is the major driving force, thus indicating small pores [58]. However, the relevant airflows needed for indoor air purification cannot be considered low. To address this, instead of the simple Darcy equation, a Darcy-Forchheimer equation (Eq. 11) is employed. At high velocities within porous media, the significance of inertial effects increases, requiring the inclusion of an inertial quadratic term, referred to as Forchheimer drag, in the Darcy equation. This term considers the kinetic energy and inertia of the fluid, as well as the non-linear relationship between fluid flow rate and pressure drop [58].

The continuity equation for the porous media flow is written as:

$$\rho \nabla \cdot \mathbf{u} = Q_m \quad (24)$$

with Q_m , the volumetric mass source per unit volume of the porous medium [$\text{kg m}^{-3} \text{s}^{-1}$]. COMSOL incorporates the theory from Equations (11) and (24) into a set of extended RANS equations. These Darcy-Forchheimer adjusted RANS equations can be described as:

$$\frac{1}{\varepsilon} \rho (\mathbf{u} \cdot \nabla) \mathbf{u} \frac{1}{\varepsilon} = \nabla \cdot [-p\mathbf{I} + \mathbf{K}] - \left(\mu \kappa^{-1} + \frac{C_F}{\sqrt{\kappa}} \rho \mathbf{u} + \frac{Q_m}{\varepsilon^2} \right) \mathbf{u} \quad (25)$$

with velocity field $\mathbf{u}$ [m/s], porosity ε [-], substrate permeability κ [m^2], the dynamic fluid (air) viscosity μ [$\text{kg m}^{-1} \text{s}^{-1}$] and the fluid (air) density ρ [kg m^{-3}]. Here, both the Darcy permeability (K) and the non-Darcian (inertial) permeability (K_1) are incorporated into the dimensionless Forchheimer coefficient C_F .

The equations for the viscous stress tensor (Eq. 26), TKE (Eq. 27), SDR (Eq. 28) and turbulent viscosity (Eq. 29) are also adapted accordingly.

$$\mathbf{K} = \frac{1}{\varepsilon} (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \frac{1}{\varepsilon} (\nabla \cdot \mathbf{u}) \mathbf{I} \quad (26)$$

$$\rho (\mathbf{u} \cdot \nabla) \frac{k}{\varepsilon} = \nabla \cdot [(\mu + \mu_T \sigma_k^*) \nabla k] + P_k + P_{k,\text{porous}} - \beta^* \rho \omega k \quad (27)$$

$$\rho \left(\frac{\mathbf{u}}{\varepsilon} \cdot \nabla \right) \omega = \nabla \cdot [(\mu + \mu_T \sigma_\omega) \nabla \omega] + \alpha \frac{\omega}{k} P_k + P_{\omega,\text{porous}} - \beta \rho \omega^2 \quad (28)$$

$$\mu_T = \rho \frac{k}{\omega \varepsilon} \quad (29)$$

3.2.3 Mass Transport Phenomena

The VOCs get transported by convection and diffusion through the biofilter's different phases. In order to solve the associated mass transfer across the phases, the convection-diffusion equation (Eq. 30) is added to the model by using the "Transport of Diluted Species Interface". This allows coupling to the airflow field determined in the previous CFD study, which is crucial as each compartment's mass transport phenomena depend on this field and the mass transfer coefficients from gas to liquid and solid phases.

$$\frac{\partial C}{\partial t} = \nabla \cdot (-D \nabla C) - \nabla \cdot (\mathbf{u} C) + R_i \quad (30)$$

Where, C is the concentration of the VOC [mol m^{-3}], D denotes the effective diffusion coefficient [$\text{m}^2 \text{s}^{-1}$], R is a reaction rate expression for the species [$\text{mol m}^{-3} \text{s}^{-1}$] and $\mathbf{u}$ is the averaged velocity vector [m s^{-1}]. The first term ($\nabla \cdot (-D \nabla C)$) accounts for diffusion whereas convection is represented by $\nabla \cdot (\mathbf{u} C)$.

3.2.3.1 Diffusivity in the air and liquid phase

In the air duct and rear air layer sections, where there is free flow the effective diffusivity (D_e) is the VOC gas diffusivity: $D_e = D_G$, and it was set to a value of $8.70 \times 10^{-6} \text{ m}^2 \text{s}^{-1}$ [59].

The substrate section of the model was defined as an unsaturated porous medium containing gas, liquid and porous matrix phases. Therefore, a percentage of the porosity is occupied by a liquid phase. The model required two diffusivity values within the unsaturated porous medium (defined within the substrate section). These are defined as the single-phase diffusion coefficients for the VOC diluted in the pure liquid and gas phases. Toluene's Diffusion Coefficient in Air (D_G) had the same value as the air duct section, and was set $8.70 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ (at 1 atm and 23 °C). This value was taken from the study by (Noël et al. 2019) ^[59].

For the liquid compartment, the diffusion coefficient (D_L) value was calculated, using the method highlighted by Gharagheizi et al. (2012). This method involves using a numerical model to predict the diffusion coefficient of organic compounds in water ^[60]. The calculation involved using the following equation (Eq. 31), were

$$\text{LOG}_{10} D^0 = A + B/T \quad (31)$$

D^0 = diffusion coefficient at infinite dilution in water, $\text{cm}^2 \text{ s}^{-1}$

A and B = regression coefficients for toluene (compound)

T = temperature, [K]

Tabulated values were found for A and B. The temperature used was 21.8 °C (294.95 K), the average temperature the validation data was collected at. The calculated value was $8.910472 \cdot 10^{-6} \text{ cm}^2/\text{s}$.

3.2.3.2 Boundary conditions

At the air duct inlet, the initial concentration ($C_{0,c}$) was set at $1300 \text{ } \mu\text{g}/\text{m}^3$, which is the initial VOC concentration injected in the chamber. The sink term for toluene removal and biodegradation was parameterized in COMSOL by the reaction rate (R_c). It was assumed that the removal of this hydrophobic VOC occurs in the liquid phase where microorganisms thrive and form a biofilm. This assumption is supported by the identification of the biofilm (and its liquid layer covering porous surfaces like the substrate particles and roots) as the major biodegrading element, and the identified adsorptive properties of water and some VOCs (section 1.12.3). Hence the mass balance for the liquid phase of the substrate compartment in Equation (32), is taking into account the fraction of porosity occupied by water θ_l .

$$\nabla \cdot \mathbf{J}_i + \mathbf{u} \cdot \nabla c_i = \theta_l R_i + s_i \quad (32)$$

Finally, the sink term R_c was experimentally derived from climate chamber experiments determining removal rate for toluene (when tested as a single VOC). Calculation of R_c followed Equation (34), attributing the removal rate to the reactive substrate volume, instead of the chamber volume. The relation for R , (Eq. 33) shows the reaction rate for removal of the chamber volume, with the experimentally determined removal constant k [h^{-1}].

$$R = -|k| \cdot C_0 \quad (33)$$

$$R_c = -|k| \cdot C_0 \cdot \frac{V_{\text{chamber}}}{V_{\text{effect}}} \quad \text{with} \quad V_{\text{effect}} = \theta_l \cdot V_{\text{substrate}} \quad (34)$$

Experimentally determined values were, $0.65279813 \text{ h}^{-1}$ for k and 0.33605 for θ_l . The value for R_c was set at $0.001960289 \text{ mol m}^{-3}\text{h}^{-1}$.

3.2.4 Linking for Multiphysics and output parameters

Both computational fluid dynamics, and transport of diluted species modules were coupled for a Multiphysics analysis, and model outputs were obtained

The response variables were the pressure drop across the substrate compartment (airflow study) and the difference in VOC concentration between both sides of the substrate (mass transport study). These were validated with the experimental findings

IV Results and Discussion

i Acclimatization process

The change in SPRE during the acclimatization of the two biofilters (ABB and MB) to a mixture of VOCs is shown in Figures 14 and 15. A summary of statistical results from ANCOVAs, the respective linear models and their analysis can be found in Appendix 1, Table 8.

Temporal trends, order of magnitude and similarities were observed in the removal of different VOCs. The effects of acclimatization on VOC removal varied depending on the specific VOC, with different patterns evident between BTEX, formaldehyde, and acetaldehyde. Overall, the SPRE values for BTEX, ranged (Min. to Max.) from 0.001472 to 0.294268 % over the course of the acclimatisation period. In contrast, the SPRE values for FA exhibited an entirely different magnitude, ranging from 4.529% to 21.599%. While previous studies report much higher SPRE values for BTEX alone (ranging 20-70% depending on the study), this pioneering method of evaluating VOCs in mixture with each other shows a much more realistic number for real indoor operating conditions ^[28,36,47,61].

4.1.1 BTEX's SPRE response

During the acclimatization period 10 times a mixture of BTEXFA was applied and SPRE values were obtained. A gradual linear increase pattern in SPRE was observed for BTEX compounds in both biofilters, suggesting improved removal efficiency with every dose. The R^2 values in Figure 14 indicate a slightly better linear fit for the ABB as opposed to the MB.

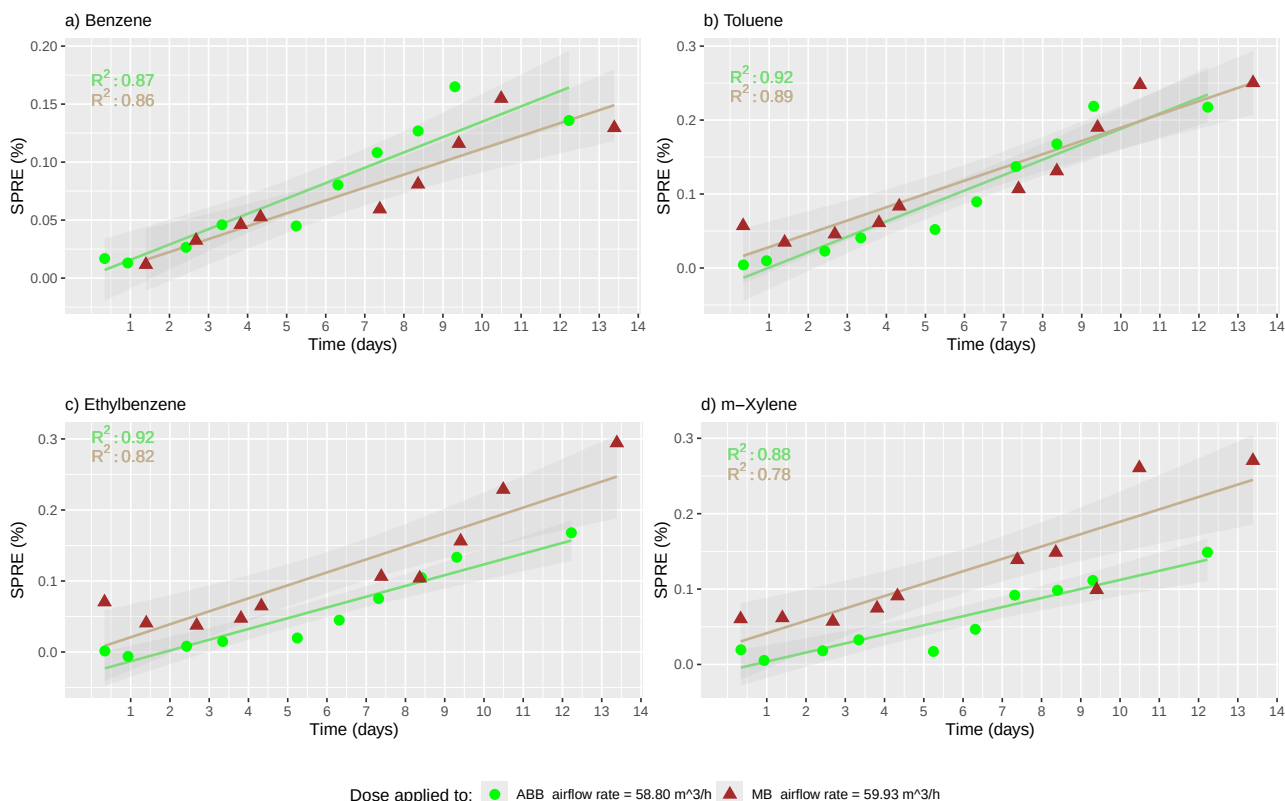


Figure 14: Single-pass removal efficiency during the acclimatization of the active botanical biofilter (ABB) and microbial biofilter (MB) to a VOC mixture. a) benzene, b) toluene, c) ethylbenzene and d) m-xylene. R^2 -values represent the linear fit between SPRE and time. "▲": dose applied but no data measured.

For ABB, the cumulative SPRE (%) increase for BTEX between the first and last doses were 0.119, 0.213, 0.166, and 0.129 for BTEX, respectively. Similar values were found for MB, which despite lacking a botanical compartment showed increases of 0.118, 0.193, 0.224, and 0.210, respectively. Notably, these observed increases are closely aligned, despite the VOCs being injected at varying concentrations. The linear models used in the ANCOVA (Table 8) revealed a strong statistically significant fit for BTEX, with a predominantly positive linear change in SPRE with every VOC exposure. The adjusted R^2 values in both experimental units ranged from 0.8219 to 0.9962, indicating that the linear models effectively accounted for the variability in SPRE. These numbers demonstrate that an acclimatization regime incorporating regular VOC doses successfully enhanced BTEX removal within a VOC mixture in both active and microbial biofilters.

For the same VOCs, the variable dose count significantly contributed the most to variation in SPRE, as evidenced by the partial coefficients of determination and the estimated coefficients. The estimated coefficients were the highest across all respective models, ranging from 0.0124432 to 0.0522164, implying with every dose a predicted increase in SPRE. Furthermore, time significantly influenced the variation in SPRE for benzene in ABB and for ethylbenzene in ABB and MB. While not always significant, this variable was included in almost all models for BTEX, demonstrating very similar estimated coefficients ranging from -0.0151689 to -0.0392608. These coefficients, when significant, predict how SPRE changes if all other explanatory variables are kept constant while time increases by one day. Additionally, this negative impact suggests that the response variable (SPRE) may decrease over time under certain conditions, potentially indicating a degradation of acclimatization effects when the biofilter is not operated regularly.

Interestingly, interaction term (time:dose count) was strongly significant in every linear model except for benzene, revealing a combined effect between time progression and dosage frequency. Its estimated coefficients ranged from 0.0015520 to 0.0025625, indicating a positive effect on SPRE, albeit with a lower magnitude than time and dose count separately.

Results of the effect of environmental variables such as initial temperature in the chamber had a significant positive impact only for ethylbenzene. The same applies to net CO_2 production, but only for benzene in the ABB. When significant, these variables had estimated coefficients ranging from 0.0055653 to 0.0077657.

4.1.2 FA's SPRE response

The aforementioned trends were less apparent for FA. A simple linear regression revealed only a sufficient linear fit for SPRE of acetaldehyde in MB (R^2 values Figure 15). However, the multifactor linear models reveal a bit more nuance. Likewise, none of the multifactor linear models sufficiently fit the data in for the ABB, except for acetaldehyde's SPRE in MB, but initial mass showed a better fit and more significant effect in variation (ANOVA), than both time and dosecount. This linear model projects an increase of 4.66 in SPRE (%) with each kg of initial mass gained, assuming other explanatory variables remain constant ($\text{Pr}(> |t|) = 1.15 \cdot 10^{-5}$). The increase of mass over time is most like due to water accumulating in the substrate.

For BTEX, initial mass did not significantly contribute to variability (ANCOVA), always had the lowest partial coefficients of determination of all variables (partial $R^2 < 0.01$), and was consequently left out of every linear model. In contrast significant mass SPRE relations were found for FA.

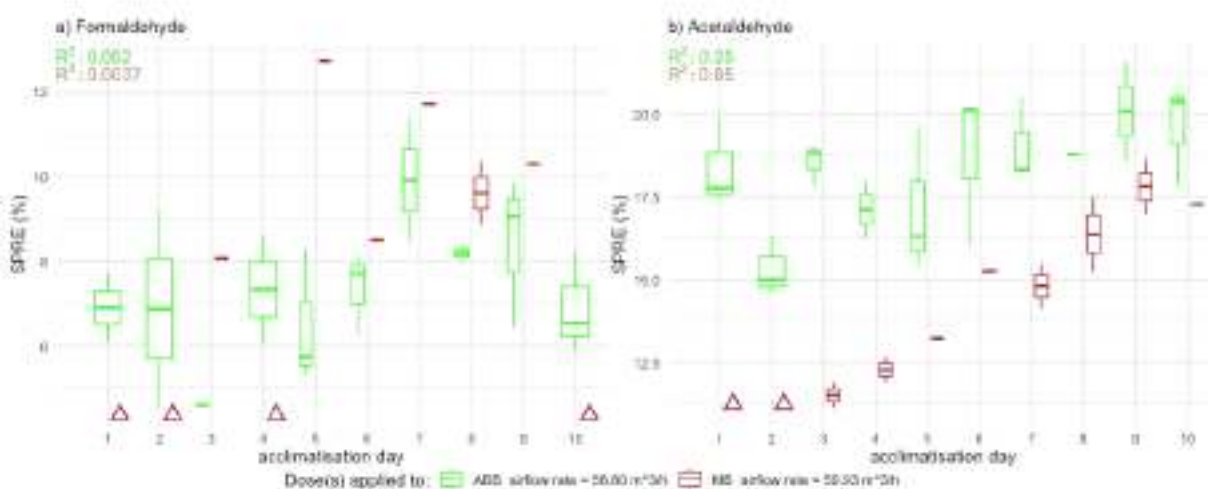


Figure 15: Single-pass removal efficiency during the acclimatization of the active botanical biofilter (ABB) and microbial biofilter (MB) to a VOC mixture. a) formaldehyde and b) acetaldehyde. R^2 -values represent the linear fit between SPRE and time. "Δ": dose applied but no data measured. Boxplots represent repeated decay measurements taken during one batch test.

In the case of acetaldehyde, both ABB and MB demonstrated increasing removal efficiency over time, with a significant increase only in MB. In Figure 15 b, ABB showed already higher removal efficiency from the start of the acclimatization period in contrast with the MB, linearly catching up.

Considering that both units were operated at the same airflow rate ($60 \text{ m}^3\text{h}^{-1}$), this difference in removal trend is highly likely due the presence of the botanical component. It is possible that due to the plant component, ABB already had a better-established biofilm or more preferential polar adsorption sites from better water retention by the root systems^[47]. The MB on the other hand may have had to rely on gradual biofilm development over time in order to distribute a stable hydrophilic layer for adsorption and breakdown throughout the substrate. Furthermore, it was established (by the upcoming modelling section) that the absence of a botanical component can lead to more permeability in the substrate and thus less resistance protecting the MB from drying out. This would make clear why the ABB was able to retain its water content and consequently its initial mass better over the acclimatization period, leading to the stable acetaldehyde removal efficiency depicted in Figure 15 b. It is also noteworthy that the initial mass significantly contributed to the variation in ABB for FA, despite the models exhibiting poor fit. Even in these scenarios, the initial mass significantly influenced SPRE variation. The trends observed for acetaldehyde removal were not evident in the case of formaldehyde, suggesting a reduced sensitivity of formaldehyde-SPRE to initial mass and possibly to the water content in the substrate.

It has been suggested in previous work on acclimatization that biofilters can be limited by the availability of the substrate for MEK removal and limited by the number of degraders present for toluene removal^[54]. The results of the acclimatization study show a similar comparison between the more hydrophilic FA and the very hydrophobic BTEX. Availability of the substrate for acetaldehyde most likely limited

adsorption in the MB, while the much slower acclimatization and limited BTEX removal before start-up suggest limited populations of BTEX degraders were present [54].

ii Impact of operational parameters

4.2.1 Airflow variation

Removal data for all individually performed tests are visualised in Figure 21 and Figure 22 in Appendix 2, showing the impact of the sequential order in which the airflows were tested within each trial (also referred to as “testing order” or “airflow order”). An airflow being tested as first, second or third in a trial is referred to as the airflow order translate into 3 separate classes order-1, order-2 and order-3. Estimated effects by the LMM were always compared to the control category, order-1. Visualisations of simple linear fits between SPRE or CADR against airflow rate (and LMM ANOVA p-values) can be found in Appendix 3, Figure 23 and Figure 24 respectively.

1.1.1.1 Single pass removal efficiency

The single-pass removal efficiencies for the airflow rate variation in the ABB are illustrated in Figure 16 a. On average, SPRE values ranged from $0.11 \pm 0.02\%$ to $0.81 \pm 0.04\%$ for BTEX. In contrast, the SPRE of formaldehyde varied between $3.42 \pm 1.49\%$ and $8.63 \pm 1.38\%$, while acetaldehyde ranged from $18.75 \pm 1.09\%$ to $29.13 \pm 0.71\%$. Similar to the results of the acclimatization period, SPRE values for FA are in a different magnitude compared to BTEX. This confirms the logic that biofilters face important limitations when applied for the treatment of poor water-soluble compounds due mass transfer limitations [62].

The ABB achieved the highest SPRE for all BTEXFA compounds at the lowest airflow setting (1x) operating at $59.80 \text{ m}^3\text{h}^{-1}$. Conversely, the lowest SPRE values were observed at the highest airflow rate ($170.34 \text{ m}^3\text{h}^{-1}$). The maximum SPRE values for each VOC were; benzene: $0.32 \pm 0.01\%$, toluene: $0.72 \pm 0.02\%$, ethylbenzene: $0.81 \pm 0.04\%$, m-xylene: $0.63 \pm 0.04\%$, formaldehyde: $8.63 \pm 1.38\%$, and acetaldehyde: $29.13 \pm 0.71\%$ respectively.

A Tukey test revealed that the lowest airflow setting (1x) resulted in significantly higher SPRE values than both the 2x and 3x airflow settings ($p < 0.05$) for benzene, xylene, and acetaldehyde. Compared to 1x, there was a significant decrease in SPRE at the higher airflow rate (3x) for all tested VOCs. Specifically, this decrease for BTEXFA was 0.21, 0.44, 0.48, 0.41, 3.50, and 10.55 respectively ($p < 0.05$). When testing formaldehyde (alone) at similar inlet concentration, Abedi et al. (2022) found similar SPRE decreases when increasing airflow, albeit at much lower airflow rates, resulting in SPREs of 85% to 97% [35].

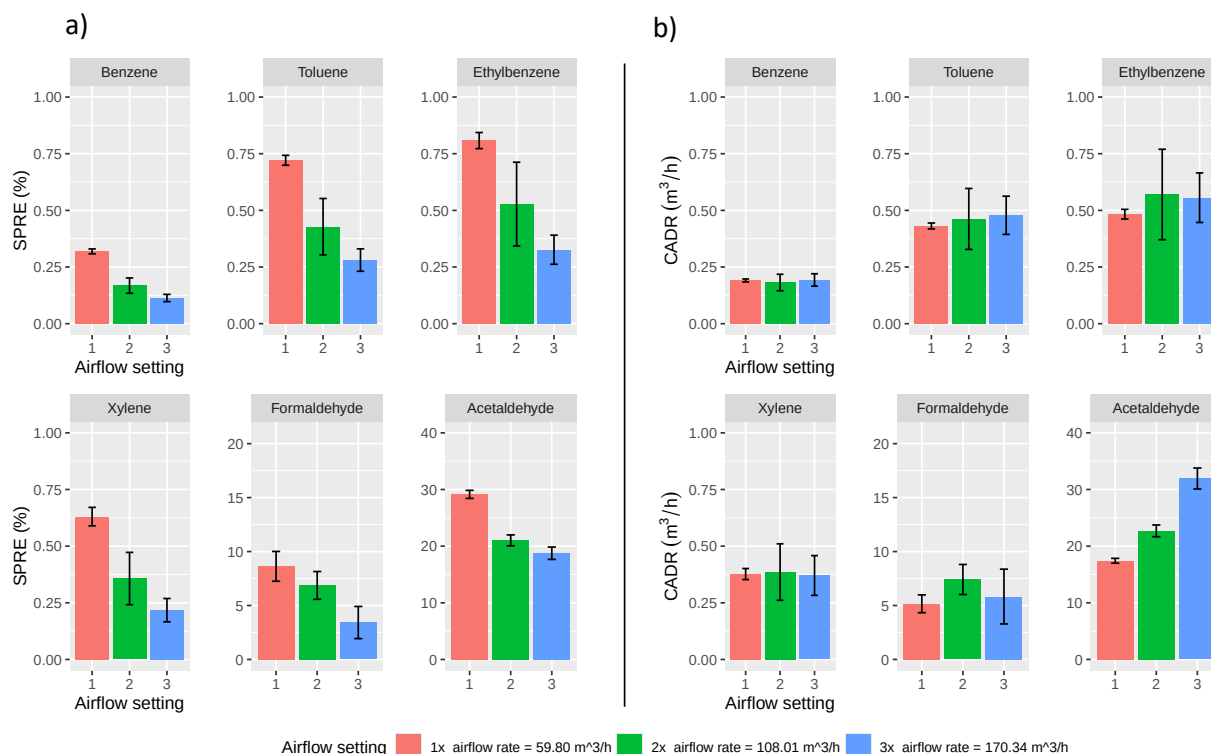


Figure 16: Average single-pass removal efficiency (SPRE) (a) and clean air delivery rate (CADR) (b) for single VOCs in a BTEXFA mixture in the active botanical biofilter (ABB). The airflow settings (1x, 2x, 3x) produced the airflow rates (59.80, 108.01, 170.34 m³h⁻¹). Error bars represent standard error of the mean.

For BTX and acetaldehyde, the airflow rate, the order in which airflow rates were applied in each trial (airflow-order), and their interaction significantly affected SPRE variation (ANOVA of LMM; for p-values, see Figure 23, Appendix 3).

For BTEX and acetaldehyde, increasing the airflow rate had a clearly significant negative impact on SPRE. In contrast, for formaldehyde, only the interactive flow-order component contributed significantly to SPRE variation (ANOVA, $p = 0.024$), with all fixed effect estimates negatively impacting SPRE.

In the case of ethylbenzene, only the fixed effect of airflow rate was significant (Estimate = -0.010657, $p = 0.02538$). Furthermore, for BTX, the model estimates for airflow order showed a negative impact of order-2 and, to a lesser extent, order-3. However, for acetaldehyde, a strong increasing effect for order-3 was observed, suggesting that applying airflow in the third order leads to an increased SPRE response.

The interaction between airflow rate and airflow order was significant (ANOVA) for BTEXFA, excluding ethylbenzene. The significant interaction term indicated that the established decreasing effect of airflow

rate on SPRE varies depending on the order in which they are tested. This finding suggests that understanding the modifying effects of testing order on the more dominant effect of airflow rate is crucial.

For BTX, the interactions between airflow rate and airflow order-2, and between airflow rate and airflow order-3, had positive fixed effect estimates with respective p-values: (B) 0.015, 0.018; (T) 0.038, 0.089; (X) 0.078, 0.18. This indicates that although testing an airflow in the 2nd or 3rd order generally reduced SPRE, the negative effect of increasing airflow rate is mitigated by the interactive effect of a specific flow and testing order combination. This suggests some antagonistic dynamics between the SPRE-reducing effect of increased airflow and SPRE-enhancing effects when specific rates and orders are combined.

Though, the modifying effect of testing order on the effect of the rate was established in this study, it is essential to understand what these modifying effects are, and to recognise that these may be very different in nature and cause. This becomes apparent when observing the following general trends.

The similar effects found for BTX contrast with the effects for formaldehyde and acetaldehyde. In BTX an interactive effect related to the ABB unit being tested for the second or 3rd time in a row, had an SPRE -increasing effect, likely compensating the negative effect of increasing airflow. Conversely SPRE-decrease for formaldehyde was solely explained by the LMM by these same interactive effects. These differences in behaviour for BTX and F may very well be due to different underlying mechanisms, or the lack thereof. Acclimatisation effects could potentially explain this observation, as in previous sections it was established that the SPRE increased for BTEX during sequential testing. Yet, these same acclimatisation effects were not present in formaldehyde removal.

When ruling out the acclimatisation effect for formaldehyde, a possible explanation why only the interactive effect led to SPRE reduction, and why differences in airflow rates were not significant, could be that increased airflow reduces SPRE depending on a physicochemical memory effect (on the substrate) by previously applied (higher) airflow rates.

For Acetaldehyde it is more plausible that a combination led to the decreasing trend in Figure 16 a. The LMM predicted a separate fixed effect of airflow rate decreasing the SPRE considerably (estimates coefficient: -0.07334, $p < 0.02$). On top of this, the other fixed effects may be caused by an SPRE-increasing or -decreasing, memory effect depending on what airflow is applied first.

4.2.1.1 *Clean air delivery rate*

The ABB clean air delivery rates (CADRs) for each tested airflow rate are illustrated in Figure 16 b. Tukey tests revealed no significant differences in CADR between the three applied airflow rates for BTEXF. Acetaldehyde was the only compound with significant differences among all three applied airflow rates.

The maximum achieved CADRs by the ABB were 0.190 ± 0.006 , 0.48 ± 0.08 , and $0.56 \pm 0.11 \text{ m}^3\text{h}^{-1}$ for benzene, toluene, and ethylbenzene (BTE), respectively. For xylene and formaldehyde, the maximum CADRs were $0.39 \pm 0.12 \text{ m}^3\text{h}^{-1}$ and $7.41 \pm 1.40 \text{ m}^3\text{h}^{-1}$ at an airflow rate of $108.01 \text{ m}^3\text{h}^{-1}$. Acetaldehyde

was the only VOC in the mixture exhibiting a peak performance at the highest airflow rate of 170.34 m³/h, achieving a CADR of 31.94 ± 1.85 m³h⁻¹.

No significant linear relationships could be fitted between airflow rate and CADR for benzene, toluene, and ethylbenzene (BTE). This finding is counterintuitive because CADR is roughly proportional to airflow rate by definition, suggesting a strong overshadowing effect could be expected. When the testing order was selected as the explanatory variable, the linear mixed models (LMMs) for BTE appropriately fit the data. CADR significantly increased with test order, as all fixed effect estimates were positive with p-values ≤ 0.02. This increase was most notable in the third test. For xylene, no significant effects or trends were identified for any tested explanatory variables.

Both acetaldehyde and formaldehyde exhibited significant interaction effects between airflow rate and airflow order on CADR. In both cases, the interaction term “airflow-rate:airflow-order” was statistically significant, indicating that the impact of airflow rate on CADR depends on the testing order. Additionally, airflow rate independently shows a significant positive effect on FA's CADR, as evidenced by (t-test) p-values well below 0.05 (1.48e-05 for acetaldehyde and 0.01102 for formaldehyde). This indicates that increasing the airflow rate generally increases the CADR for both substances. Previous research confirms this trend as well for formaldehyde [35]. However, the effect of testing order most likely overshadows this in formaldehyde's CADR in Figure 16 b.

4.2.1.2 SPRE and CADR: a dual evaluation approach

Before continuing, the very nature of the performance metrics SPRE and CADR merits some discussion. These measures provide complementary yet nuanced perspectives on the effectiveness of the ABB system.

SPRE offers insights into the removal efficiency under highlighted operational conditions by accounting for (normalising by) the airflow rate, providing a standardised measure of contaminant removal relative to the volume of air processed. Specifically, SPRE is calculated as $SPRE = (CADR/Q) \times 100$, where Q represents the airflow rate, underscoring how it is corrected when varying airflow. In contrast CADR quantifies the raw volume of clean air delivered per unit of time, effectively reflecting the system's operational capacity within the test set-up. Thus, by nature it is intrinsically linked to the airflow rate.

It is pertinent to note that the lack of statistical insignificant differences observed in CADR versus airflow rate (Figure 16 b), may stem from the intrinsic characteristics of the CADR metric. Since CADR and airflow rate are inherently linked—where changes in one generally induce proportional adjustments in the other—the resulting intrinsic changes in CADR as response variable may very well cancel out the true effects of airflow rate on removal. As a consequence, CADR values may exhibit less sensitivity within the linear mixed models employed, as they represent the raw mass of VOCs removed over time without the corrective influence of airflow rate, unlike SPRE.

This distinction carries significant implications for interpreting the performance outcomes of the ABB. CADR provides a snapshot of volumetric air processing, essentially only filtering out the strongest effects. In contrast, SPRE reveals the efficiency of the removal process across different operational conditions, allowing for a more thorough understanding of the biofilter's VOC removal capabilities with

enough sensitivity to explore effect trends. The dual SPRE/CADR-lens depicted by Figure 16 summarises trade-offs between additive, interactive and confounding effects, that are distinct between the BTEXFA compounds. Similarly to the research field of biological gas treatment, it can be confirmed that an ABB is not either mass transfer or kinetically limited, but is a complex combination of both [62].

4.2.2 Testing VOCs singular vs in a mixture

Figure 17 shows a comparison of removal of benzene and toluene tested in mixture (Phase II) vs tested alone (Phase III). Conditions like initial VOC concentration, airflow rates and airflow rate testing order (sequentially) were maintained constant for this comparison.

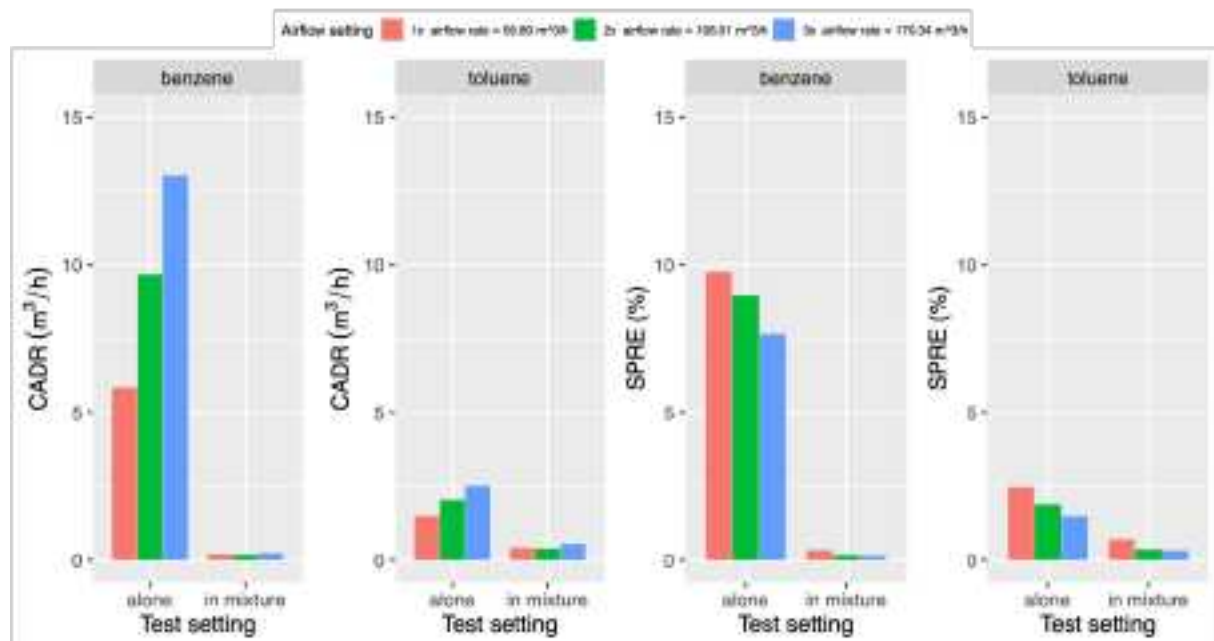


Figure 17: Comparison of the removal metrics (SPRE and CADR) for benzene and toluene in the active botanical biofilter (ABB) when tested as a single VOC vs in a BTEXFA mixture. The initial VOC concentration in both cases was 50 and 1300 $\mu\text{g m}^{-3}$ for benzene and toluene respectively.

It is clear that both VOCs exhibited higher removal (in both metrics) when tested in isolation. For instance, single Benzene showed a CADR with a corresponding SPRE that was 29.0 to 54.1 times greater than when tested in mixture (depending on the airflow rate). Similarly, when Toluene was tested without the presence of the other BTEXFA-compounds, the CADR and SPRE were 3.5 to 5.2 times larger. Consequently, the data presented in Figure 17 demonstrates an increase in removal metrics for both benzene and toluene when other VOCs (in similar concentration range) are absent.

The full removal of benzene in mixture took roughly 6 hours. Similar removal was observed in the study by Siswanto et al. (2020) of where benzene in cigarette smoke (also a VOC mixture) was also fully removed 6 to 8 hours in similar testing set-up to the one used for this dissertation [51].

Removal tests when applying benzene alone yielded SPREs just below 10%. This is on the low side compared to similar research on ABBs (without active carbon) reporting a range 28.7% to 36% SPRE for benzene [47]. However, within the state of the art as presented in Table 3, the single benzene removal tests in this work were performed at the lowest inlet concentration tested to date

A notable difference between the two VOCs in Figure 17 is that when toluene was co-removed within a BTEXFA mixture, it exhibited higher values for CADR and SPRE across all tested airflow rates compared to benzene. However, this trend reverses when substances are tested in isolation, as benzene's removal metrics appear markedly higher under these conditions. This discrepancy may be attributed to proportional differences in the total concentration of polar VOCs (BTEX). Benzene's inlet concentration ($50 \mu\text{g m}^{-3}$) was significantly lower than that of toluene ($1300 \mu\text{g m}^{-3}$), indicating that benzene may face more competition with other VOCs, sharing similar physicochemical properties, for binding sites in the botanical biofiltration system, compared to toluene.

While the differences outlined in this section are noteworthy, they must be interpreted with caution due to the lack of replication. Additional testing with more replicates is necessary to validate and expand upon these preliminary findings.

iii The model

4.3.1 Characterisation of substrate airflow kinetics

The aerodynamic properties of the biofilters (ABB, MB, MB2) including their airflow rates, pressure drop and calculated Reynold numbers (Re) for each fan setting can be found in Table 7.

Table 7: Results of pressure drop and airflow experiments, and further derived airflow characteristics for ABB, MB and MB2. Re number "free flow": Re for sections with free airflow kinetics i.e., pipe and duct ($Re > 2300$ turbulent). Re number "porous flow": Re for flow inside the porous medium i.e., the substrate ($Re > 10$ turbulent).

Unit	Fan setting	Airflow rate [$\text{m}^3 \text{h}^{-1}$]	Pressure drop [Pa]	Re number 'free airflow'	Re number 'porous flow'	Darcy permeability (K) [m^2]	non-Darcian permeability (K_1) [m]	Dimensionless Forchheimer coefficient (C_2) [-]
ABB	1x	59.80	4.56	9428	44.43	9.81×10^{-8}	3.42×10^{-4}	0.92
	2x	108.01	11.73	16968	100.04			
	2.5x	126.03	14.93	19797	103.77			
	3x	170.34	29.77	27058	113.29			
MB	1x	59.93	-	8204	-	-	-	-
	2x	95.39	-	13057	-			
	3x	167.89	-	22981	-			
MB2	1x	75.42	2.76	12347	106.6	1.31×10^{-7}	9.41×10^{-4}	0.38
	2x	128.72	7.36	20657	158.53			
	2.5x	148.97	9.28	23906	185.03			
	3x	218.75	17.48	35104	278.05			

The relationship between pressure drop and Darcy velocity over the biofilter substrate is depicted in Figure 18. The second order polynomial had a good fit for both ABB and MB2 units, indicating a reliable estimation of the coefficients in the Darcy-Forchheimer relation.

The coefficient c_a for the ABB was only slightly larger between the two units. This means a higher (Darcy-) permeability for MB2, and thus less resistance in the substrate, when botanical parts are absent. The quadratic coefficient c_b for the ABB was over 2.7 times larger compared to MB2. This translates into the ABB substrate, showcasing lower (non-Darcian) permeability resulting in a more sizeable Forchheimer drag. Consequently, the inertial effects are more prominent in the ABB substrate. Most likely this is due to the lack of botanical component in MB2.

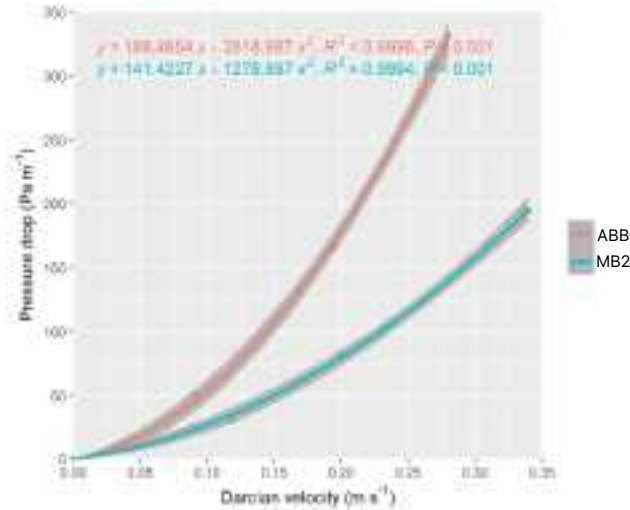


Figure 18: Regression of obtained pressure drop and Darcy velocities for the ABB and MB2.

$$\frac{\Delta P}{\Delta x} = -\left(\frac{\mu}{K}\right)q - \left(\frac{\rho}{K_1}\right)q^2 = c_a q + c_b q^2 \quad (13)$$

4.3.2 Validation of model in terms of airflow kinetics

Figure 19 depicts the 3D- velocity field of the fluid dynamics submodel for 3 different mesh resolutions. The runtimes for this submodel were 15 min, 2h 25min, 16h41 min for course (a), normal (b) and fine mesh (c) respectively. Thus, the choice of mesh can drive up the computational time for the fluid dynamics considerably.

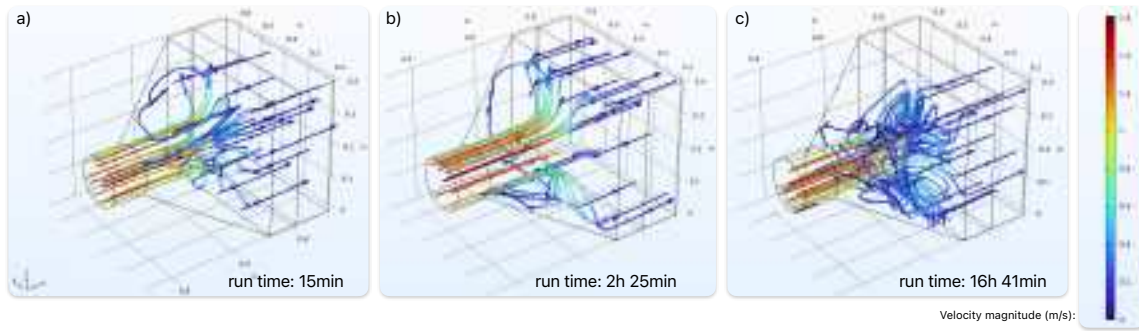


Figure 19: Streamline; Modelled velocity field of three mesh resolution at an inlet airflow rate (input) of $75.42 \text{ m}^3 \text{ h}^{-1}$. a) course, b) normal and c) fine mesh.

A grid convergence study was conducted on pressure drop (including the same mesh resolutions depicted in Figure 19) and resulted in a significant monotonic convergence ($R^2 = 0.75$) and a grid convergence index (GCI) of 0.34%. Consequently, in terms of pressure drop even the course mesh had a very accurate prediction compared to the two other resolutions.

The model validation against experimental data is shown in Figure 20. Pressure drop data was modeled by varying the inlet airflow rates corresponding to the MB2 fan settings (Table 7). These were plotted against the experimentally determined pressure drop values from MB2 (Table 7). Both experimental and modelled data have a very significant ($R^2 = 0.9965$, $p < 0.002$) linear fit, indicating a very accurate prediction by the model. Consequently, the aerodynamic submodel including airflow through all MB components model was successfully validated against experimental measurements, providing a solid framework for upcoming model builds.

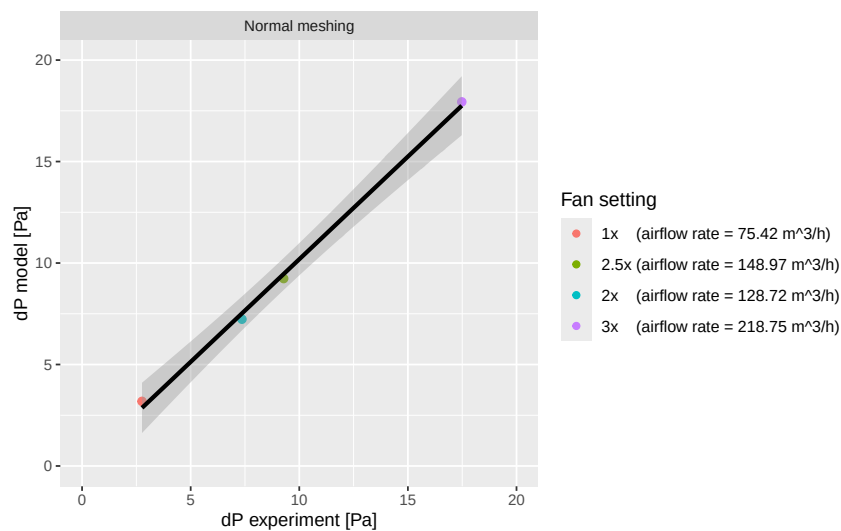


Figure 20: Modelled versus experimental pressure drop at airflow rates corresponding to 4 established fan settings.

4.3.3 Validation of the transport and removal of VOC sub-model

For validation of the full submodel, including the transport of diluted species coupled to the airflow field, experimental data from MB2 was likewise used. The sole removal of toluene (as model VOC) was experimentally obtained for MB2 by applying the lowest fan setting 1x ($75.42 \text{ m}^3\text{h}^{-1}$). MB2 yielded an SPRE of 1.038660% (CADR: $0.47 \text{ m}^3\text{h}^{-1}$).

The same boundary conditions were applied in the model (initial inlet concentration: $1300 \mu\text{g m}^{-3}$, inlet airflow rate: $75.42 \text{ m}^3\text{h}^{-1}$). The inlet and outlet toluene concentrations were obtained and the simulated SPRE was calculated. The modelled SPRE values for toluene were 0.475177305% for a course mesh, and 0.4822695035% for a fine mesh resolution.

A possible explanation why the modelled metrics are roughly half that of their experimental counterpart could be the assumptions or simplification made in the model build. It was assumed that the aqueous surface was the sole source of removal. This would totally ignore other binding sites like organic material in the porous medium not covered by biofilm or exposed to water. Nevertheless, the fact that both modelled and experimental removal are in the same order of magnitude may indicate that the model is capturing essential dynamics of the air-biofilm interactions despite its simplifications.

V Conclusions

i Acclimatisation

The effects of acclimatization on VOC removal varied depending on the specific VOC. Different acclimatization patterns characterized by both consistency and variability in SPRE were evident between BTEX, formaldehyde, and acetaldehyde. The acclimatization regime for both the ABB and MB involved 10 batch removal operations of a VOC (BTEXFA) mixture at an airflow rate of $60 \text{ m}^3\text{h}^{-1}$ for both units.

This work demonstrates that an acclimatization regime incorporating regular VOC doses and defined windows of operation successfully enhanced BTEX removal within a VOC mixture in both active and microbial biofilters. Notably, increased BTEX removals were recorded, with significant respective enhancements of 0.119, 0.213, 0.166, and 0.129 in the SPRE metric for the ABB. The MB showed very similar increases.

Analysis of linear models and ANCOVA indicated that cumulative dose count, along with the timing of dose application and their interactive effects, significantly contributed to variations in SPRE for BTEX. This suggests that adjustments to both the quantity of doses and the timing of their application, as well as possibly the resting time between doses, could lead to even more SPRE increase or even shorten acclimatization periods. Sensitivity analyses on these parameters with more repetitions might reveal optimal acclimatization conditions. This is particularly crucial in a societal context, as faster biofilter stabilization could potentially save substantial amounts of time and resources in future research.

In contrast, the removal of formaldehyde and acetaldehyde (FA) exhibited less pronounced trends during acclimatization. Although SPRE for acetaldehyde in the MB biofilter showed some improvement, the overall variability in removal efficiency was largely influenced by initial mass rather than by time or dose count. This discrepancy highlights the distinct removal mechanisms between BTEX and FA, suggesting that initial mass likely plays a more crucial role in facilitating the adsorption and degradation of certain VOCs.

Assuming that the initial mass changes are the result of water retention in the substrate, the removal trends suggest that the presence of botanical components within the ABB may confer advantages over MBs by maintaining moisture levels critical for optimal acetaldehyde adsorption or degradation. This underscores the potential of integrating biological components into biofilter design to improve SPRE for specific VOCs.

Regarding formaldehyde removal, the trends established for acetaldehyde were absent, indicating that SPRE was less sensitive to initial mass for formaldehyde. Future tests should focus on whether different critical moisture levels can be identified for different VOCs. Accordingly, for the removal of highly water-soluble VOCs, such as FA, future research may need to differentiate acclimatization trends governed by sequential VOC dosing from those by increased substrate water content.

ii Impact of operational parameter

5.2.1 Airflow variation

The main two operational metrics to analyse VOC removal in the airflow variation study, were single-pass removal efficiency (SPRE) and clean air delivery rate (CADR). The interplay between CADR and SPRE highlighted the importance of employing both metrics in assessing the overall effectiveness of biofiltration systems. SPRE proved essential to establish efficiency losses due to airflow rate, and to identifying other operational parameter effects further ameliorating or hindering removal in the substrate. SPRE offered enough sensitivity to even evaluate effect trends between different VOC compounds. However, CADR can give a more honest look at how efficiency losses are compensated by other effects like testing order under true operating conditions. Furthermore, CADR can give a first indication on how an ABB may perform for further comparison.

5.2.1.1 *SPRE*

The optimal airflow rate for achieving maximum single-pass removal efficiency (SPRE) was observed at the lowest tested setting of $59.80 \text{ m}^3\text{h}^{-1}$. Notably, further analysis through linear mixed models revealed that reducing airflow enhanced SPRE for compounds such as benzene, toluene, ethylbenzene, xylene, and acetaldehyde (in the tested range of airflow rates). The extrapolation from these models suggests even greater SPRE improvements may occur at lower airflow rates, highlighting the need for continued examination of airflow as a critical operational parameter.

Furthermore, it was determined that the order of airflow testing significantly affected SPRE variation, akin in magnitude to that of airflow rate itself. However, the nature of the testing order effect (i.e., additive, interactive, or any specific combination) was very different among VOCs, implying different, albeit subtle, SPRE behaviours and effect trends. Due to these observed trends in the LMM effects, It is likely that benzene, toluene and xylene were affected by further acclimatisation, leading to less clear differences in the observed SPRE response with varying airflow.

These findings emphasize that various factors, including sequential testing of the same ABB unit, can confound the analysis of airflow impacts. Previous literature predominantly employs single-factor linear models and ANOVA, which may overlook these critical interactions and their implications [35,36,63]. Therefore, this research advocates for the incorporation of randomized trial designs and advanced analytical models to better account for confounding variables related to experimental setups.

5.2.1.2 *CADR*

In order to identify the optimal airflow rate, achieving maximum VOC removal in the shortest time within the test chamber setup, the CADR metric was assessed. Maximum CADRs achieved by the ABB were as follows: $0.190 \pm 0.006 \text{ m}^3\text{h}^{-1}$ for benzene and $0.48 \pm 0.08 \text{ m}^3\text{h}^{-1}$ for toluene at an airflow rate of $170.34 \text{ m}^3\text{h}^{-1}$, $0.56 \pm 0.11 \text{ m}^3\text{h}^{-1}$ for ethylbenzene, $0.39 \pm 0.12 \text{ m}^3\text{h}^{-1}$ for m-xylene, and $7.41 \pm 1.40 \text{ m}^3\text{h}^{-1}$ for formaldehyde. Notably, no significant differences (TukeyHSD test) were observed with other airflow rates for BTEXF. Consequently, there was no optimal airflow rate for BTEXF removal in terms of CADR.

A lack of discernible differences in the CADR response, suggests that within the airflow range tested, other factors have an effect of equal or greater magnitude. For BTE this was most likely a continued acclimatisation effect, suggesting that for BTE removal in a mixture, airflow adjustments within the tested range will only have a significant or noticeable impact once the ABB is fully stabilised. A possible consequence is that increasing airflow in a non-acclimatized or unstabilised ABB might be counterproductive regarding energy usage. For future studies, longer acclimatization periods with more VOC doses, and a broader range of airflow rates, may be necessary to determine the conditions under which airflow rate impacts are noticeable, factoring in the trade-offs among multiple effects.

An optimal airflow rate achieving maximum in the shortest time was observed for acetaldehyde. With a maximum CADR of $31.94 \pm 1.85 \text{ m}^3\text{h}^{-1}$ at an applied airflow rate of $170.34 \text{ m}^3\text{h}^{-1}$, and further analysis by LMMs predicted more CADR increase with increasing airflow. Further inquiry in where corresponding SPRE-decreases to higher airflows may impact this CADR increase, may prove valuable in understanding the underlying removal which appears to behave differently from BTEX and formaldehyde.

5.2.2 Testing singular VOCs vs. in a mixture

The impact of single versus mixed VOC testing on their removal within the active botanical biofilter was assessed by comparing single measurements (one to one airflow variation trial comparison). The findings revealed that both benzene and toluene demonstrated higher removal metrics (SPRE and CADR) when tested in isolation as opposed to being part of a BTEXFA mixture. In isolation, benzene and toluene removal efficiencies were markedly improved, with benzene exhibiting a CADR and SPRE that were 29.0 to 54.1 times greater than in a mixture, and toluene showing increases of 3.5 to 5.2 times. This suggests that the presence of additional VOCs may competitively inhibit removal efficiency due to similarities in physicochemical properties that lead to competition for binding sites within the biofilter system. When co-removed within a BTEXFA mixture, toluene consistently showed higher removal metrics than benzene across all tested airflow rates. In contrast, benzene removal outperformed toluene's in isolation. This variation could be due to the significantly lower inlet concentration of benzene compared to toluene, resulting in higher competition with other VOCs for removal.

However, some caution should be exercised in interpreting these findings due to the limited replication of experiments. It is recommended for future studies to conduct more airflow variation trials on single VOCs to gain insight into how altering the airflow rate, affects the removal of single vs. mixed VOCs with different physicochemical characteristics. Simultaneously this could provide the statistical power needed to corroborate or contest these findings and suggested implications

iii Modelling approach

The analysis of the experimentally obtained airflow dynamics in the substrate compartment demonstrated that the active botanical biofilter (ABB) exhibited markedly higher resistance, particularly in terms of Forchheimer drag compared to the unit without plants (MB). This difference indicates a more turbulent flow within the substrate and reveals higher drag and inertial forces at play due to the botanical

components (roots and foliage). The next challenge in future research endeavors will be to validate the the substrate's aerodynamics including root system characterisation and above-ground plant organs. In this regard, it is recommended that subsequent work reevaluates mesh sensitivity and apply higher resolution settings where feasible to refine the results further.

The airflow model on the aerodynamic characterisation for the substrate compartment presented in this work was successfully validated against experimental measurements of pressure drop across the system. This validation implies that this CFD aerodynamic submodel is robust and can serve as a foundation for future more comprehensive models. In addition, it was found that even at coarse mesh resolutions, the model maintains accuracy, which is beneficial in the context of botanical biofiltration due to the lower computational resources and running times (15 minutes) required.

The preliminary 3D multiphysics model of the substrate compartment of the active botanical biofilter was developed using a novel approach that characterises airflow in the biofilter components through CFD calculations. Subsequently, the resulting airflow fields, contained in a first submodel, were coupled with a second submodel addressing the transport and removal of a single VOC based on its physicochemical characteristics.

While the model presented provides a solid framework for understanding the biofiltration process for single VOC removal (toluene) in MB2, further refinements to the complete MB model are necessary to fully capture the complexities of the removal interactions at play before validation with experimental removal metrics (i.e., SPRE and CADR) is successful. Future research should focus on integrating additional, or more complex, pathways for removal and conducting sensitivity analyses to better understand the influence of various model parameters on the output results.

VI Societal finality of the research and possible valorisation of the results

This dissertation presents a pioneering examination of the often-overlooked effects of acclimatization in ABBs. Understanding that both the timing and number of exposures during the start-up phase of ABBs substantially influence removal efficiency, underscores the necessity for additional research. Recognising that optimal acclimatization parameters, such as resting time, water content and dose frequency, can vary for different VOCs serves as a crucial foundation for future studies aimed at stabilizing system performance.

The results contributed significant insights into the practical relevance of ABBs within the context of indoor air quality management. It has become evident that the commonly published removal metrics for ABBs may not accurately reflect their performance in real-world scenarios. Traditional approaches test individual VOCs, leading to removal metrics (like CADR) that can be misleadingly elevated when extrapolated to mixtures of VOCs that are encountered in everyday environments ^[9,64]. Such discrepancies pose a potential risk for claims regarding performance and safety in real-world applications.

This dissertation also highlights the ability of ABBs to remove VOCs with diverse physicochemical characteristics, including BTEXFA compounds. It stands to reason that reporting removal metrics for

polar and (nonpolar) lower removal rate VOCs, such as BTEX, could significantly enhance the credibility of ABBs in the air purification industry. Currently, individual consumer air filters primarily emphasize the removal of highly polar and water-adsorptive VOCs, such as formaldehyde, methyl ethyl ketone (MEK) [64–66]. Notably, botanical biofilters that are emerging on the market tend to follow this trend, thereby limiting the comprehensive understanding of ABB capabilities by consumers and retailers alike [64,66].

As a means to promote informed consumer choices, it is imperative that future studies refine and expand test metrics to encompass both mixed VOCs and CADR values relevant to indoor air concentrations and room dimensions. This endeavour would not only aim to ensure transparency but also aspires to affirm the real-world effectiveness of ABB technology.

The resource-intensive nature of this research—which involved 6–8-hour test times and extensive care for the botanical components—highlights the need for advanced modeling techniques to streamline the investigative process. The novel use of 3D-Multiphysics modeling within this thesis marks an essential step towards more efficient methodologies in the field of botanical biofiltration. By facilitating simulations of various reactor designs and operational parameters, future research can focus valuable resources on optimizing real-world applications.

This work lays the groundwork for future modeling, optimization, design and eventually deployment of ABBs. It is our hope that subsequent research will further explore the integration of botanical biofilters into complex urban and indoor environments, ultimately enhancing air quality management solutions and contributing to the sustainability of indoor living spaces.

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VIII Appendices

Appendix 1. Statistical analysis of BTEXFA removal response to acclimatization

Table 8: Summary of multi factor linear models and ANCOVAs performed for the acclimatization study. “:” indicates an interactive effect.

Unit	VOC	ANCOVA summary		Linear model summary			
		Contributing variables in the linear model	p value -- Pr(>F)	Adjusted R ²	P-value (fit)	coefficient estimate	Pr(> t)
ABB	Benzene	time [days]	0.02873	0.9748	0.00008034	-0.0281976	0.02026
		dose count	0.009393			0.0422658	0.00414
		net CO2 production over total run time [ppm/h]	0.02574			0.0055653	0.04483
		time : dose count	0.08600			0.0007233	0.08600
ABB	Toluene	time [days]	0.349586	0.9826	0.000003399	-0.0392608	0.00922
		dose count	0.0005562			0.0522164	0.00241
		time : dose count	0.004034			0.0019068	0.00403
ABB	Ethylbenzene	time [days]	0.004662	0.9962	0.000007231	-0.0195482	0.00279
		dose count	0.00008962			0.0124432	0.02618
		T _{start} [°C]	0.001734			0.0077657	0.01434
		time : dose count	0.00005695			0.0024075	0.000057
ABB	Xylene	time [days]	0.31730	0.9243	0.0002758	-0.0151689	0.286
		dose count	0.0000534			0.0147000	0.301
		time : dose count	0.02503			0.0015520	0.025
ABB	Formaldehyde	time [days]	0.77203	0.2648	0.04731	1.7891	0.0344
		dose count	0.23909			-1.1103	0.0260
		T _{start} [°C]	0.04718			0.5464	0.2087
		initial mass [kg]	0.02680			7.6106	0.0268
ABB	Acetaldehyde	time [days]	0.8476724	0.5615	0.00045	-2.14706	0.01530
		dose count	0.0008531			0.46802	0.00540
		net CO2 production over total run time [ppm/h]	0.0020655			0.81114	0.00108
		initial mass [kg]	0.0780066			-6.40266	0.03892
		time : dose count	0.0273736			0.02658	0.02737
MB	Benzene	time [days]	0.1956817	0.922	0.001051	-0.0213665	0.1152
		dose count	0.0001988			0.0366628	0.0281
		time : dose count	0.2856502			0.0006988	0.2857
MB	Toluene	time [days]	0.354750	0.9523	0.00006952	-0.0312865	0.07833
		dose count	0.00001325			0.0330488	0.07563
		time : dose count	0.008437			0.0025625	0.00844
MB	Ethylbenzene	time [days]	0.0116297	0.9954	0.0001847	-0.0189736	0.01127
		dose count	0.000001928			0.0127470	0.04641
		net CO2 production over total run time [ppm/h]	0.0009332			0.0005865	0.74333
		T _{start} [°C]	0.0052395			0.0066717	0.16141
		time : dose count	0.0018781			0.0023238	0.00188
MB	Xylene	time : dose count	0.000184	0.8219	0.000184	0.0016387	0.000184
MB	Formaldehyde	time [days]	0.13544	0.9649	0.02324	-2.9907	0.00852
		dose count	0.27592			-0.8922	0.07588
		T _{start} [°C]	0.23859			7.3039	0.00997
		initial mass [kg]	0.00626			27.5687	0.00626
MB	Acetaldehyde	initial mass [kg]	0.00003823	0.8444	0.00001433	4.6600	0.0000115
		T _{start} [°C]	0.3401			-0.97449	0.34009

Appendix 2. Airflow variation of active botanical biofilter (ABB): individual test results with emphasis on testing order.

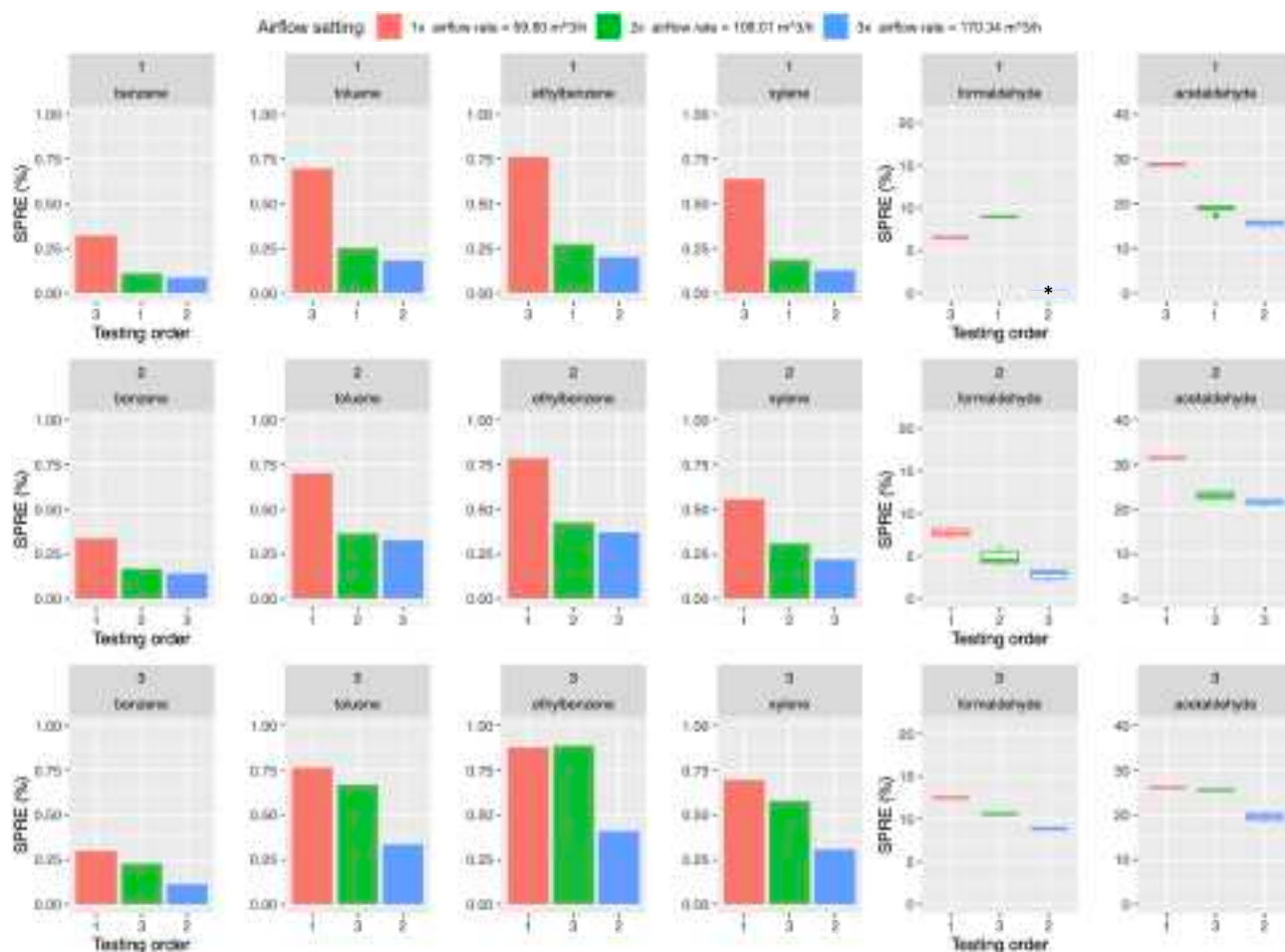


Figure 21: Airflow variation in the active botanical biofilter (ABB): single-pass removal efficiency (SPRE) for single VOCs in a BTEXFA mixture. “*”: no data available due to measuring error.

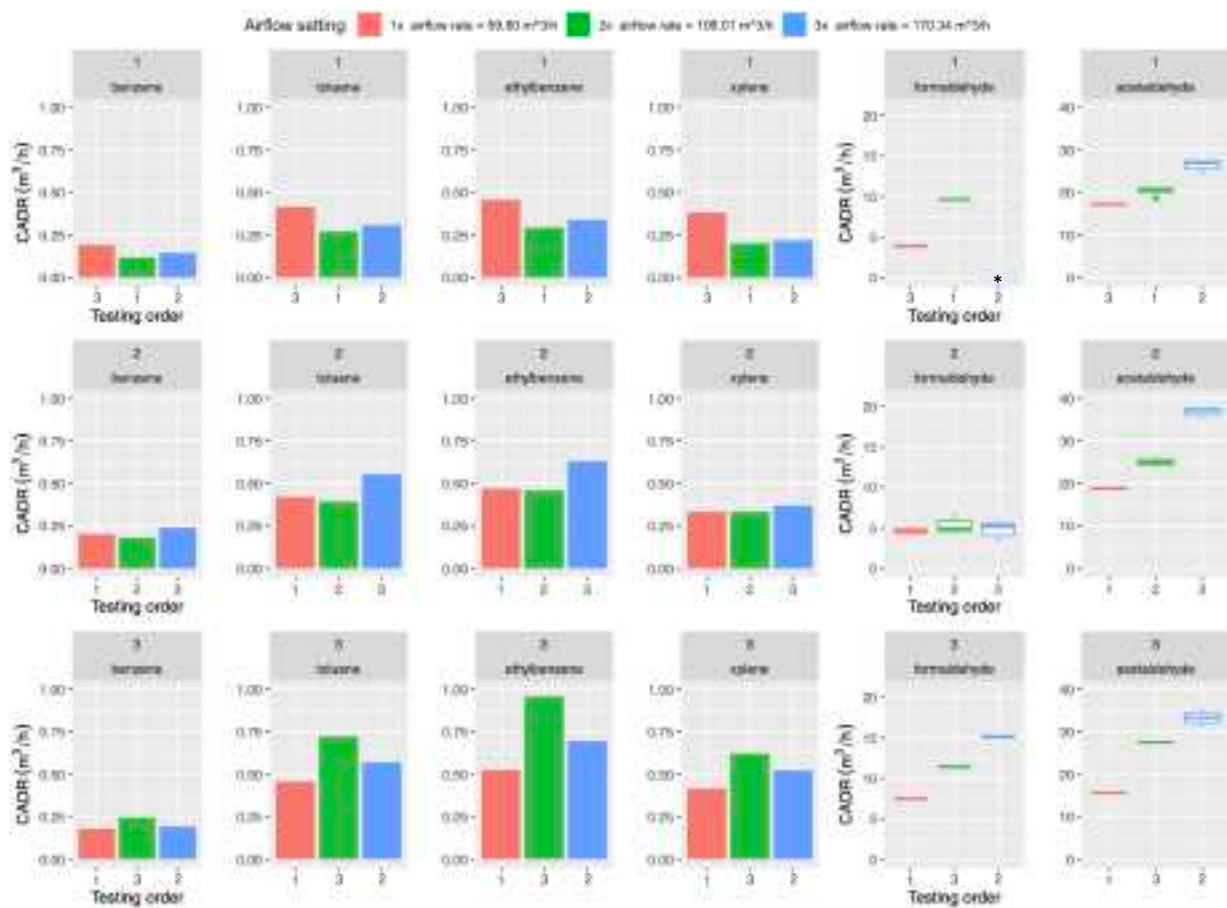


Figure 22: Airflow variation in the active botanical biofilter (ABB): Clean air delivery rate (CADR) for single VOCs in a BTEXFA mixture. "*": no data available due to measuring error.

Appendix 3. Single factor linear models, linear mixed models ANOVA on airflow variation data.

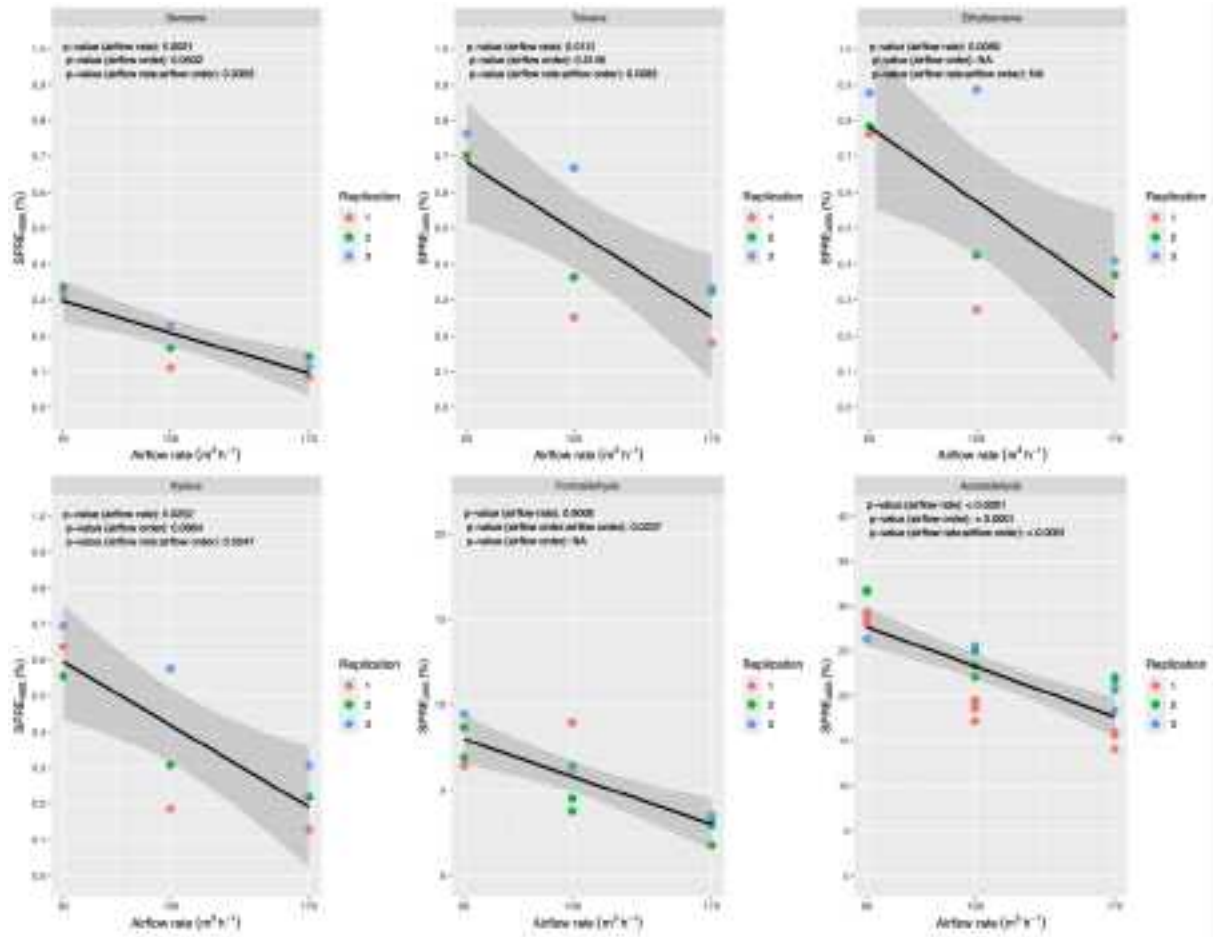


Figure 23: Linear relation between the single-pass removal efficiency (SPRE) and airflow rate reduction in the active botanical biofilter (ABB). p-values correspond to the actual contribution to variation in the linear mixed model (LMM). “NA” means the variable was left out of the LMM due to lack of significance.

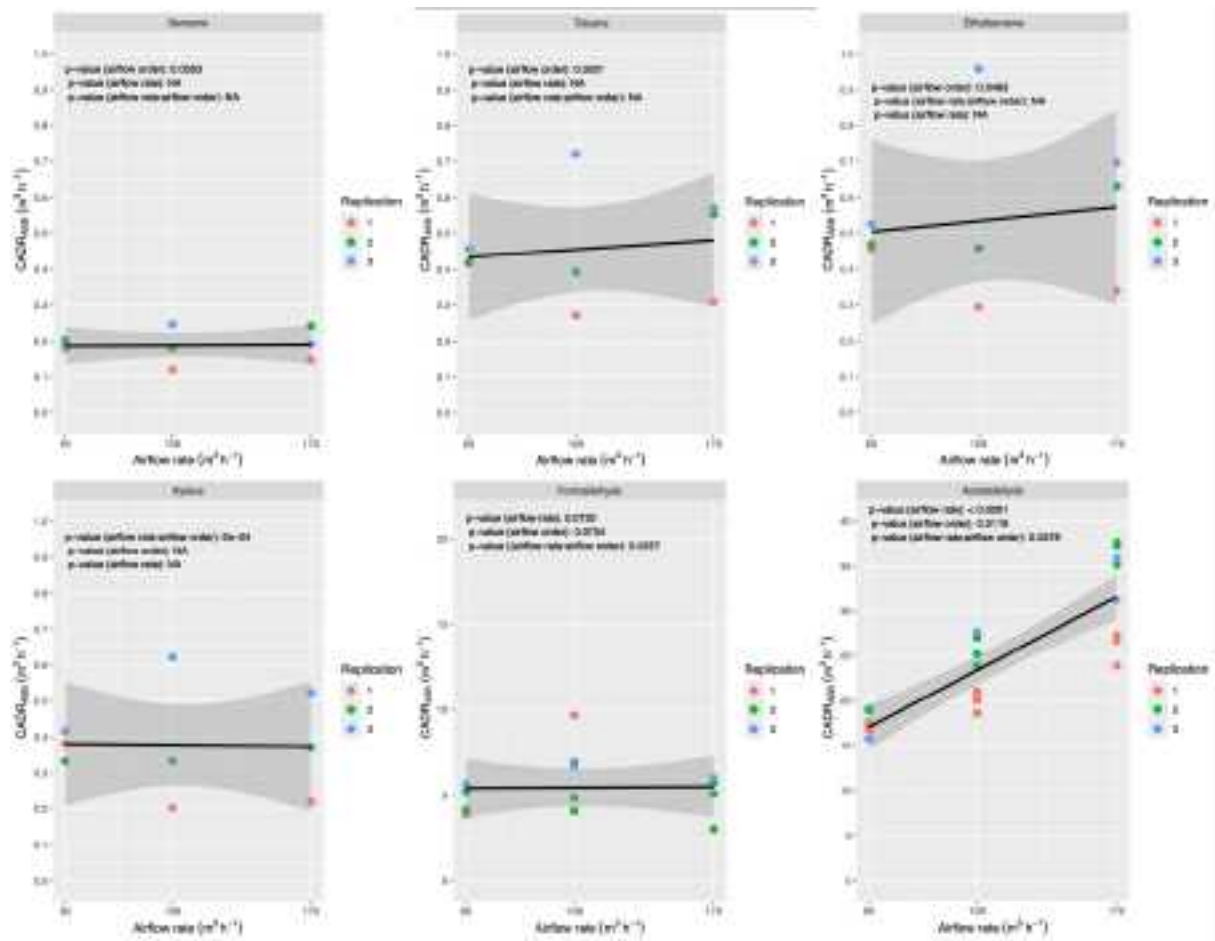


Figure 24: Linear relation between the clean air delivery rate (CADR) and airflow rate variation in the active botanical biofilter (ABB). p-values correspond to the actual contribution to variation in the linear mixed model (LMM). "NA" means the variable was left out of the LMM due to lack of significance.

Appendix 4. Raw output for linear mixed model and ANOVA analysis of airflow variation data.

+++ SPRE +++

Benzene

[illegible]

Toluene

```

>>> from itertools import combinations
>>> combinations('ABCD', 2)
<itertools.combinations object>
>>> list(combinations('ABCD', 2))
[('A', 'B'), ('A', 'C'), ('A', 'D'), ('B', 'C'), ('B', 'D'), ('C', 'D')]
>>>

```


Xylene

75

Formaldehyde

```

> fitPoissonGLM = glm(factors ~ offset(log(factors)), data = fittedData)
> summary(fitPoissonGLM)

glm model results:

Data: fittedData
Model: glm(formula = factors ~ offset(log(factors)), data = fittedData)
Df: 1
Deviance: 0
AIC: 1.07
BIC: 1.07
P-value: 1

```

Acetaldehyde

+++ CADR +++

BENZENE

77

```

Random effects:
             Sum             Variance: 550.866
Intercept    0.0000000 0.0000000 0.0000000
airFlow,trial 0.0000000 0.0000000 0.0000000
Residual     0.0000000 0.0000000 0.0000000
Number of obs: 9, groups: trial, 3; airFlow,trial, 3

Fixed effects:
             Estimate Std. Error      df t value Pr(>|t|)
(Intercept)  0.26140    0.00905 2.16198    6.528  0.010 *
airFlow,trial 0.01736    0.00413  0.00000    4.190  0.000 *
airFlow,order 0.00070    0.00000  0.17163    0.344  0.838 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Correlation of Fixed Effects:
             (Intercept)
airFlow,trial -0.220
airFlow,order -0.001
) ##>##>===== Table for Fixed Effects (Type III Sum of Squares) =====

---- ANOVA Table for Fixed Effects (Type III Sum of Squares) ----
> anova(lm.model)
Type III Analysis of Variance Table with Satterthwaite's method
              Sum Sq   Mean Sq  NumDF  DenDF  F value    Pr(>F)
airFlow,order 0.0042375 0.0021188        2        2  27.336 0.00029 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```

Toluene

```

##>##>===== Table for random ----
> summary(lm.model)
Linear model using OLS by RLM. 4 effects use Satterthwaite's method ["numMakersFor"]
Formula: lm0 ~ airFlow,order + (1 | airFlow,trial) + (1 | trial)
Data: 9, 1999, 1999

RMSE criterion of convergence: 10.0

Scaled residuals:
      Min       1Q   Median       3Q      Max
-0.0286 -0.0000  0.0070  0.0000  0.0100

Random effects:
             Sum             Variance: 550.866
Intercept    0.0000000 0.0000000 0.0000000
airFlow,trial 0.0000000 0.0000000 0.0000000
Residual     0.0000000 0.0000000 0.0000000
Number of obs: 9, groups: trial, 3; airFlow,trial, 3

Fixed effects:
             Estimate Std. Error      df t value Pr(>|t|)
(Intercept)  0.26140    0.00905 2.16198    6.528  0.010 *
airFlow,trial 0.01736    0.00413  0.00000    4.190  0.000 *
airFlow,order 0.00070    0.00000  0.17163    0.344  0.838 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

Correlation of Fixed Effects:
             (Intercept)
airFlow,trial -0.220

```

```

---- ANOVA Table for Fixed Effects (Type III Sum of Squares) ----
> anova(lm.model)
Type III Analysis of Variance Table with Satterthwaite's method
              Sum Sq   Mean Sq  NumDF  DenDF  F value    Pr(>F)
airFlow,order 0.0042375 0.0021188        2        2  27.336 0.00029 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1

```

Ethylbenzene

```

--- ANOVA Table for ethylbenzene ---
+ summary(lme_model)
Linear mixed model fit by REML. t-tests use Eigenström's method [Eigenström2007]
Formula: code ~ airFlow,order + (1 | airFlow,trial) + (1 | trial)
Data: E1Trial_data

REML criterion at convergence: 8.2

Scaled residuals:
      Min       1Q   Median       3Q      Max
-0.59636 -0.20862  0.04624  0.28134  0.50000

Random effects:
              Name                Variance Std.Dev.
trial         (Intercept)  9.986289  3.15903
airFlow,trial (Intercept)  0.000027  0.01643
Residual              0.000001  0.00099
Number of obs: 9, groups: trial, 3; airFlow,trial, 3

Fixed effects:
              Estimate Std. Error      df t value Pr(>|t|)
(Intercept)    0.12228      0.18028  1.270e+01  0.902 >
airFlow,order2  0.66750      0.04581  1.5027e+01  0.000 *
airFlow,order3  0.25750      0.05272  1.5027e+01  0.000 *
---
Dgeff, codes: 0 =*** 0.001 ** 0.01 * 0.05 . 0.1 . 1
Correlation of Fixed Effects:
              (Intercept)
airFlow,order2  0.234
airFlow,order3  0.288  0.744

```

```

--- ANOVA Table for Fixed Effects (Type III Sum of Squares) ---
+ anova(lme_model)
Type III Analysis of Variance Table with Eigenström's method
              Sum Sq  Mean Sq  NumDF  DenDF  F value    Pr(>F)
airFlow,order2 0.055284  0.017682       2       18  29 0.00028 *
---
Signif. codes:  0 =*** 0.001 ** 0.01 * 0.05 . 0.1 . 1

```

Xylene

```

--- ANOVA Table for xylene ---
+ summary(lme_model)
Linear mixed model fit by REML. t-tests use Eigenström's method [Eigenström2007]
Formula: code ~ airFlow,order+airFlow,order + (1 | airFlow,trial) + (1 | trial)
Data: E1Trial_data

REML criterion at convergence: 20

Scaled residuals:
      Min       1Q   Median       3Q      Max
-0.45449 -0.06472  0.00733  0.09135  0.09933

Random effects:
              Name                Variance Std.Dev.
trial         (Intercept)  7.100e+01  8.426107
airFlow,order (Intercept)  9.160e+01  9.573340
Residual              4.340e-01  0.658540
Number of obs: 9, groups: trial, 3; airFlow,trial, 3

Fixed effects:
              Estimate Std. Error      df t value Pr(>|t|)
(Intercept)    4.525e+01  0.347e+01  1.999e+01  7.358  0.018 *
airFlow,order2  1.238e+01  1.031e+01  5.586e+00 -09.762  0.000 *
airFlow,order3 -1.870e+00  1.080e+01  5.586e+00 -04.361  0.000 *
airFlow,order4 -1.945e+00  1.080e+01  5.586e+00 -03.349  0.000 *
---
Dgeff, codes:  0 =*** 0.001 ** 0.01 * 0.05 . 0.1 . 1
Correlation of Fixed Effects:
              (Intercept) airFlow,order2
airFlow,order2  0.000
airFlow,order3  0.000  0.001
airFlow,order4  0.000  0.000  0.900
---
+ anova(lme_model)

```

```

--- ANOVA Table for Fixed Effects (Type III Sum of Squares) ---
= anova(flm, model)

Type III Analysis of Variance Table with lmerAnova() method
              Sum Sq  Mean Sq  NumDF  DenDF  F value    Pr(>F)
arFlow_rate arFlow_order 0.001512 0.001512    1      2  0.002 0.999215 ***
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1.


```

Formaldehyde

```

--- OLS Results for Formaldehyde ---
= summary(lm, model)

Linear model using OLS by OLS. 1 factor and lmerAnova() method ["lmerAnova"]
Formal: mod = arFlow_rate ~ arFlow_order + (1 | arFlow_order) + (1 | Site)
Data: lmerAnovaData

RMS: criterion of convergence: 50.7

Scaled residuals:
      Min       1Q   Median       3Q      Max
-1.0493  -0.2075  -0.0000  -0.0000  -0.2002

Number of obs: 15, group: 1000, 0, arFlow_order, 0

Fixed effects:
              Estimate Std. Error    DF t value Pr(>|t|)
(Intercept)  -0.04507    2.13673  7.99999  -0.467  0.6505
arFlow_rate   0.00750    0.87063  7.99999   0.007  0.9538
arFlow_order  -0.00000    0.70345  7.99999  -0.000  0.9999
arFlow_order2  0.00000    0.65030  7.99999   0.000  0.9999
arFlow_order3  0.00000    0.60000  7.99999   0.000  0.9999
arFlow_order4  0.00000    0.55000  7.99999   0.000  0.9999
arFlow_order5  0.00000    0.50000  7.99999   0.000  0.9999
arFlow_order6  0.00000    0.45000  7.99999   0.000  0.9999
arFlow_order7  0.00000    0.40000  7.99999   0.000  0.9999
arFlow_order8  0.00000    0.35000  7.99999   0.000  0.9999
arFlow_order9  0.00000    0.30000  7.99999   0.000  0.9999
arFlow_order10 0.00000    0.25000  7.99999   0.000  0.9999
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1.

Correlation of Fixed Effects:
              (Intercept) arFlow_order2 arFlow_order3
arFlow_order 0.960
arFlow_order2 0.772 0.760
arFlow_order3 0.520 0.560 0.680
arFlow_order4 0.300 0.300 0.300 0.300
arFlow_order5 0.100 0.100 0.100 0.100 0.100
arFlow_order6 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order7 0.000 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order8 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order9 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order10 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000

Type III Analysis of Variance Table with lmerAnova() method
              Sum Sq Mean Sq NumDF DenDF  F value    Pr(>F)
arFlow_rate   0.2448  0.2448    1      2  4.4705 0.02332
arFlow_order  30.8455  3.4273    9      2  3.8613 0.07509
arFlow_order2 31.8335  3.5371    2      2  3.9333 0.02175 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1.


```

Acetaldehyde

```

--- OLS Results for acetaldehyde ---
= summary(lm, model)

Linear model using OLS by OLS. 1 factor and lmerAnova() method ["lmerAnova"]
Formal: mod = arFlow_rate ~ arFlow_order + (1 | arFlow_order) + (1 | Site)
Data: lmerAnovaData

RMS: criterion of convergence: 100.7

Scaled residuals:
      Min       1Q   Median       3Q      Max
-1.0233  -0.2000  -0.0000  -0.0000  -0.2119

Number of obs: 15, group: 1000, 0, arFlow_order, 0

Fixed effects:
              Estimate Std. Error    DF t value Pr(>|t|)
(Intercept)   0.0000  2.4442  7.9999  0.000  0.9999
arFlow_order  -0.2134  0.9402  7.9999  -0.227  0.9845
arFlow_order2  0.7985  1.0404  7.9999   0.766  0.4430

---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1.

Correlation of Fixed Effects:
              (Intercept) arFlow_order2 arFlow_order3
arFlow_order 0.960
arFlow_order2 0.430 0.680
arFlow_order3 0.500 0.500 0.611
arFlow_order4 0.300 0.300 0.300 0.300
arFlow_order5 0.100 0.100 0.100 0.100 0.100
arFlow_order6 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order7 0.000 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order8 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order9 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000
arFlow_order10 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000 0.000


```

```

--- ANOVA Table for Fixed Effects (Type III Sum of Squares) ---
= anova(flm, model)

Type III Analysis of Variance Table with lmerAnova() method
              Sum Sq Mean Sq NumDF DenDF  F value    Pr(>F)
arFlow_rate   380.850 380.850    1  27.299 84.7000 3.97e-06 ***
arFlow_order   22.312  22.312    2  20.827  4.4075  0.0129 *
arFlow_rate:arFlow_order  24.400   7.467    2  20.825  4.4075  0.0129 *
---
Signif. codes:  0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1.


```