Mémoire

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Assessment of the effect of passive green walls on volatile organic compounds in an office sized chamber

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Abbreviations

[C]	Concentration
°C	Degrees Celsius
°K	Degrees Kelvin
µg	Micrograms
µL	Microliters
B.E.M.S.	Building Energy Monitoring and Simulation
E.E.D.	*Eau-Environnement-Développement*
G4IW	Green4Indoor Wallonia
GW	Green walls
H	Hour
IAQ	Indoor air quality
Kow	Octanol-water partition coefficient
L	Liters
m^2	Square meters
m^3	Cubic meters
min	Minutes
mL	Milliliters
MVOC	Microbial volatile organic compound
ng	Nanograms
ppb	Parts per billion
ppm	Parts per million
S.A.M.	Sensing of Atmospheres and Monitoring
SBS	Sick building syndrome
T°	Temperature
TVOC	Total volatile organic compounds
VOC	Volatile organic compound

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Introduction

Indoor air quality is a subject of increasing concern. Indeed, indoor air quality can be worse than outdoors (Rehwagen et al., 2003) due to high concentrations of volatile organic compounds and particulate matter for example. Given the amount of time we spend indoors, it is of utmost importance to maintain an acceptable degree of air quality in homes, schools and workplaces.

Natural ventilation and HVAC systems are the main strategies for regulating indoor air quality. Unfortunately, these methods have some shortcomings (Guieysse et al., 2008). Because of this, alternative methods of air quality control are a topic of interest as there is research highlighting the phytoremediation potential of plants. Phytoremediation has been investigated in various forms such as potted plants and green walls. Plants also have secondary benefits such as increased biophilic satisfaction. They could also be a response to the energetic needs associated with the modulation of air temperature as well as to the limits of traditional ventilation systems (Guieysse et al., 2008; Pettit et al., 2019).

In this context, we find the "Green4Indoor Wallonia" project. This project funded by UR SPHERES and conducted in collaboration with Sound Ecology[1] and Cita Verdi[2] has for objective the study of green wall systems according to various criteria such as general air quality in terms of VOCs, particulate matter and molds as well as thermal comfort and energetic needs/ insulative properties associated with the use of such technology.

This project entails the collaboration of multiple teams, namely the S.A.M., B.E.M.S and E.E.D. teams, of the Arlon campus dedicated to environmental sciences of the University of Liège.

For each team, students participated in this project as part of their Master's thesis or Bachelor training. The present Master's thesis concerns the analysis of VOCs by means of adsorbent cartridges (TENAX®TA and Radiello®) under supervision of the S.A.M. team. Another student among the S.A.M. team, Tetekpor Komi Dayane, assessed molds, formaldehyde and particulate matter. In the B.E.M.S. team, Simonis Nathalie undertook the analysis of thermal comfort and energy needs associated with the green walls. Among the E.E.D. team, Delperdange Alexandra assisted in the technical aspect of formaldehyde analysis as well as on the irrigation needs of the green wall system. Because of this, repetitions are bound to occur between our works.

The specific objective of this master's thesis is to evaluate the influence of green walls on indoor air in terms of VOCs inside a realistically sized experimental chamber by means of Tenax®TA and Radiello® sampling methods. Furthermore, the limits and constraints of the methodology used will be explored as well in order to suggest improvements for future experiments in the context of the G4IW project.

[1] "Biodiversity Management Luxembourg| Sound Ecology Sàrl |," n.d. https://www.sound-ecology.com/
[2] "Cita Verdi | *Murs et toits végétalisés, jardins et mobilier urbain*," n.d. https://www.citaverdi.com/

PART 1

1. Volatile organic compounds

1.1. VOCs & indoor air quality

As presented in the introduction, the indoor air contaminants of interest for this thesis are volatile organic compounds (VOCs). Unfortunately, there is no unanimous definition of VOC (Guieysse et al., 2008). The *Council Directive 1999/13/EC of 11 March 1999 on the limitation of emissions of volatile organic compounds due to the use of organic solvents in certain activities and installations*, for example, poses that the term volatile organic compound designates every organic compound characterized by a vapor pressure of at least 0.01 kPa at 293.15°K or with a corresponding volatility in particular conditions of use.

VOCs are important indoor pollutants. Indeed, many VOCs have been found in indoor air, many of which can be detrimental to our health (Jones, 1999). Furthermore, their indoor concentration is generally higher than outdoors and is also higher in winter than in summer (Rehwagen et al., 2003). Individually, indoor VOC concentrations are generally low in the µg/m3 range, however a great number of different VOCs can be found which amounts to greater TVOC levels as described by Guieysse et al. (2008).

Table 1. VOCs of interest, their potential sources and health effects (Ruiz-Jimenez et al., 2022)

Compound	**Source**	**Health effect**
Formaldehyde	Wood panels, adhesives, resins, fiberboards, particle boards, plywood	Irritation, cancer, asthma
BTEX	Wood materials, particle boards, paint, laminate, furniture	Anemia, cancer, immunological effects, irritation, nervous system effects, respiratory system, liver and kidney damage
Phthalates	Paints, plastics, vinyl flooring, wall coverings	Male reproductivity issues, male hormonal issues, issues in neurological development
Terpenes	Wood based materials	Irritation
Chlorinated compounds	PVC polymers	Irritation, toxicity, possibly carcinogenic

Many families of compounds are present in the indoor environment. The most prominent are terpenes, then aromatics and alkanes. This is in contrast with outdoor environments where aromatics are the most prominent (Rehwagen et al., 2003). These compounds can be emitted by various sources such as furniture and building materials and can have various detrimental health effects, as shown in table 1 (Ruiz-Jimenez et al., 2022). Table 2 also shows VOCs found in office buildings in USA by means of Tenax®TA sampling by Subramanian et al. (2000). It is also important to note that VOC emissions from building materials can increase due to higher temperatures and humidity levels (Huang et al., 2016; Zhou et al., 2019).

Table 2. Compounds found in office buildings in USA by Tenax®TA sampling (Subramanian et al., 2000)

Compounds					
Ethyl acetate	Heptane	Toluene	Naphthalene	Cl3-ethene	Cl3C-CH3
Butyl acetate	Octane	Et-benzene	CH2C12	Cl4-ethene	Hexane
Limonene	Decane	Styrene	CHCl3	1,4-dichlorobenzene	2-Butanone
Pinene	Dodecane	o,m,p-xylenes	CCl4	HCHO	MIBK
		1,2,4-trimethylbenzene	Benzene		

While the building itself is responsible for a large portion of indoor VOC emissions (Missia et al., 2010), other sources can be found. Indeed, we can find biogenic sources of VOCs leading to microbial volatile organic compounds ("MVOCs") for example, which are emitted by fungi and bacteria (Korpi et al., 2009). The variety of MVOCs can be quite large as shown by Fiedler et al. (2001). In their study, they found over 150 volatile compounds of different families such as alcohols, aldehydes, ketones, saturated and unsaturated hydrocarbons, aromatic hydrocarbons, ethers, esters, terpenes, as well as nitrogen and sulfur containing compounds. A relationship between higher levels of MVOCs and respiratory problems and irritation of the eyes has been found (Elke et al., 1999). Problematic buildings have shown maximum levels of individual MVOCs ranging from 0.1 to 10µg/m3 but much higher levels have also been reported (Korpi et al., 2009).

On another note, humans themselves are sources of VOCs as well. We can emit through our breath and ozonolysis of the lipids on our skin for example (Liu et al., 2016). We can also contribute to poor indoor air quality through our activities such as cooking and cleaning (Tran et al., 2020).

Secondary air pollutants as well are problematic for indoor air quality. Many terpenes such as α-pinene or d-limonene for example can react with ozone to form secondary pollutants as described by Nazaroff and Weschler (2004).

The presence of VOCs in indoor air is of concern as chronic exposure is associated with negative health effects as reported by Rumchev et al. (2004). These authors found an association between asthma diagnosis in children and indoor VOC concentrations of particular compounds such as benzene, ethylbenzene and toluene. They also add that an analysis based solely on total VOCs may undermine the risks associated with specific compounds. The effects of poor air quality on children have also been described in the research compiled by Buka et al. (2006), showing that many adverse effects can be attributed to poor IAQ such as increased mortality, adverse pregnancy outcomes, altered immunity and adverse respiratory health outcomes among others. Additionally, an association between chronic exposure even at relatively lower concentrations of VOCs and negative health effects has been found (Khanchi et al., 2015 in Pettit et al., 2019). These findings illustrate the importance of the development of air cleaning tactics/technologies.

Another health condition potentially related to indoor VOCs is sick building syndrome ("SBS"). SBS is a term used to describe non-specific symptoms such as headaches, respiratory tract issues, and fatigue among others. Reports of SBS have become more and more common as more airtight and energy efficient buildings dependent on HVAC systems have come to replace older buildings with natural ventilation (Redlich et al., 1997).

Norback et al. (1990) have shown a significant relation between volatile organic compounds (specifically n-alkanes, butanol, terpenes and aromatics) and chronic symptoms. In their study of SBS symptoms among hospital workers, Chang et al. (2015) have described positive relationships between VOC concentrations and various symptoms typical of SBS.

Furthermore, Suzuki et al. (2021) conducted a particularly compelling study meant to determine if two practically identical buildings with different VOC concentrations would lead to building related symptoms. They found that the probability of developing symptoms in the building with low VOC concentrations was significantly lower. Interestingly, Suzuki et al. (2021b) have also shown that psychological factors are associated with SBS. Given the "biophilia effect" (Gaekwad et al., 2022; Grinde and Patil, 2009), the use of phytoremediation technologies could theoretically help ease symptoms of poor indoor air quality on a psychological level as well.

Based on the research presented, VOC concentrations do seem to be of interest in the determination of interior air quality despite the difficulty in assessing what exactly causes sick building syndrome.

1.2. VOC emissions from plants

Given the negative effects associated with poor indoor air quality, phytoremediation appears to be a particularly interesting solution. However, it is important to note that plants themselves can be sources of VOCs (Lerdau and Keller, 1997).

Plant volatiles can be described as low molecular weight compounds that can be classified into 3 main groups, namely terpenoids, phenylpropanoids/benzenoids and fatty acid derivatives (Dudareva et al., 2006). A non-exhaustive list of VOCs, mainly terpenes, potentially emitted by plants can be found in table 3 based on the study of 40 Mediterranean plant species by Owen et al. (2001).

Table 3. Compounds emitted by 40 Mediterranean plant species (based on Owen et al., 2001)

a-Pinene	Limonene	a-Thujene
Camphene	Cineole	a-Fenchene
Sabinene	gamma-Terpinene	Cymene
b-pinene	Linalool	Ocimene
Myrcene	a-Terpineol	Linalool oxide
a-Phellandrene	Isoprene	Thymol
3-Carene	Tricyclene	Camphor

Plants typically emit VOCs in response to various stresses as evidenced in the literature review conducted by Holopainen and Gershenzon (2010). These authors have highlighted how VOC emission by plants can relieve the stress that induced it. Stress can come in various forms such as abiotic (light intensity, water stress, oxidative stress) or biotic (herbivory, oviposition,…) (Holopainen and Gershenzon, 2010). Herbivory for example has been shown to trigger the emission of terpenes and green leaf volatiles (Dudareva et al., 2006). The emission of terpenes could be problematic for IAQ given the possibility of secondary pollutant formation from reactions with ozone as previously presented (Nazaroff and Weschler, 2004).

Another factor affecting the emissions of plants is the neighboring community. Kigathi et al. (2019) have shown that an increased plant richness in the community changed the emissions from the studied plants under effect of herbivory. This illustrates the complex effect that plant to plant interactions can have on emissions.

It is clear that plants can be sources of VOCs. It is therefore important to contrast phytoremediation capabilities with plant emissions in order to accurately determine the effect

that they can have on interior air quality. Furthermore, it is also necessary to limit stress to the plants in order to lower VOC emissions, especially in the context of phytoremediation studies.

2. General air cleaning methods

One of the simplest ways to remediate indoor air quality is to allow natural ventilation by opening windows for example. However, this is less often done in winter months because of the colder temperatures and the need to conserve heat inside the home. This could result in higher VOC concentrations indoors during that period. In fact, higher levels of VOCs have been reported during winter compared to summer (Rehwagen et al., 2003). Furthermore, the periodic ventilation obtained through natural ventilation may simply be insufficient to offset continuous indoor emissions (Guieysse et al., 2008).

Air remediation can also be done through Heating, Ventilation, and Air Conditioning systems (HVAC). The objective of these systems is to provide conditioned air for the purposes of maintaining good air quality and comfort (Sugarman, 2020). These are more commonly found in newer buildings designed to be energy efficient by making them more airtight for example. Because of this, these buildings tend to rely on forced mechanical ventilation (Redlich et al., 1997).

HVAC systems are generally programmed in such a way as to remediate poor indoor air quality based on carbon dioxide emissions from the inhabitants (Sugarman, 2020). This however overlooks indoor air quality based on VOCs. While it has been shown that HVAC systems can be effective in reducing formaldehyde and TVOC concentrations in the context of office buildings (Li et al., 2002), these same systems can also be sources of VOCs. Indeed, the filters, ducts, humidifiers and heat exchangers could be pollution sources (Bluyssen et al., 2003). Furthermore, smells emanating from filters that could be indicative of microbial growth have been reported (Pasanen et al., 1991 in Schleibinger and Rüden, 1999). It is therefore not only important to consider all pollution types present indoors when deciding on ventilation rate, but also to ensure proper maintenance of HVAC systems (Bluyssen et al., 2003).

Technologies for maintaining indoor air quality other than forced mechanical ventilation exist as well. These would be particularly useful in specific situations where outdoor air is even more polluted than indoor air (Mata et al., 2022). In their literature review of cleaning technologies for indoor air, Mata et al. (2022) outlined the following technologies :

- Ultraviolet light
- UV-Photocatalytic Oxidation
- Air ionization
- Phytoremediation

While many alternative methods for treatment of indoor air exist, they can be costly in terms of operation and can also produce secondary waste (Sriprapat et al., 2014). In this context, phytoremediation is particularly interesting as it can be cost effective and environmentally friendly (Mudliar et al., 2010). It has been proposed that phytoremediation, specifically active botanical filters, have potential for use in conjunction with HVAC systems (Matheson et al., 2023).

3. Phytoremediation

3.1. Plant physiology and interactions with the environment

There are multiple aspects to consider when evaluating the capacity of plants to remove VOCs in the air. Indeed, plants are complex in their physiology as well as in their interactions with the environment. Based on this, it is possible to assess phytoremediation capabilities according to the aerial parts of plants as well as the rhizosphere and growing media (Matheson et al., 2023).

Among the aerial parts of plants, we find stomata. Stomata are pores whose major function is to allow entrance of CO2 for the purposes of photosynthesis. They also serve as an exit for water for the process of transpiration (Willmer and Fricker, 1996). The aperture of these pores varies according to factors such as time of day. Many species of plants open their stomata during daytime conditions and close them during nighttime conditions (Sriprapat and Thiravetyan, 2013). This is however not the case for all plant species as demonstrated in Crassulacean Acid Metabolism plants (CAM). These plants present a particular metabolism adapted to arid environments and as such show closed stomata during the day and open stomata during nighttime (Ting, 1985).

Another part of the physiology of aerial parts of plants is the cuticle. The cuticle is a waxy membrane covering the aerial parts of the plant. Its functions are protection against the environment and regulation of gas exchange/ water loss among others. It can also contribute to a favorable microenvironment for fungi and bacteria (Domínguez et al., 2011).

We also find complex bacterial communities on the above ground parts of plants. This microbiome is referred to as the phyllosphere. The microbiota in the phyllosphere can be inoculated by the soil as well as the air (Sohrabi et al., 2023).

The underground parts of plants are in constant interaction with the soil. The complex environment influenced by plant roots is referred to as the rhizosphere. The rhizosphere is characterized by higher microbial densities than in the adjacent soil because of excreted photosynthates from plant roots. These microbes can affect the plant in beneficial or detrimental ways, but the nature of their relationship can simply be neutral as well. The interaction between the plant and the rhizosphere is such that the rhizosphere can be likened to the human gut in terms of the functions of the microbial communities found (Berendsen et al., 2012).

3.2. Remediation capabilities of plants

The purification capacity of plants has been shown in multiple studies. Sriprapat and Thiravetyan (2013) for example demonstrated that *Z.zamiifolia* had the capacity to uptake benzene, toluene, ethylbenzene and xylene through stomata as well as through the cuticle. The stomata however were the privileged means of uptake. The effect of stomata was also assessed according to light conditions given that light influences stomatal conductance. They showed that among well-watered plants, BTEX uptake was higher during day time conditions which is in accordance with stomatal conductance rhythms. Interestingly, water stressed plants showed better performance during dark conditions when compared to well-watered plants.

Sriprapat et al. (2014) assessed the capacity of different plant species to uptake toluene and ethylbenzene. They verified the number of stomata and compared it with pollutant removal rates but found no particular correlation between these 2 factors.

In that same study, the authors assessed the capacity of the cuticle to uptake the same pollutants. In order to do so, they considered the total mass of cuticle per surface area as well as the nature of the wax. They concluded that the relationship between cuticle mass and pollutant removal was unclear but found that plants whose wax was higher in hexadecenoic acid had greater absorption of pollutants. Another factor they explored was the octanol-water partitioning coefficient (Kow) of toluene (2.69) and ethylbenzene (3.15). Based on this, they proposed that ethylbenzene may be more readily adsorbed onto the waxy cuticle.

The importance of physico-chemical properties of compounds has also been brought forth by the results of Irga et al. (2019) who found that plant species more fit for ethyl acetate phytoremediation, a more hydrophilic species, were less so for benzene and vice versa.

In the same vein of looking at composition of wax, Treesubsuntorn et al., 2021 assessed phytoremediation capability in different species according to whether their wax was chloroform soluble, ethanol soluble or hexane soluble. In their study, they found that species with ethanol soluble wax had higher particulate matter and VOC remediation efficiencies.

The ability of phyllosphere communities to degrade VOCs has been shown by Sandhu et al. (2007). In their study, plants inoculated with phenol degraders showed significantly higher phenol mineralization in comparison with non-degrading mutants. These microbial communities are therefore of interest given their ability to metabolize VOCs (Junker and Tholl, 2013). They can however also emit biogenic VOCs according to internal and external factors (Peñuelas and Staudt, 2010).

It is clear that the ability of aerial parts to uptake and/or metabolize VOCs is complex and dependent on many factors. These factors can be intrinsic to the plant (cuticle composition, stomatal conductance, phyllosphere composition, etc.…) but also external (light, water stress, physico-chemical properties of compounds, etc.…).

The underground parts are also capable of remediating air quality. The ability of the underground parts to remove benzene for example has been demonstrated as early as 1989 by Wolverton et al. (1989). These authors demonstrated this capacity by removing foliage and

showed that the pot and soil alone were capable of removing pollutants from the air. The importance of soil microbes has been demonstrated by Yang and Zhao (2019). In their experiment, they added cultured microorganisms to the rhizosphere of different plant species and observed better removal rates of formaldehyde.

While the microbial activity is seen as the main mechanism for air purification in terms of VOCs (Teiri et al., 2022), it can be interesting to consider the plant as a complex system with interdependent parts given the interaction between aboveground and underground parts. This interaction has been briefly described in a literature review by Matheson et al. (2023). These authors refer to a study by Aydogan and Montoya (2011) who found independent formaldehyde removal from both the aerial and underground parts but with better results for the root zone. They then refer to Hörmann et al. (2017) who found similar rates but while covering the substrate. The authors then link these findings to the observations of Su and Liang (2015, 2013), who determined that foliage delivers VOCs to the rhizosphere, as a potential explanation behind the similar removal rates. Furthermore, the plant itself can have an inoculation effect on the microbial community of the soil as demonstrated by Mikkonen et al. (2018). These observations illustrate the complexity behind the phytoremediation potential of plant-substrate systems.

4. Advantages of green wall technologies

Many experiments aiming to assess the ability of potted plants to purify air have been conducted (Fooladi et al., 2019; Mosaddegh et al., 2014; Parseh et al., 2018; Song et al., 2011; Sriprapat et al., 2014; Sriprapat and Thiravetyan, 2013). These studies are usually carried out in sealed glass chambers with single injections of particular compounds at the start of the experiment and pollutant concentrations are assessed after certain time periods.

While these studies have shown that plants do have the capacity to clean the air, they serve mainly as proof of concept given that the results are not easily applicable to in situ situations. Indeed, the plants usually represent an unrealistic volume inside the chamber. Furthermore, a single injection at the start of an experiment is not representative of in situ emissions which are continuous in nature. Also, the concentrations used tend to be in the ppm range which is very high in comparison to what is usually found indoors (ppb). Finally, the reductions potentially attained by the air exchange rate of a building itself should also be taken into account for the sake of comparison. These limits have been brought forth in a compelling publication by Cummings and Waring (2020) titled “Potted plants do not improve indoor air quality: a review and analysis of reported VOC removal efficiencies”. In their publication, the authors demonstrated the ineffectiveness of potted plants by calculating the unrealistically high plant densities necessary for their remediation effect to be comparable to typical air exchange rates found in buildings. Based on this, Cummings and Waring (2020) suggested to focus on other aspects of phytoremediation such as the mechanisms themselves as well as alternative biofiltration technologies among others.

A potential answer to the limits of potted plants would be vertical planted systems. These systems would allow a higher density of plants relative to the volume of the room with minimal floorspace requirements. In this respect, we find both passive and active green walls (Bandehali et al., 2021).

Indoor passive green wall systems can be made of modular panels attached to the wall. These panels are filled with growing medium as substrate for the plants (Modirrousta and Mohammadi, 2015). While these systems address a major shortcoming of potted plants by allowing a higher plant density, pollutant removal is still limited by the diffusion rate of pollutants into the soil/plant just like potted plants (Baduru et al., 2008; Matheson et al., 2023).

Active green wall systems on the other hand are not limited by pollutant diffusion into the substrate/plant tissues because they make use of active airflows. Because of this active airflow, the rate at which pollutants can be treated by the system is increased (Pettit et al., 2019). This can make the system more effective in comparison to passive walls and potted plants as demonstrated by Pettit et al. (2019). In their study, they showed not only that the active green wall system significantly outperformed the passive system and the potted plants in terms of VOC removal, but it also provided better air quality than the HVAC system it was compared to.

5. Description of sampling and analysis techniques

5.1. Thermal desorption associated with gas chromatography and mass spectrometry

Thermal desorption

Thermal desorption is a technique by which a sample is transferred to a gas chromatography unit. For the usage of this technique, samples have to be adsorbed on adsorbent cartridges. Adsorbent cartridges are filled with a material capable of trapping volatile organic compounds such as a polymer in the case of TENAX TA® cartridges or graphite carbon for Radiello® passive sampling tubes.

Different adsorbents have different properties and allow for an adequate or inadequate adsorption of specific compounds based on these properties. It is therefore important to choose an appropriate adsorbent material based on the particular substances we wish to sample. The breakthrough volume is a useful metric when choosing an adsorbent. This volume represents the volume of a vector gas that elutes an analyte through 1 gram of adsorbent at a given temperature. A high breakthrough volume implies that the substance is strongly trapped. Based on this characteristic, we can determine the temperature range at which adsorption is possible as well as the adequate temperature to reach inside the thermal desorption system (figure 1) in order to desorb the analytes from the sampling media. It is also important to desorb the samples in the opposite direction of the sampling flow.

After desorption of the sample, it can also be “focused” thanks to a “cold trap”. This trap cools the sample which focuses it in a smaller volume. It is subsequently heated again and transported to the gas chromatography equipment. This allows for the passage of a narrower band inside the column which increases its performance.

Figure 1. td-100xr thermal desorption unit of Markes International, the type of unit used for the experiments (“Thermal Desorption With TD100-xr | Markes International,” n.d.)

Thermal desorption is a useful technique that limits the amount of procedures needed to analyze samples. It also bypasses the need for liquid solvents and allows for the reuse of sorbent cartridges, making it a powerful technique in the context of sample analysis.

Gas chromatography

After thermal desorption, the sample is transported by a vector gas to the gas chromatography equipment. Gas chromatography is a technique that allows the separation of the specific compounds comprising a sample.

Gas chromatography makes use of capillary columns. These columns can be of different types according to the nature of their inner surface coating which is referred to as the "stationary phase". Based on the affinity that the specific compounds comprising a sample have for this stationary phase, they will be more or less retained by it. Because of this, different compounds will exit the capillary phase at different times which effectively separates them from each other. These times are referred to as "retention times".

The capillary column is held inside an oven which can be heated according to a specific program. This allows for a control of the temperature of the column as the sample is carried through which can alter the retention time of the compounds comprising a sample. Thanks to this, different temperature ramps can be programmed for a better separation of molecules.

The compounds are transported to detection equipment once they exit the capillary column. In the case of TD-GCMS, the mass spectrometry equipment serves as a detector. The result of gas chromatography analysis is a graph known as a chromatogram. This graph represents the abundance as a function of retention time and can effectively be used to determine the mass of an analyte by means of the area of its peak provided a calibration curve has been made.

Mass spectrometry

In TD-GCMS, the capillary column of the GC equipment leads to an ionization chamber after separation of the analyte and the vector gas. Ionization creates ions through electronic impact (among other techniques) with the analyte. Those ions are fragments of the analyte that can then be "selected" according to their mass and charge. The different fragments resulting from the impact "carry" information of the structure of the initial molecule.

After impact, the fragments move towards an analyzer. This analyzer can be a quadrupole analyzer among others. The quadrupole analyzer functions by paired potentials between the poles, communicating an oscillatory movement to the ions. This allows for ions presenting specific mass/charge ratios to attain the detector whereas others do not reach. Different mass/charge ratios are analyzed in sequential order through the control of the potentials of the poles.

The detector is an electron multiplier. It comprises an ion collecting cathode to which a high potential is communicated. The collision between an ion and the cathode results in the ejection of electrons constituting the cathode. These electrons are then focused by the use of dynodes which results in the ejection of secondary electrons. This electron multiplication leads to a higher signal.

Mass spectrometry allows for the creation of a spectrogram that represents abundance as a function of the mass/charge ratio. This spectrogram can be interpreted as a sort of signature

of a given molecule which can then be identified by comparison with an existing database for example.

Associating gas chromatography and mass spectrometry is a powerful means of quantifying and qualifying molecules thanks to the resulting chromatogram and spectrograms. Because a spectrogram is available for each unit of time on the chromatogram, it is possible to determine which molecule a specific chromatogram peak can be attributed to.

5.2. Tenax®TA adsorbent cartridges

Tenax®TA adsorbent is used for active sampling of VOCs. Tenax®TA is a porous polymer resin with the capability to adsorb VOCs. Its low affinity for water is a major advantage for the purposes of this thesis because the green walls have to be watered, which could lead to higher levels of humidity.

The adsorbent is housed inside tubes specifically designed for thermal desorption. These tubes have an identifier and a sampling direction is specified on them. This specification is to ensure that sampling and thermal desorption are done in opposite directions.

As specified before, the breakthrough volume is an important metric to take into account for sampling. Generally, if the breakthrough volume is higher than 10L then trapping of VOCs at the corresponding temperature is adequate. The molecules for which the known breakthrough volume is not adequate at 20°C are shown in table 4.

Table 4. Molecules for which Tenax® TA is inadequate at 20°C ("Tenax® TA Breakthrough Volume Data," n.d.)

Family	Compound		
Alcohols & Glycols	Methanol 2-methyl-2-propanol	Ethanol 2-methyl-2-butanol	2-propanol
Alkenes	1-Butene	1-Pentene	2-Pentene
Acetates & Acids	Acetic Acid		Methyl Acetate
Aldehydes & Ketones	Acetaldehyde	Propanal	Acetone
Halogens	Chlorodifluoromethane Dichlorofluoromethane Monochloromethane	Vinylchloride Trichlorofluoromethane Monochloroethane	1,1-Dichloroethylene Methylenechloride 1,2-Dichloroethylene
Amines	Tert-Butylamine	Methylamine	Ethylamine
Aromatics & terpenes		/	

These adsorbent tubes need to be used in conjunction with a pump, making this an active sampling technique. It is important to measure the total volume sampled which, in conjunction with the mass of analyte determined by TD-GCMS analysis, is used to calculate the concentration of said analyte in the sample volume.

A potential problem when using Tenax®TA cartridges is the adsorption of O_3 and NO_2 onto the cartridge. This has multiple consequences during the desorption process (Helmig, 1997; Klenø et al., 2002):

- Reaction with the adsorbent polymer leading to artefacts of benzaldehyde, phenol and acetophenone among others
- Degradation of terpenes which leads to underestimation of actual concentrations

Unfortunately, possibility of adsorbent and terpene degradation was not considered during the experiments described in this thesis.

5.3. Radiello® adsorbent tubes[3]

Passive sampling of VOCs was carried out with Radiello® adsorbent tubes (figure 2). These adsorbent tubes made of a stainless steel mesh surrounding the adsorbent material (carbograph) are used in conjunction with a diffusive body. This combination allows for components to adsorb onto the tubes according to their diffusion coefficient as well as the concentration differential between the inside and outside of the barrier. The radial configuration of Radiello® samplers allows for a high surface area which in turn increases the total adsorbable mass of analytes in a given time thanks to the increased trapping flow.

Figure 2. Radiello® sampling material ("Radiello passive samplers. | Markes International," n.d.)

It is necessary to know the total exposure time as well as the average temperature during sampling in order to properly assess the concentration of a given analyte by means of these adsorbent tubes. While the influence of pressure is usually minimal, temperature has an important influence on the diffusion coefficient.

The average concentration of a given analyte during the sampling period is calculated according to the following formula :

$$Concentration\left[\frac{\mu g}{m3}\right] = \frac{mass\ [\mu g]}{Qk\left[\frac{ml}{min}\right] * time[min]} * 1{,}000{,}000$$

Qk represents the trapping flow at temperature K for a given analyte. This flow can be calculated by using the known flows at 298°K and the average T° according to the following formula:

$$Qk = Q298\left(\frac{K}{298}\right)^{1,5}$$

[3] ("Diffusive sampler for monitoring pollution. How it works.," n.d.)

PART 2

1. Description of the experimental chamber

The experiments presented in this thesis were conducted inside a temperature controlled chamber. This chamber was surrounded by an external zone referred to as the buffer zone (figure 3).

The chamber zone is 3.68m long, 2.63m wide and 4.82m in height for a total volume of 46.65m^3. The walls are covered with aluminum in order to limit adsorption and diffusion interactions with VOCs. That being said, there is an open ventilation vent connecting the chamber to the buffer zone and the walls in the buffer are not covered. Because of this, adsorption and diffusion dynamics can still occur.

The buffer zone surrounding the chamber is 6.72m long, 6.22m wide and 4m in height. The walls are made of oriented strand boards.

The chamber and buffer are in a closed circuit, meaning that there are no air exchanges with the external environment unless specifically programmed. The only air exchange is between the buffer and chamber themselves.

The purpose of the buffer zone is to simulate a particular climatic sequence (winter or summer) for the experiments of the B.E.M.S. team. That being said, these climatic sequences have an important impact on the measurements for the S.A.M. team, particularly because of the connection between the two rooms. The climatic sequences are simulated through a variable temperature programming in the buffer. They also require a two to three day period of stabilization before the tests can be started.

The winter sequence is meant to simulate winter conditions with a need for heating inside the chamber. The chamber temperature is kept at approximately 21°C while the buffer zone fluctuates between 2 and 3°C. For the summer sequence, the chamber temperature is kept at 25 to 26°C whilst the buffer zone fluctuates between 32 and 35°C. Two subtypes of summer sequence were tested : with climatization and without climatization.

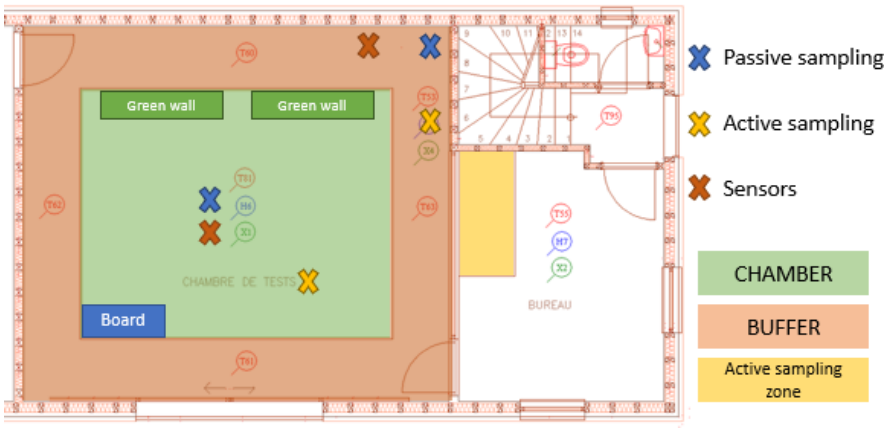

Figure 3. Schematic of the working area with approximate sampling positions – the dimensions of the walls and board on this schematic do not reflect their actual size

Green walls

Two green walls were installed inside the chamber for the last portion of the experimental campaign. These green walls were freely provided by *Sound Ecology* and *Cita Verdi*. Each wall is 140cm by 210cm and the substrate used is sphagnum moss. This substrate is held by galvanized steel baskets attached to the wall (figure 4). A tarp is put on the wall behind the green walls to protect it from moisture. The following species were planted on the wall :

1. *Aglaonema commutatum 'silver bay'*
2. *Epipremnum aureum*
3. *Nephrolepis exaltata 'Bostoniensis'*
4. *Dracaena fragrans*
5. *Chamaedorea elegans*
6. *Spathiphyllum wallisii 'sensation'*
7. *Chlorophytum comosum 'Ocean'*
8. *Hedera helix 'Pittsburgh'*
9. *Begonia rex 'Alaska creek'*
10. *Tradescantia zebrina*

Since there is no active airflow generated by these green walls, they are considered to be passive. That being said, the ventilation vent leading to the buffer is located between the 2 walls.

Figure 4. Picture of both green walls – the lamps are highlighted in red

The walls are lit up by two 50W FloraLED UV lamps, lent for the research efforts by the company itself[4], for 10 hours a day.

The walls are watered by percolation once to twice a week with 30L of water for each wall. This watering is assured by means of pumps and solenoid valves used to control the process. The excess water is collected in bins and removed. Eventually, this method was changed because of overwatering. The new system was based on a floater that would ensure watering until 300mL of excess water (run-off) had percolated into a collecting bottle, which would be detected by the floater system, at which point the watering would automatically be shut off.

[4] "FloraLED - *Leader FR LED horticole - Eclairage horticole LEDs de culture*" n.d. https://www.floraled.fr/

2. General methodology

The purpose of the experimental campaign in the context of this master's thesis was to evaluate the effect of green walls on indoor air VOCs. For this purpose, 3 different cases were considered :

1. Empty chamber (No VOC source and no green wall)
2. Chamber with an additional VOC source but no green walls
3. Chamber with an additional VOC source and two passive green walls

For each of these cases, multiple tests were scheduled. These tests followed the same general methodology as each other but a specific climate simulation was programmed in the buffer zone for each, whereas the test chamber was maintained at a specific temperature range. The many tests comprising the analysis campaigns spanned 7 days each and are referred to as climatic sequences in figure 5.

Initially, three sequences with the three different climate simulations were planned for each part but some of these tests had to be dropped due to planning constraints (shown in red in figure 5). Additionally, a "flush", which is a period of ventilation with outdoor air meant to renew the air inside the chamber and buffer so as to evacuate the VOCs before the start of a test, was programmed. This flush was maintained until the total VOC reading, according to a metal oxide based eNose from "Comon-invent", became stable, after which the stabilization period could be started. Unfortunately, the readings of the eNose are not available for download but only for online view in real time and therefore cannot be shown in this document.

It is important to note that the flush wasn't conducted for the empty chamber tests which is an oversight in the methodological approach.

VOC source	Green wall	CLIMATIC SEQUENCE	FLUSH	Sampling days
NO	NO	WINTER	X	1/7
		SUMMER		
		SUMMER WITHOUT CLIMATISATION		
YES	NO	X WINTER X	V	3/7
		X SUMMER X		
		SUMMER WITHOUT CLIMATISATION		
YES	YES	WINTER	V	3/7
		SUMMER		
		SUMMER WITHOUT CLIMATISATION		

Figure 5. Schematic overview of the experimental campaign as it pertains to VOC sampling

During a given test week, 3 sampling days are scheduled. The general procedure for a given test of a specific climatic sequence, except for empty chamber tests, is as follows[5] :

Day 1

Firstly, a gypsum board is painted and introduced into the chamber to serve as a VOC source. Immediately after, a passive sampling cartridge is set up inside the chamber and 2 mold samples are taken. After leaving the chamber, another passive VOC sampling tube is set up inside the buffer and 2 more mold samples are taken.

About an hour and a half later, two VOC samples are taken from the chamber and two from the buffer. Once these are done, a single aldehyde sample is taken from the chamber as well as from the buffer. The sampling data is collected on a document for review (sample type, sampled zone, volume sampled, sampling day and time,…).

Day 4

- Mold sampling in the same manner as day one
- Active VOC sampling in the same manner as day 1
- Active aldehyde sampling in the same manner as day 1

Day 7

- Mold sampling in the same manner as day one
- Active VOC sampling in the same manner as day 1
- Active aldehyde sampling in the same manner as day 1

Day 8

- Recovery of the passive VOC sampling tubes
- Removal of the painted gypsum board

This general test scheduling was followed for tests with the green walls plus a VOC source as well as the tests with a VOC source only. This scheduling wasn't followed for the tests with an empty chamber however as the concentration of VOCs in those tests was assumed to be at equilibrium throughout the 7 day span, therefore only a single sampling day was considered (see figure 5). An error in the methodology was to not proceed in the same manner for the empty chamber tests as for the others. Ideally, a flush should've been programmed as well as three sampling days instead of the single one for the empty chamber tests in order to offer a true comparison between the different cases and limit potential confounding factors.

General precautions

In order to avoid contamination of the chamber, specific precautions were taken. The people in charge of sampling had to wear gloves, an ffp3 face mask, a lab coat and shoe covers upon entrance. Furthermore, they were also instructed to avoid using particularly odorant products (shower gel, shampoo, perfume, etc.) on sampling days.

The data regarding the sampling and entrances into the chamber was systematically collected and shared with the teams working on the project.

[5] The specifics will be elaborated on in the later parts of this document

3. Gypsum board painting

In order to introduce additional VOCs into the chamber, a painted gypsum board was used. The painting procedure was as follows :

1. The paint container is agitated, then turned upside down and back 15 times, and finally agitated once more
2. 100mL of paint (based on the covering capacity as displayed on the paint bottle) are poured in a cut plastic bottle (100 mL are marked on the bottle beforehand)
3. The paint is thinly poured across a 60cm by 130cm gypsum board and then spread as evenly as possible with a wide paintbrush except for two 15cm by 10cm areas blocked out to grab onto the board
4. The leftover paint in the plastic bottle is used in the end to fill in the less painted areas as best as possible

Initially, a solvent based paint described to contain a maximum of 300g/L of VOCs was used. Unfortunately, the results from that test had to be discarded because such a concentrated paint source led to unexploitable chromatograms. The test was therefore repeated with a water based paint described to contain a maximum of 1g/L of VOCs.

The 1g/L paint used was a wall and ceiling mat white paint made by Sencys (figure 6). No information regarding the specific composition of the paint is given besides for 1,2-benzisothiazole-3(2H)-one and 2-methyl-2H-isothiazole-3-one.

Figure 6. Peinture mur & plafond Sencys extra couvrant mat blanc 1L

4. VOC sampling and sample treatment methodology

4.1. Material, equipment and software used

The material, equipment and software used were the following :

- RAD145 Radiello® tubes
- Markes and CAMSCO Tenax®TA cartridges
- Sampling pumps : GilAir plus from Sensidyne®
- Thermal desorption unit : TD100-xr from Markes international
- Gas chromatography equipment : Thermo Electron Trace GC Ultra
- Gas chromatography capillary column : fused silica Rxi-624Sil MS column
- Mass spectrometry equipment : Trace DSQ II MS
- Data treatment and visualization : Rstudio version 2021.09.2 build 382

4.2. Active sampling of volatile organic compounds

The active sampling of VOCs was done by means of TENAX TA® adsorbent cartridges. The sampling took place in an office outside of the chamber and buffer by means of two lengths of Teflon® tubing connected to both zones. This allowed for simultaneous sampling of the buffer and the chamber from the active sampling zone shown in yellow in figure 3 (page 20). Each of the two pumps used was attributed to a specific zone in order to make the procedure as reproducible as possible between different sampling repetitions.

In preparation of active sampling

Before proceeding to the sampling, the adsorbent cartridges are conditioned according to the thermal desorption program shown in annex I.a.

Afterwards, a blank measure has to be taken. This blank will serve to eliminate background “noise” as well as peaks that aren’t a result of the sample, from the subsequent sample analysis. The thermal desorption program is shown in annex I.c and the temperature settings for the chromatography oven are shown in annex II.

Before being used, the cartridges are well closed with adequate caps to prevent sample contamination.

It is also necessary to calibrate the equipment that will be used for the sampling, namely the GilAir pumps from Sensidyne®. These pumps are calibrated by means of a soap bubble flowmeter. The pump is connected to the flowmeter and a bubble is generated. This bubble travels a known volume as the apparatus is pumping. By measuring the time needed to traverse this volume, the bubble flowmeter computes the flow. The flow on the pump is corrected on the basis of the average flow measured by at least 3 measurements and is then checked again until the measured flow is in accordance with the programmed flow.

Active sampling procedure

The TENAX®TA cartridges are connected to the pumps (which are downstream of the cartridge) as well as to the tubing connected to the buffer on one side and to the chamber on the other. The sampling flow is 200mL per minute for 30 minutes in the direction specified on the cartridge, giving a total sample volume of 6L. When possible, two samples were taken for each zone one after another (meaning 2 from the chamber and 2 from the buffer).

Once the samples were taken, the cartridges were closed and covered in aluminum foil. They were also placed in a desiccator before analysis. These measures were taken to avoid contamination or losses.

After sampling

The samples were then taken for TD-GCMS analysis according to the same methodology presented earlier for the blank measures.

Once the analysis was completed, an automatic report was generated with Xcalibur software. This report contained specifics on the nature of the compounds as well as their absolute area and relative area (in relation to total chromatogram area).

The analysis of all peaks in a chromatogram is unrealistic given their high number and the fact that some of them are extremely small as well as very difficult to accurately qualify. Therefore, only the peaks representing at least 1% of the total area on the chromatogram were kept for further inspection.

It is important to note that this method of proceeding can introduce a certain bias because different samples don't present the same total area. Some peaks may indeed be common to two different chromatograms but could be ignored in one and taken into account for the other simply because the total area of one is higher than the other.

The inspection entailed a verification of the area as well as a verification of the nature of the molecules in question by means of Xcalibur and AMDIS software. Furthermore, peaks resulting from the GC column (typically compounds containing silica) were removed from the data.

Another problematic peak was occasionally found in blank measurements at 12.1 minutes retention time. This peak was attributed to 1,3,5-trifluoro-benzene in the automatic reports (maybe erroneously). The peak was systematically removed based on retention time without verification of the actual compound. On certain occasions, it was found that 2-butanone also had this same retention time. Because of this, 2-butanone was ignored in the results presented in this thesis even though it may be a compound of interest.

Calibration

It is necessary to establish a calibration curve in order to quantify the mass adsorbed onto the cartridges. Given the variety of molecules analyzed, a single calibration with toluene was considered. This means that every mass reported for the TENAX®TA analysis is expressed in toluene equivalents.

In order to establish the calibration curve, a solution of toluene and analytical methanol was prepared. This solution served as the basis for subsequent dilutions (table 5). It was prepared inside a 20mL glass vial equipped with a septum.

The various injections and samplings were done with syringes. These syringes were cleaned 5 times with technical methanol, then 5 times with technical acetone and finally 3 times with the solution they were destined to sample before the actual injections.

In order to obtain a relatively precise volume of methanol, two 20mL vials of methanol were prepared with a closed septum. This allowed for a more precise sampling of the solvent volume as it is possible to "prime" the syringe used instead of directly sampling 20mL from an open vial or flask. The methanol was extracted from these vials for transfer into the source solution vial.

The priming process is important because it eliminates air bubbles in the syringe, allowing for a more precise sampling. In order to prime a syringe, the vial is turned upside down with the syringe inserted into the septum. The liquid is then pumped and expulsed in order to expel the air bubbles that might end up in the syringe before taking the wanted volume.

For the source solution, a 10 mL syringe was used to fill the source solution vial with 20mL of methanol. It was therefore necessary to fill the vial in two steps. It would be preferable to fill the 20 mL at once in order to avoid the accumulation of procedural errors but it was impossible to do so given the available material.

Once the methanol was introduced, 5µL of toluene were injected directly into the methanol with a 10µL syringe. The vial was closed immediately after with the septum by means of a setter.

Table 5. Preparation of toluene standards for Tenax®TA calibration

Source solution							
Substance	**Toluene volume (µl)**	**Purity**	**Solvent volume (µl)**	**density (mg/µl)**	**Corresponding mass (ng)**	**Solution volume (µl)**	**Concentration (ng/µl)**
Toluene	5.0	0.99	20000	0.866	4300000	20005	210

Standard solutions							
	Solvent volume (µl)	**Volume of source solution (µl)**	**Solution volume (µl)**	**Corresponding toluene mass from source solution (ng)**	**Concentration (ng/µl)**	**Volume injected on cartridge (µL)**	**Injected mass (ng)**
1	5000	10.0	5010	2140	0.428	5.0	2.14
2	1000	10.0	1010	2140	2.12	5.0	10.6
3	1000	25.0	1025	5360	5.23	5.0	26.1
4	1000	60.0	1060	12900	12.1	5.0	60.6
5	1000	125	1125	26800	23.8	5.0	119

These standards were then adsorbed onto TENAX TA® cartridges through a loading rig. This device allows for a passage of helium while injecting a volume of a given standard with a syringe into a cartridge. For this calibration, a flow of 80mL/min was used.

The procedure for each injection was as follows :

1. The cartridge is set up on the loading rig
2. A flow meter is connected to the end of the cartridge
3. The helium flow is turned on and adjusted to 80mL/min with the flow meter, then turned off
4. The syringe is primed and the adequate volume of standard is sampled
5. The flow is turned back on, the syringe is inserted and the standard volume is injected, at which point a 2 min timer is turned on
6. After 15 seconds of the timer have passed, the syringe is removed
7. After the 2 minutes are over, the flow is turned off, the cartridge is removed and the caps are put on

Each standard was adsorbed onto 2 cartridges so that each injected mass is represented by at least 2 analysis results. Once the analysis was complete, the injected masses were plotted as a function of their corresponding areas in the resulting chromatograms. A linear trend is established and its equation can be used to determine an unknown mass in samples (see figure 7).

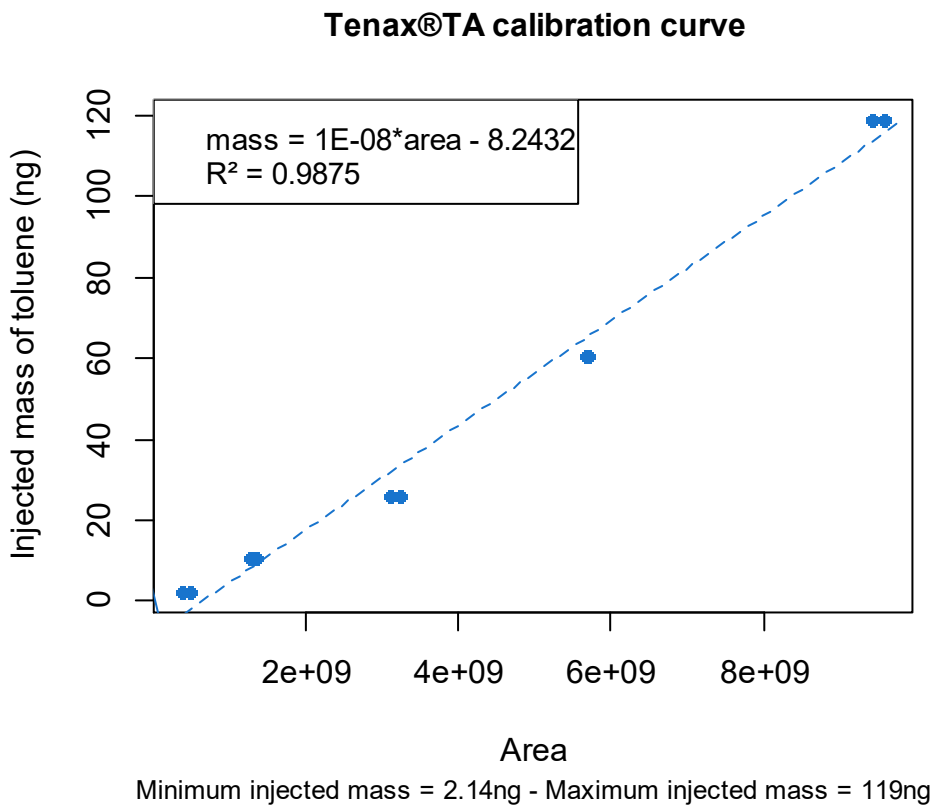

Figure 7. Calibration curve for Tenax®TA analysis results

4.3. Passive sampling of volatile organic compounds

Before sampling

The Radiello® tubes are put inside empty tubes destined for thermal desorption. While wearing a lab coat, gloves and an ffp3 mask, the following procedure was followed :

1. A small amount of quartz wool is packed inside the thermal adsorption cartridge that will house the Radiello® adsorbent tube
2. While working on a paper towel laid out underneath the working space, the Radiello is removed from its vial with pincers
3. The carbon excess on the surface outside of the mesh of the Radiello® tube is cleaned with a toothbrush
4. The adsorbent tube is slid inside the thermal desorption cartridge and the cartridge caps are put on

Then they are conditioned in the thermal desorption unit according to the thermal desorption program described in annex I.b. Once the conditioning is over, the tubes are put back inside their plastic vials while using the appropriate equipment presented above.

Passive sampling procedure

The Radiello® tubes are kept inside a closed plastic vial before use. At the beginning of a test, as we first enter the chamber, a Radiello is set. The vial is opened and the Radiello® is slid inside the yellow diffusive body. The diffusive body is then screwed onto the plastic support. This is repeated in the buffer. The identifiers of each cartridge and the zone in which they were set are noted. The date and time at which they are deposited is noted as well. Seven days later, the Radiello® are recovered and put inside their plastic vial. Once again, the date and time are noted.

After sampling

In order to analyze the samples, the Radiello® tubes have to be placed inside empty tubes destined for thermal desorption according to the aforementioned procedure.

The TD-GCMS analysis procedure is the same as for the TENAX TA® cartridges with the exception of the thermal desorption program which is described in annex I.d.

The treatment of results is also the same as for the TENAX TA® cartridges with automatic reports, selection of peaks exceeding 1% of total area and removal of unwanted peaks. The results are also verified.

Calibration

The calibration curve for Radiello® analysis requires a particular setup as proposed by the product provider. It is done by using a gas chromatography unit, specifically the injector to which a piece of capillary column is attached. This column is linked to the cartridge containing the Radiello® by means of Swagelock® joints. 1µL of the methanol solution is injected with a nitrogen flow of 50mL/min for 2 minutes. The injector has to be heated to 200°C during the process.

Unfortunately, the available equipment made it impossible to proceed in this manner. Therefore the same methodology as for the TENAX®TA calibration was used with a minor change. The actual concentration of the standards was different from that of the TENAX®TA calibration (table 6).

Table 6. Preparation of toluene standards for Radiello® calibration

Source solution							
Substance	**Toluene volume (µl)**	**Purity**	**Solvent volume (µl)**	**density (mg/µl)**	**Corresponding mass (ng)**	**Solution volume (µl)**	**Concentration (ng/µl)**
Toluene	20.0	0.99	20000	0.866	17100000	20020	856

Standard solutions							
	Solvent volume (µl)	**Volume of source solution (µl)**	**Solution volume (µl)**	**Corresponding toluene mass from source solution (ng)**	**Concentration (ng/µl)**	**Volume injected on cartridge (µL)**	**Injected mass (ng)**
1	5000	60.0	5060	51400	10.2	1	10.2
2	1000	25.0	1025	21400	20.9	1	20.9
3	1000	50.0	1050	42800	40.8	1	40.8
4	1000	300	1300	25700	198	1	198
5	1000	1000	2000	856000	428	1	428
6	100	1000	1100	856000	779	1	779

It is important to note that this method was not compared with the actual method proposed by the Radiello® providers and therefore cannot be deemed adequate. Because of this, the results concerning Radiello® analysis shown in the present document can only be compared between themselves. The method used for this project and the method presented by the providers should both be tested and then the results compared in order to evaluate the applicability of the method.

As for the technical aspect of the calibration, a small change had to be made from the Tenax®TA methodology. Because the Radiello® are inserted into empty cartridges (the same type used for Tenax®TA), they have a tendency to slide out during the injection on the loading rig. To remedy this, a small cap was put at the end of the cartridge during the loading process (see figure 8). A hole was drilled into this cap in order to allow for the flow of helium. The calibration curve is shown in figure 9.

Figure 8. Thermal desorption cartridge containing a Radiello® tube fixed onto the loading rig - note the white cap on the end of the tube

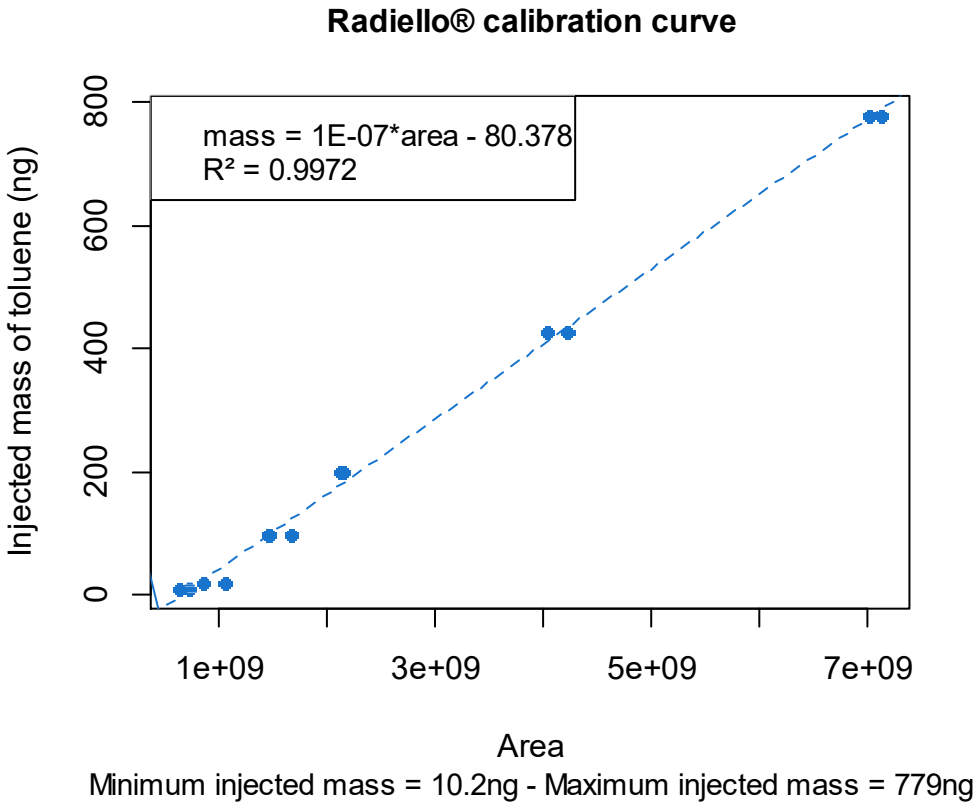

Figure 9. Calibration curve for Radiello® results

PART 3

1. General campaign results

Initially, nine test weeks were planned according to the presence of an added VOC source as well as the presence of the green walls. As explained before, planning constraints made it impossible to proceed with all the tests with a VOC source and without the green walls because the green wall installation was prescheduled. Given this fact, only 8 test weeks could be completed. They were all named from S1 to S8 according to their order. A schematic overview of the campaign is shown in figure 10.

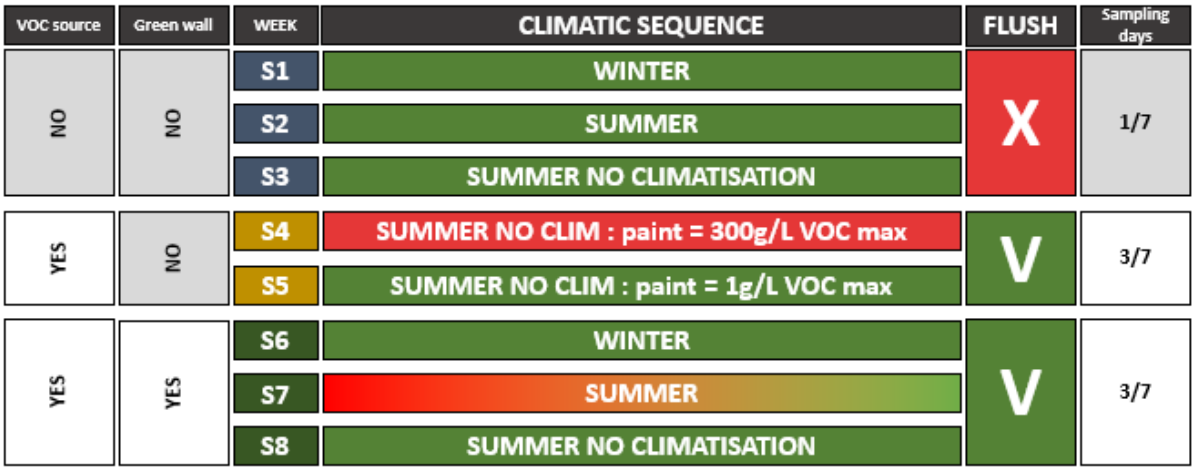

Figure 10. Schematic overview of the experimental campaign

Firstly, all planned test weeks with the empty chamber were completed (S1, S2 and S3). Unfortunately, the methodology as it relates to the flush as well as to the sampling days was different for those tests than for the others. Those results can still yield useful information and so will be discussed nonetheless.

As for the tests with a VOC source and no green walls, it was only possible to complete a test for the summer without climatization mode. Initially, 3 tests were planned for each climatic mode as specified before. However, there was only enough time to complete two test weeks before the installation of the green walls. Because of this, the summer without climatization sequence was privileged as it represented the worst case scenario for VOC emission. Unfortunately, the results of the first trial with VOC source and no green walls (S4) were unusable as the VOC concentration was simply too great when using a solvent based paint (at a maximum of 300g/L of VOCs) as an added source, which led to unexploitable chromatograms. The results were therefore discarded for the purposes of this thesis. To remedy the problem, a water based paint (at a maximum of 1g/L of VOCs) was used for another trial (S5) with the same climatic sequence. The results of that trial allowed for exploitable chromatograms that visually presented a few different peaks from the empty chamber trials. This same paint was then used to prepare the VOC source for the following test weeks. Because this is the only test with exploitable results for the trials with an added VOC source and without the green walls, it will be used as a comparison with the subsequent trials even though the climatic sequences differ. Given the major differences between climatic

sequences (mainly between winter and summer modes) in terms of buffer temperature, and given the fact that airflow is maintained between the buffer and chamber, S5 results aren't a proper reference point with differing climatic modes. Indeed, temperatures influence major factors of interest such as building VOC emission and surface adsorption dynamics among others. That being said, the conditions between regular summer mode and summer without climatization are very similar.

Finally, three test weeks were completed with a VOC source and green walls. Unfortunately, certain problems occurred. For the winter climatic sequence (S6), there was a problem on the level of the equipment that resulted in a higher buffer T° than programmed (10°C on average instead of approximately 5°C). Furthermore, no proper references are available for comparison with winter mode as the empty chamber methodology was different and the planned test with VOC source but no green walls in winter mode had to be abandoned. The results for S6 will be discussed nonetheless.

For the summer climatic sequence (S7), a problem occurred at the level of the TD-GCMS equipment. This made it impossible to obtain the blanks for the Tenax® TA cartridges and to analyze already obtained samples. Radiello® results however are available for that week as they do not necessitate a blank measure and the samples can be kept for a longer period of time.

The summer without climatization trial with an added VOC source and green walls was successfully completed as it pertains to VOC sampling by means of Tenax®TA and Radiello® adsorbent cartridges. The punctual sampling times for tests with multiple sampling days are described in table 7.

Table 7. Sampling times for Tenax®TA

S5 : added VOC source only – summer no climatization			
Time of day	**DAY 1**	**DAY 4**	**DAY 7**
~13H00	Climate sequence start		
~13H30	Introduction of painted board		
14H00-15H00		Tenax®TA sampling	Tenax®TA sampling
15H00-16H00	Tenax®TA sampling		
S6 and S8 : green wall modes			
Time of day	**DAY 1**	**DAY 4**	**DAY 7**
~14H00	Climate sequence start		
~14H30	Introduction of painted board		
15H00-16H00		Tenax®TA sampling	Tenax®TA sampling
16H00-17H00	Tenax®TA sampling		

General test and sampling conditions can be found in table 8 for Tenax®TA and table 9 for Radiello®. Note the difference in terms of average week temperature in table 9 for the buffer in S1 and S6, illustrating the problems encountered in S6 at the level of the cooling system.

Table 8. Test conditions and data for Tenax®TA sampling

Week	Date		Avg T° during sampling		Number of chromatograms		N sampling days
	Start	Finish	Buffer	Chamber	Buffer	Chamber	
S1	14 Feb	21 Feb	7°C	21°C	1	1	1
S2	24 Feb	3 Mar	31°C	25°C	1	1	1
S3	6 Mar	13 Mar	30°C	28°C	2	2	1
S5	24 Mar	31 Mar	30°C	28°C	6	6	3
S6	21 Apr	28 Apr	11°C	23°C	6	6	3
S7	9 May	16 May	X	X	X	X	X
S8	23 May	30 May	31°C	28°C	5	6	3

The number of sampling days are specified for Tenax®TA in table 8. Generally speaking, two replicas were made for each zone per sampling day. However, the replicas for S1 were used to test different split flows in the TD-GCMS analysis. For S2, two samples per zone had initially been taken but they were analyzed according to an erroneous split flow by mistake. Another sample per zone was then taken for analysis with the adequate split flow. The only test to have two samples per zone per day among the empty chamber tests is S3. For the tests S5 and S6, two samples per zone and per day were taken which amounts to 12 total samples for each week. S8 follows the same sampling methodology but it was only possible to obtain a single sample for the buffer on one of the sampling days (day 1). S8 is therefore represented by 11 chromatograms (5 from the buffer and 6 from the chamber).

Table 9. Test conditions and data for Radiello® sampling

Week	Date		Avg week T°		Number of chromatograms		Exposure time (min)
	Start	Finish	Buffer	Chamber	Buffer	Chamber	
S1	14 Feb	21 Feb	5°C	20°C	1	1	8636
S2	24 Feb	3 Mar	21°C	24°C	1	1	10080
S3	6 Mar	13 Mar	22°C	25°C	1	1	10063
S5	24 Mar	31 Mar	25°C	27°C	1	1	10056
S6	21 Apr	28 Apr	10°C	23°C	1	1	10049
S7	9 May	16 May	26°C	25°C	1	1	10003
S8	23 May	30 May	25°C	25°C	1	1	10002

Another difficulty encountered was the fact that the experimental campaign began right at the start of the present Master's thesis. This meant that there was no time to make the calibration curves prior to the beginning of the tests. It was therefore only possible to make them after the experimental campaign was over. The consequence of this is that no changes could be made to the sampling method according to the calibration limits during the experimental campaign since these limits were yet unknown.

Furthermore, maintenance of the TD-GCMS equipment was scheduled for shortly after the end of the experimental campaign. This implies that the calibration couldn't be repeated with different injection masses if needed because the maintenance has an effect on the equipment, meaning that any calibration made after the maintenance would not be usable for samples analyzed before said maintenance.

2. Lighting and watering of the green walls

The photoperiod consisted of daily 10H periods of light. While this was mostly respected, some differences can be seen between weeks. For S6 and S7, the lights were generally turned on at 12H30 and turned off at 22H30. For S8 however, the lights were turned on at 8H17 and turned off at 18H17. As seen on figure 11, the green walls received much more light during S6 as there was a malfunction of the system that made the photoperiod last multiple days. S8 presents the lowest total light period and there was no photoperiod the day before the 1st test day. The sampling by Tenax®TA adsorbent cartridges (16H00-17H00 on day 1 ; 15H00-16H00 on days 4 and 7) was done while the lights were turned on for all test weeks.

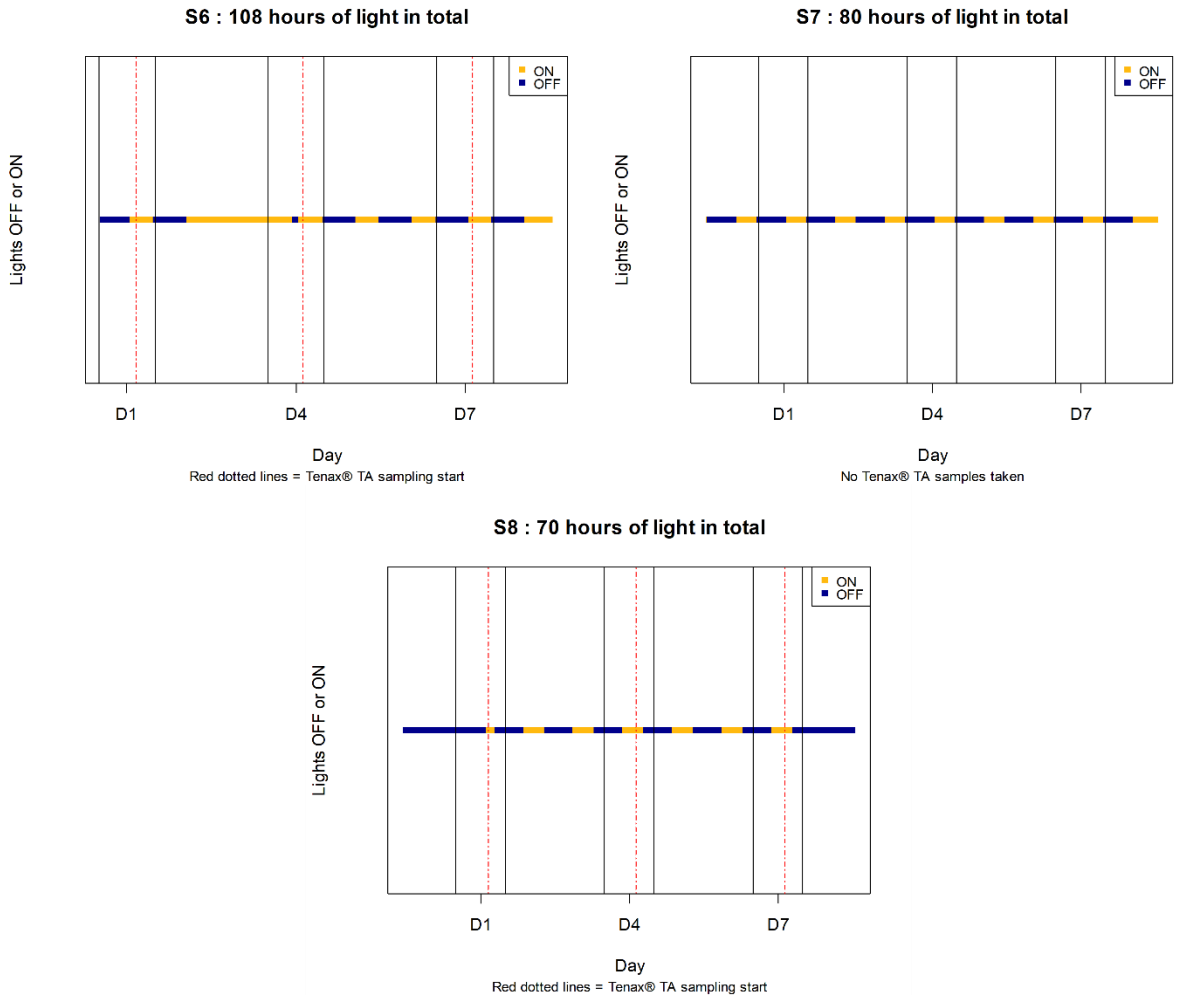

Figure 11. Graphs representing the photoperiods during test weeks with plants

For the watering of the walls, they were initially watered with very high amounts of water (192L) on two days to wet the dry substrate (table 10). For the subsequent planned watering days, only 32 liters were used for each wall for a watering time of 30 minutes.

As seen on table 10, the watering was less and less frequent as the campaign progressed, with three waterings during S6, two during S7 and only one during S8. The watering frequency was lowered because a watering volume of 32L per wall was simply too much and there was a visible decline in plant health on the green walls. Later on, the watering system was changed to be based on a floater system that allowed for a stop as soon as the run off volume reached about 300mL. This change however was only made after the experiments presented in this thesis were finished.

Table 10. Watering volumes for both green walls

	Green wall A		Green wall B	
Date	**Watering liters**	**Run off (liters)**	**Watering (liters)**	**Run off (liters)**
11-04-23	192	?	192	?
13-04-23	192	?	192	?
17-04-23	32	?	32	?
21-04-23	**START OF S6**			
20-04-23	32	3.83	32	2.48
24-04-23	32	4.95	32	1.42
26-04-23	32	7.07	32	3.12
28-04-23	**END OF S6**			
01-05-23	32	4.07	32	0.3
04-05-23	32	5.83	32	0.65
08-05-23	32	7.74	32	2.46
09-05-23	**START OF S7**			
11-05-23	32	9.28	32	3.29
15-05-23	32	8.92	32	3.36
16-05-23	**END OF S7**			
23-05-23	**START OF S8**			
27-05-23	32	?	32	?
30-05-23	**END OF S8**			
06-06-23	32	?	32	?

3. Compound qualification

In order to analyze the results, a report was automatically generated for each chromatogram. In each report, only the peaks representing more than 1% of the total area of a given chromatogram were used for analysis. As previously mentioned, this creates a bias as a specific compound may indeed be common to two different chromatograms, with the same area under the peak in both, but it may be ignored in one and not the other because the total area of one chromatogram may be higher than the other. It is important to keep this in mind when reading the results of this thesis.

Once the peaks of interest were selected, the molecules were verified through analysis of the spectrograms by means of comparison with an existing database. This verification was done through AMDIS software. On certain occasions, peaks were also simply analyzed through specific evaluation of the mass spectrogram at individual times inside a peak.

The compounds identified in the Radiello® Chromatograms (peaks >1% area) are identified in table 11 and the ones for Tenax®TA in table 12. The results in these tables have to be considered critically because of the bias mentioned earlier.

The compounds colored in green are those whose verification was good according to match factors and, because of their reoccurring nature, can be more confidently attributed.

The compounds colored in orange in the tables are those for which qualification was repeatedly difficult. In this group we find notably 3-furaldehyde, furfural, xylene and nonane who were often represented in the same peak (hence the interrogation marks in the tables). A similar occurrence happened between hexanoic acid and octanol although oftentimes a separation of the 2 peaks could be observed. Finally, we find benzaldehyde for which the qualification was complicated. Often the peaks could either be attributed to benzaldehyde or a variety of different terpenes. Because benzaldehyde presented the best match, it was chosen as a representative of that peak for the purposes of this thesis. It is however important to note that for the results for S5 in the chamber for Tenax®TA analysis, that specific peak clearly presents a separation with the left portion better attributed to benzaldehyde whereas the right to terpinene. The difficulty of adequately assessing the nature of the molecule is particularly important in this case as this specific, often reoccurring peak was usually of major importance in terms of area in the chromatograms analyzed.

The difficulties encountered for some of the peaks suggest that improvements should be considered in the gas chromatography method used. Given that the first peaks generally appear after 10 minutes with very few exceptions, a faster increasing temperature ramp could be programmed in the future in order to better separate problematic peaks.

The uncolored compounds in the tables are not necessarily badly attributed, they might even present good match factors, but they were either less often seen or other very similar compounds could also be attributed to those specific peaks with good match factors.

Table 11. Radiello® compound identification data – the compounds in green were often found and therefore their identification is more likely to be correct, the compounds in orange were often difficult to adequately identify – B = buffer; C = chamber

RT	Compound (Radiello®)	S1		S2		S3		S5		S6		S7		S8	
		B	C	B	C	B	C	B	C	B	C	B	C	B	C
13.9	Acetic acid	x	x	x	x	x	x	x	x	x	x	x	x	x	x
14.4	Benzene	x	x			x				x	x				x
16.7	Pentanal	x	x	x	x	x	x	x	x	x		x	x	x	x
18.3	Propanoic acid									x					
19.4	Toluene	x	x	x	x	x	x	x	x	x	x	x	x	x	x
20.4	2-Octene or 1-Pentanol													x	
21.3	Propylene Glycol	x	x	x	x	x	x	x	x			x		x	
21.5	Hexanal	x	x	x	x	x	x	x	x	x	x	x	x	x	x
24.2	Furfural	?		?	?			?	?	?	?		?	?	?
24.2	Furaldehyde		?												
24.2	Nonane				?										
24.2	Xylene	?	?	?		?	?	?	?	?		?	?		?
25.4	Styrene		x	x	x	x	x		x			x	x		x
26.1	Heptanal								x			x			
26.6	α-Pinene	x	x	x	x	x	x	x	x	x	x	x	x	x	x
27.5	Camphene	x	x	x	x	x	x		x		x	x	x	x	x
28.2	Hexanal, 2-ethyl-										x	x	x		x
28.4	Decane	x	x			x	x	x	x	x	x	x	x	x	x
28.5	Alkane or alkene			x											
28.5	Benzene, 1-methyl-4-(3-methylethyl)-	x													
29.1	1,3-Hexadiene, 3-ethyl-2,5-dimethyl-		x												
29.4	Nonane, 2,6-dimethyl-							x							
29.7	Benzaldehyde or various terpenes	x	x	x	x	x	x	x	x	x	x	x	x	x	x
30.1	Hexanoic Acid						?			x					
30.3	Octanal			x		x	?	x	x	x		x	x	x	x
30.3	Organic acids or Butane, 2-methoxy-2-methyl-				x										
30.4	Benzene, 1-methyl-3-(1-methylethyl)-								x			x		x	x
30.5	Limonene	x	x	x	x	x	x	x	x	x	x	x	x	x	x
30.5	Benzene, 1-methyl-4-(1-methylethyl)-	x		x						x					x
30.6	Benzene, 1-methyl-2-(1-methylethyl)-		x		x	x	x	x			x	x	x	x	
32.1	Phenol	x	x	x	x	x	x		x		x	x	x	x	x
32.3	Undecane	x	x				x	x	x	x	x	x	x	x	
33.0	Benzene, 4-ethenyl-1,2-dimethyl-	x	x							x	x				
33.2	Benzene, 1-methyl-4-(1-methylethenyl)-	x	x	x	x	x	x	x	x	x	x	x	x	x	x
33.9	Acetophenone											x	x	x	
34.1	Nonanal		x	x	x		x	x	x	x	x	x	x	x	x
35.7	6-Dodecene		x												
35.8	Dodecene									x					
35.9	3-Dodecene E or Z	x	x												
35.9	Dodecane	x	x	?	x	x	x	x		x	x	x	x	x	x

Table 12. Tenax®TA compound identification data – the compounds in green were often found and therefore their identification is more likely to be correct, the compounds in orange were often difficult to adequately identify – B = buffer; C = chamber

RT	Compound (Tenax®TA)	Family	S1		S2		S3		S5		S6		S8	
			B	C	B	C	B	C	B	C	B	C	B	C
7.5	Pentane	Alkane									x			
8.5	Isopropyl Alcohol	Alcohol										x	x	x
9.5	Pentane, 2-methyl-	Alkane									x			
13.8	Acetic acid	Org. Acid	x	x	x	x	x	x	x	x	x	x	x	x
14.4	Benzene	Aromatic									x			
15.0	Heptane	Alkane					x							
16.3	2-Pentanone	Ketone										x		
16.6	Pentanal	Aldehyde	x	x	x	x	x	x	x	x	x		x	x
19.4	Toluene	Aromatic	x	x	x	x			x		x	x	x	x
20.4	1-Pentanol	Alcohol					x						x	x
20.8	Propanoic acid, 2-methyl-	Org.acid	x				x	x	x					
21.1	Propylene Glycol	Glycol	x	x	x	x	x	x	x	x	x		x	x
21.5	Hexanal	Aldehyde	x	x	x	x	x	x	x	x	x	x	x	x
22.4	Propanoic acid, 2-hydroxy-, ethyl ester	Org. Acid					x							
24.1	3-Furaldehyde	Aldehyde	?				?			?		?		?
24.1	Furfural	Aldehyde				?	?	?	?	?	?	?	?	?
24.1	Nonane	Alkane				?	?	?		?		?	?	?
24.1	Xylene	Aromatic	?	?	?	?		?	?	?	?	?	?	?
24.1	1,4-Decadiyne	Alkyne							x					
24.8	2-Hexanone oxime or 1-Hexanol	Oxime or alcohol								x				
25.4	Styrene	Aromatic			x	x		x					x	
26.0	Heptanal	Aldehyde			x	x	x		x				x	
26.2	Pentanoic acid	Org.acid			x	x	x	x	x	x	x		x	x
26.5	α-Pinene	Terpene	x	x	x	x	x	x	x	x	x	x	x	x
26.9	Nonane, 2-methyl-	Alkane								x				
28.2	Hexanal, 2-ethyl-	Aldehyde									x	x		
28.3	Decane	Alkane	x	x					x	x	x	x	x	x
28.5	Heptane, 2,2,4,6,6-pentamethyl-	Alkane									x	x		
28.7	b-Pinene	Terpene		x		x		x						
29.0	1,3-Hexadiene, 3-ethyl-2,5-dimethyl-	Alkene	x	x		x		x						
29.2	Heptane, 5-ethyl-2-methyl-	Alkane								x				
29.3	Decane, 4-methyl-	Alkane							x	x		x		
29.4	Nonane, 2,6-dimethyl-	Alkane								x				
29.7	Benzaldehyde or various terpenes	Aldehyde or terpene	x	x	x	x	x	x	x	x	x	x	x	x
29.7	Terpinene	Terpene								x				
30.1	Hexanoic acid	Org. Acid	x	x	x	x	x	x	x	x	x	x	x	x
30.2	Octanal	Aldehyde			x	x	x	x	x		x	x		x
30.4	Cyclohexane, butyl-	Cycloalkane								x				
30.5	Limonene	Terpene	x	x	x		x	x			x	x		
30.6	Heptane, 4-ethyl-	Alkane								x				
30.8	Decane, 2-methyl-	Alkane							x	x				
31.1	1,3-Dioxolane, 2-heptyl-4-methyl-	Dioxolane					x							
31.2	Decane, 3-methyl-	Alkane								x				
31.3	1-Hexanol, 2-ethyl-	Alcohol	x	x	x	x	x	x	x	x	x	x	x	x
32.0	Phenol	Aromatic	x	x	x	x	x	x	x	x	x	x	x	x
32.2	Undecane	Alkane							x	x	x	x	x	x
32.6	1,3-Dioxolane, 4-methyl-2-pentyl-	Dioxolane						x						
32.9	1-Decanol, 2-methyl-	Alcohol							x					
33.0	1-Octanol	Alcohol											x	
33.0	Benzaldehyde, 2-hydroxy-	Aldehyde											x	
33.9	Acetophenone	Ketone									x	x		
34.1	Nonanal	Aldehyde	x	x	x	x	x	x	x	x	x	x	x	x
35.8	Dodecane	Alkane							x	x	x	x		x
37.9	Decanal	Aldehyde		x	x						x	x	x	
38.5	Benzoic acid	Org. acid									x	x		

Radiello® results

Looking at the results for Radiello® analysis, certain compounds were always found in every week and every zone, and others were found very often across all three situations (namely empty chamber, with VOC source and with VOC source + green walls) (table 13).

Table 13. Commonly found compounds across different test weeks for Radiello®

Radiello	Compounds		
Always present	Acetic acid	Toluene	Hexanal
	α-Pinene	Benzaldehyde	Limonene
	Benzene,1-methyl-4-(1-methylethenyl)-		
Mostly present	Pentanal	Styrene	Camphene
	Decane	Benzene, 1-methyl-2-(1-methylethyl)-	
	Phenol	Undecane	Nonanal
	Dodecane		

Based on table 11 for Radiello® analysis, no particular pattern can be discerned with maybe the exception of propylene glycol. We can see that the compound is present in every zone in week S1, S2 and S3 (empty chamber) as well as in week S5 (VOC source only). In the tests with the green walls, it is found in both S7 and S8 but only in the buffer zone.

In order to evaluate if this observation concerning propylene glycol is of interest based on the 1% bias, the total chromatogram areas as calculated on the automatic reports were used. As shown on figure 12, weeks 7 and 8 present higher total areas than the other weeks, meaning that it is possible that propylene glycol's absence in the chamber date for those weeks is simply due to the bias introduced by only looking at peaks with areas exceeding 1% of the total area. That being said, week 6 presents total areas that are similar to the empty chamber tests, if not lower as seen on the buffer results. Therefore the bias does not explain the absence of propylene glycol in the results above 1% of total chromatogram area for S6 meaning that there may have been an actual effect associated with the green wall tests. No confident conclusion can be made however given the very low amount of data available. The graphs of total area per week will be discussed further in the later parts of this thesis.

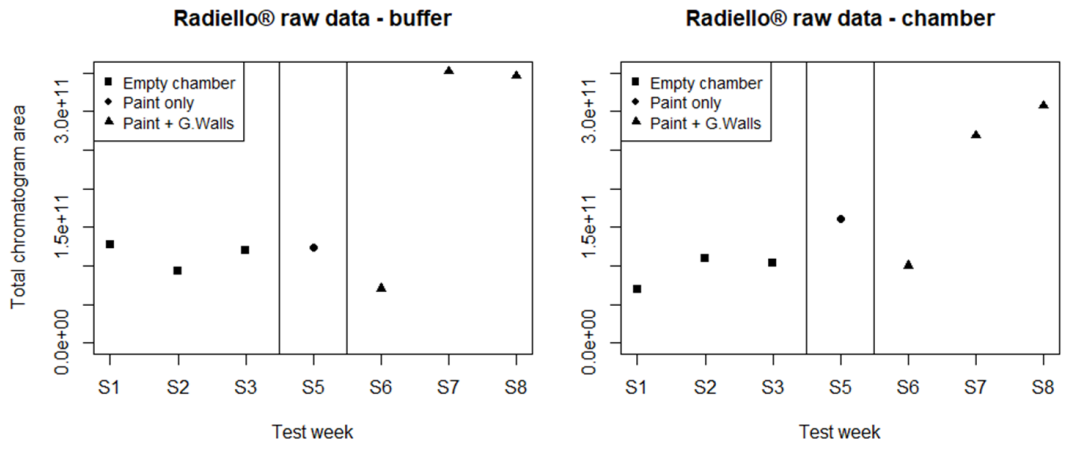

Figure 12. Total area comparison (Radiello®)

Tenax® TA results

As for the Tenax®TA results, a summary of the compounds always present and those mostly present is available in table 14. It is important to note however that the weeks S1 and S2 are only represented by 1 sample per zone, and S3 by 2 samples per zone. S5 and S6 are represented by 6 samples per zone and S8 is represented by 5 samples for the buffer and 6 samples for the chamber.

Table 14. Commonly found compound across different test weeks (Tenax®TA)

Tenax®TA	Compounds		
Always present	Acetic acid	Hexanal	α-Pinene
	1-Hexanol, 2-ethyl-	Phenol	Nonanal
	Benzaldehyde		
Mostly present	Pentanal	Toluene	Propylene glycol
	Pentanoic acid	Hexanoic acid	Octanal

Looking at the results for Tenax®TA in table 5 (peaks > 1% total area), certain interesting patterns can be seen :

- Certain compounds are only found in tests with green walls, namely isopropyl alcohol (S6 chamber, S8 chamber and buffer) and acetophenone (S6 buffer and chamber)
- Others are only found in S5 (paint only), namely 2-methyl-decane, 3-methyl decane and 4-ethyl-heptane, all of them being alkanes

Once again, the total chromatogram areas will be looked at in order to see if these trends could potentially be explained by the bias resulting from the data treatment method. Acetophenone is only seen for S6 which also presents the lowest total areas as seen on figure 13. This means that acetophenone's presence in S6 and not the others may simply be due to the 1% bias. An acetophenone peak could also be an artefact resulting from polymer degradation because of O_3 and NO_2 as seen in the literature presented in part 1.

Isopropyl alcohol on the other hand may be of interest as it was found in S8 buffer zone which also presents a similar range of total areas as S5 buffer zone. This may mean that isopropyl alcohol is characteristic of the green walls. However, it was also used to disinfect the mold sampling equipment and will therefore be considered a contaminant.

As far as the alkanes are concerned, it does seem more likely that they are due to the presence of paint as S5 generally presents a range of total areas higher than the other weeks (especially in chamber zone), meaning that the 1% bias would not come into play.

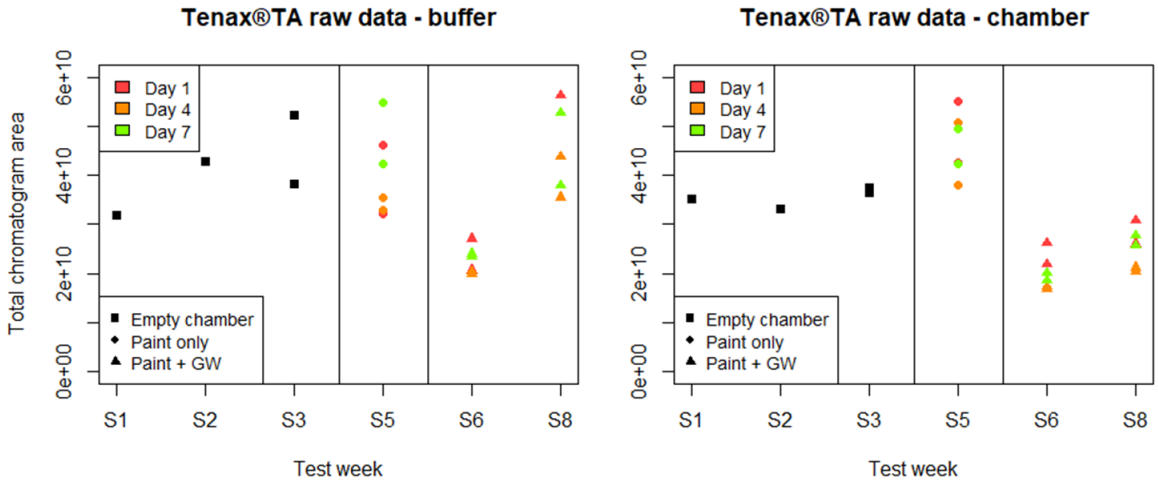

Figure 13. Total chromatogram area comparisons (Tenax®TA) – as previously specified, two replicas per sampling day were made from S3 onward except for day 1 in S8 (buffer zone)

These total area results will be discussed further in later parts of this document.

4. Radiello® quantification results

4.1. Total and individual area comparison

Firstly, the total areas of the chromatograms obtained will be explored further. Certain peaks in those chromatograms were not a result of the sample but of the GC column (typically silica containing compounds). These peaks were removed before plotting the total areas in order to make them more representative of the samples themselves (figure 14). It is important to note however that the total exposure time for S1 was only 8636 minutes vs the usual 10000 (approximately). Because of this, the areas shown for S1 would be lower than for other weeks if they hypothetically presented the same concentrations during the experiments.

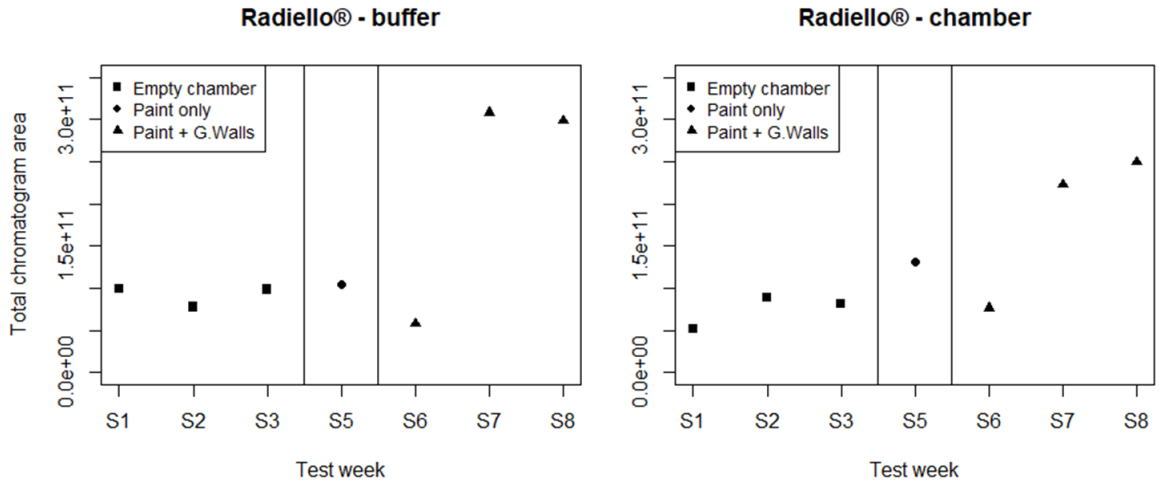

Figure 14. Comparison of total chromatogram areas without GC column peaks (Radiello®)

Figure 14 shows that the highest total areas are found in S7 and S8 which correspond to summer modes with the green walls and added VOC source. Those total areas seem to be about 2 to 3 times higher than the ones in the empty chamber tests (S1, S2, S3) and added VOC source only test (S5). Interestingly S6, which is winter mode with green walls and an added VOC source, presents lower or equivalent total areas than empty chamber tests.

There also doesn't seem to be a great difference between buffer and chamber except maybe for S7 and S8. Because the amount of data for each case is so low, remarks can only be made by visual analysis of data as statistical analysis isn't possible. The low number of samples per case is a general issue in the experimental campaign, even for Tenax®TA results.

Generally speaking, it is difficult to interpret this data since both the highest and lowest total areas are found among the tests with green walls. There is also an absence of reference in winter mode with paint only with which to compare the results of S6 directly. As far as S7 and S8 are concerned (summer mode with and without climatization respectively), they present higher total areas than S5 (summer without climatization).

The high total areas in S7 and S8 are particularly interesting as those tests do not seem to present a great difference with the other tests according to the nature of the compounds encountered as seen on table 11. The higher areas may then be due to greater concentrations

of the same compounds found before or they may present themselves in different ratios between different tests.

Figure 15 shows the distribution of individual peak areas (>=1%). It is possible to see that S7 and S8 present more than 25% individual areas that exceed the calibration range for the chamber and around 50% for the buffer.

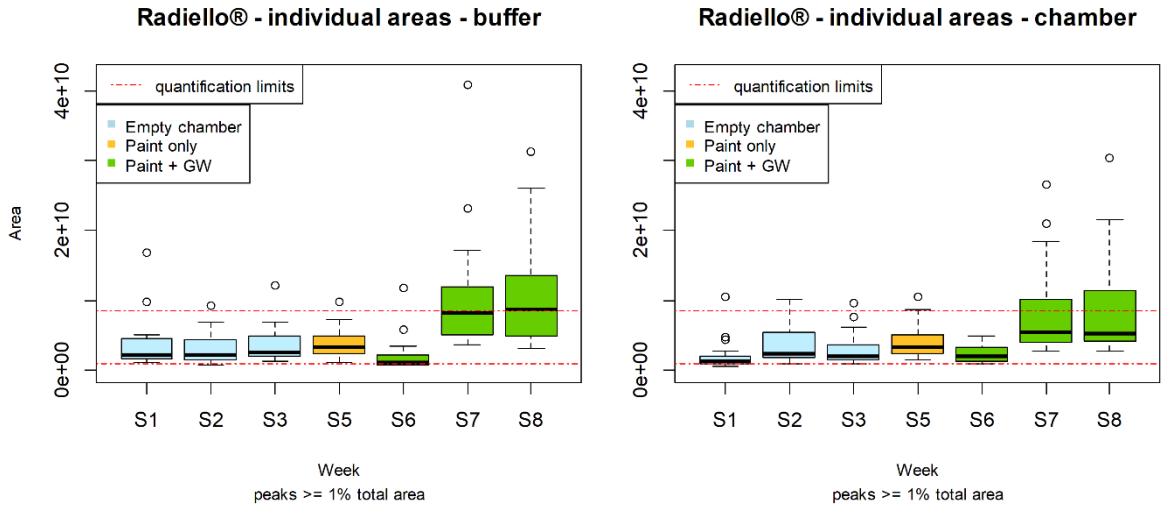

Figure 15. Boxplots showing the distributions of individual areas (Radiello® results)

The 5 greatest peaks and their corresponding mass in toluene equivalents according to the calibration for S7 and S8 are shown in annex III per zone. The injected masses of toluene used for the calibration range from 10.2ng to 779ng. As seen on the annex, the compounds greatly exceed this range and cannot be accurately quantified in toluene equivalents with this range without verifying the linear relationship with higher injected masses. Furthermore, the calibration method has not been validated as previously mentioned.

Generally speaking, benzaldehyde seems to be a major compound found in S7 and S8 as well as a few more aromatic compounds. We also find acetic acid among chamber samples but it is also present in the buffer (but not in the 5 peaks with the highest areas). Comparing different compounds based on their mass in toluene equivalents is possible but may be misleading as different compounds can have a different detector response even if the same mass is analyzed. Furthermore, different compounds have different adsorption rates onto the Radiello® adsorbent tubes, meaning that comparisons between different compounds according to their chromatogram area can also be misleading. These remarks also apply to the comparison of total chromatogram areas presented earlier but the differences between S7 and S8 in comparison with all the other tests are so visible that the information is still useful. That being said, comparing the adsorbed mass in toluene equivalents for the same given compound across different weeks is logical.

4.1. Specific compound quantification

Determining the average concentration of compounds adsorbed onto Radiello® cartridges requires the knowledge of the flow at which they are trapped. These flows are given for specific compounds by the Radiello® providers. Because of this, only a select amount of

compounds, those found in the experiments for which a trapping flow is provided, are going to be explored in terms of their concentration in toluene equivalents. Those compounds are specified in table 15, together with their trapping flow at 298°K. While a trapping flow is available for xylene, it will not be explored as confident classification of xylene was difficult as discussed previously.

Table 15. Trapping flows (Radiello®)

Compound	Trapping flow [mL/min] (at 298°K)
α-Pinene	6.4
Benzene	27.8
Decane	22.3
Limonene	12.8
Styrene	27.1
Toluene	30.0
Undecane	12.0

The specific flows were all corrected for each week in order to take the average week temperature in each zone into account. Furthermore, the concentrations obtained were adjusted to be representative of their equivalent at 20°C.

The results are graphically represented in annex IV. The red dotted lines represent the lower and upper concentration values for adequate quantification calculated according to the following factors :

- The minimum and maximum masses of toluene used for calibration (10.2 and 779ng)
- A reference exposure time of 10080 minutes (7 days)
- The specific trapping flow of the compound analyzed at 20°C

The quantification limits were added in order to keep concentrations outside of the calibration rate for visualization purposes. Because the calibration range is not adequate for all peaks, some concentrations will appear as negative which obviously doesn't reflect reality.

A summary of the results by compound is available in table 16. As shown on annex IV, decane presents higher concentrations in tests where a VOC source was added than in empty chamber tests. This is especially the case for S5, which is also the test with only the added VOC source and no green walls. S5 presents the highest concentrations whereas the following weeks have somewhat lower concentrations but still higher than the empty chamber tests.

Limonene presents quite higher concentrations in S7 and S8 than the other tests. This is also the case for toluene which reaches 2µg/m^3 at most in S8.

Generally speaking, the results for the specific compounds seem to follow the trends seen in the total area comparisons. It is particularly interesting that the tests with green walls can present the highest concentrations (summer modes) while also relatively low/ the lowest ones (S6 winter mode).

Table 16. Summary of the results comparing concentrations of green wall tests with S5 (added VOC source without green walls) based on annex IV

Compound	Buffer			Chamber		
	S6	S7	S8	S6	S7	S8
A-pinene	Lower	Higher	Higher	Lower	Higher	Higher
Benzene	?	Comparable	?	Higher	Comparable	Higher
Decane	Lower	Lower	Lower	Lower	Lower	Lower
Limonene	Lower	Higher	Higher	Lower	Higher	Higher
Styrene	Lower	Higher	Comparable	Lower	Higher	Higher
Toluene	Lower	Higher	Higher	Comparable	Higher	Higher
Undecane	Lower	Comparable	Comparable	Lower	Higher	Lower

The main difference between summer and winter modes is the buffer temperature. Because the chamber and buffer are connected by a ventilation vent, buffer temperatures can indeed affect the chamber. The differing dynamics of adsorption and building material emission (among other factors) in the buffer zone between different modes (winter vs summer) could have an effect. That being said, building material emissions should affect S2, S3, and S5 in a similar manner as S7 and S8 because they are all summer modes but those first weeks do not present the same high levels as S7 and S8.

While it was previously mentioned that S1, S2 and S3 could not be used as controls for confident comparisons with the rest because of the differing methodology, in this case a lack of flush should theoretically lead to even higher concentrations than if a flush was indeed programmed. Because of this, using the results of the controls as a way to set this hypothesis aside for now is sensical. By adopting this thought process, we do make the assumption that no contamination could come from the flushing process which could be an error.

As for the chamber temperature itself, it was 23°C on average during S6 and during S7 and S8 was 25°C on average. The temperature inside the room could be of interest because it can stress the plants if it is too high as it is known that heat stress can induce higher VOC emission in plants. In this case however, the temperatures don't seem to be too different but the stress on the plants may accumulate as the weeks advance if the temperature isn't adequate.

Other differences found between S6 and S7/S8 are the photoperiod, the watering, and the health of the green walls. Indeed, during S6 the plants received much more light than the other weeks as well as water. Furthermore, the health of the plants deteriorated as the weeks advanced, likely because of excessive watering.

We could also consider a combined effect from higher humidity in green wall tests due to watering and summer mode temperatures that could lead to higher building emissions in summer modes with green walls, in comparison with summer modes without green walls. In this case, building emissions could still be the cause of the higher adsorbed quantities found in S7 and S8 compared to the summer modes without walls.

Furthermore, the compounds found in S6, S7 and S8 are often the same ones found in the other tests without green walls, mainly benzaldehyde and other aromatics/ terpenes as well as propylene glycol. This might also suggest that the increased emissions may be the result of increased building emissions. However, this is not necessarily the case as there is an overlap

between the types of VOCs emitted by wood based building materials, plants, and microbes ,mainly terpenes, as presented in the earlier parts of this thesis. Also the peak corresponding to benzaldehyde, as discussed earlier, could also be attributed to various terpenes. These factors will be further discussed in the later parts of this thesis.

5. Tenax®TA quantification results

5.1. Total and individual area comparison

The results of total chromatogram area, from which the peaks associated with the GC column were removed, are shown in figure 16. In this case, the volumes sampled were all 6L with less than 1% difference between them generally.

The buffer results show a similar range of total areas between S5 and S8, whereas the Radiello® results showed S8 areas to be clearly higher than S5. S6 however seems to present the lowest total areas which is in accordance with the Radiello® results. The results for S1, S2 and S3 are represented by very few samples, it is therefore difficult to interpret them in relation to the others other than the fact that they seem very similar in the chamber zone.

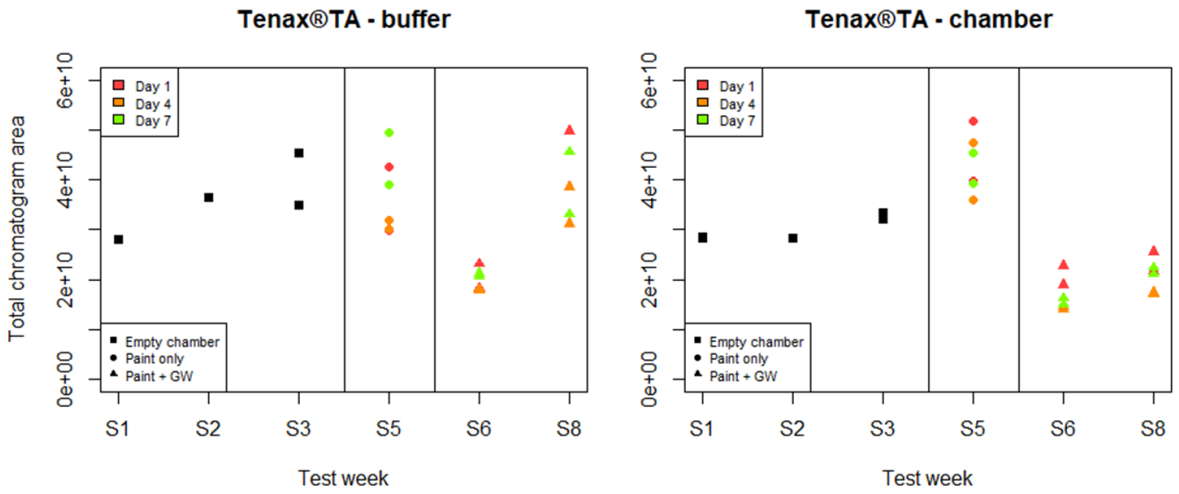

Figure 16. Total area comparison without peaks associated with the GC column

The chamber results seem to differ from the buffer for S8 as they are also lower than all the others with the exception of S6. This is interesting as S6 follows a similar trend in Tenax®TA results as in Radiello® results, but S8 presents opposite trends between the two sampling methods. S5 generally presents a larger range of areas in comparison with other test weeks.

Generally speaking, no particular trend seems to appear according to the sampling day, especially when considering that the difference between replicas (same day samples) can be quite large.

As seen on figure 17, A large number of individual peaks are not quantifiable[6] according to the calibration range used in toluene equivalents, with many test weeks presenting above 50% of non-quantifiable peaks among those with an area that already exceeds 1% of the total. Because of this, increasing the total sampled volume could be a useful methodological change in the future.

[6] **For the purposes of this thesis, the term « non-quantifiable » will repeatedly be used to designate compounds whose areas fall outside of the range available from the calibration curves used.**

The chamber results show that S5 has a larger range of values in comparison to the other weeks. There are also quite a few compounds that present areas much higher than the general range.

Furthermore, the results for S6 in the chamber show the lowest median value and no outliers, which isn't the case for the other boxplots.

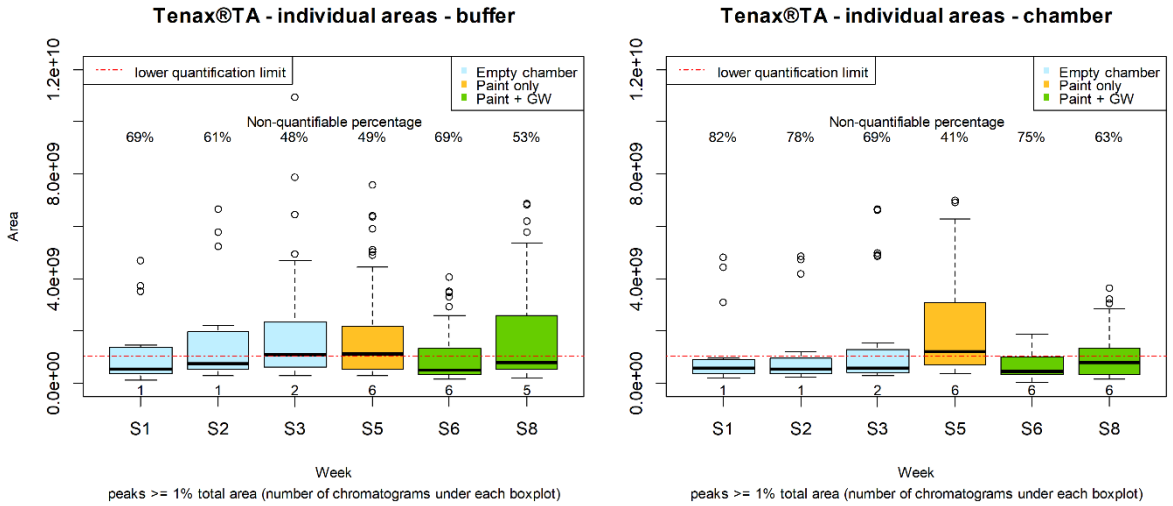

Figure 17. Boxplots of the individual areas for each test week (Tenax®TA results)

5.2. Total concentration analysis according to compound families

The concentration of each component was calculated according to the Tenax®TA calibration curve and the sampled volume. The temperature during sampling was used to calculate the concentrations at their equivalent at 20°C.

In order to explore the data in a little more detail, individual compounds were aggregated by family according to the specifications on table 12. For this purpose, the results will be shown as comparisons between S5 and the green wall modes. The empty chamber results will also be presented.

The concentrations of a given compound in each chromatogram were added according to the families present. For days where 2 replicas were taken, both values of total concentration by family were averaged into one. When a compound wasn't quantifiable according to the calibration range, its concentration was input as 0. Because of this, if one replica presents a compound in a quantifiable quantity and the other one presents the compound but in insufficient quantities to be quantifiable, the average of both will underestimate the actual concentration. This implies that the concentrations shown in the following graphs tend to be underestimations of the actual concentrations (in toluene equivalents).

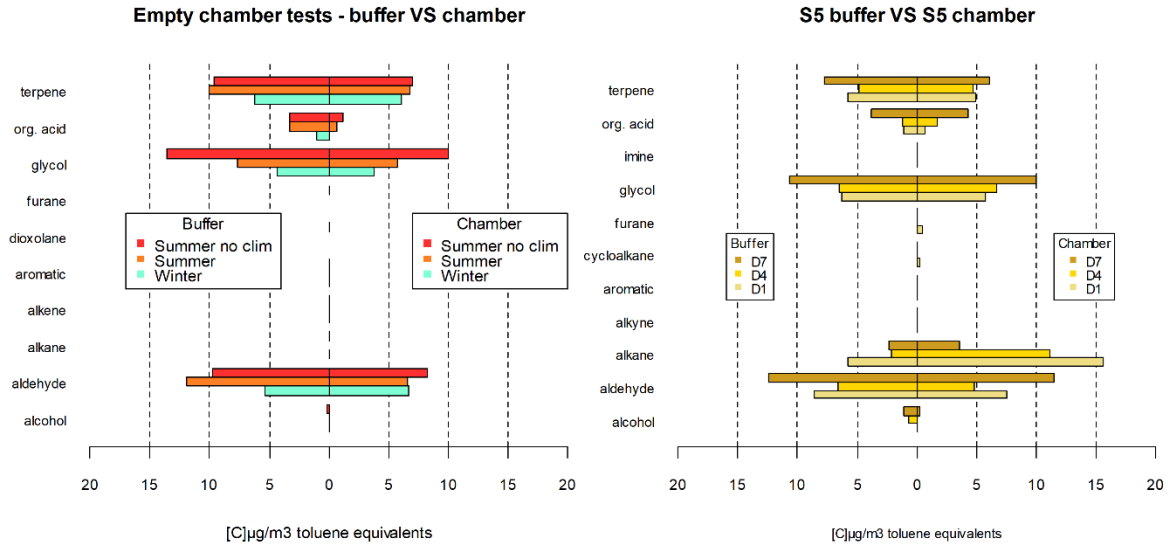

Figure 18. Empty chamber tests and paint only test

Figure 18 shows the total family concentrations for the empty chamber tests on the left. If a family/ group is shown but is represented by an empty bar, it signifies that said group was found in either the buffer or chamber but in insufficient quantities to be quantified according to the calibration range.

The major families are aldehydes, terpenes, and glycols, in empty chamber tests. Organic acids are also present. The presence of terpenes and aldehydes is expected given the OSB walls of the buffer zone. Generally speaking, winter mode presents the lowest concentrations. Summer mode without climatization presents the highest total glycol concentration. As shown previously, very few compounds were quantifiable among all peaks in the empty chamber tests.

Also shown on figure 18 to the right are the total concentrations per sampling day during S5 (paint only, summer no climatization mode). Tendencies seem to mirror each other when comparing buffer and chamber except for alkanes as they seem much more present in the chamber. Alkanes may be a result of VOC emission from the paint used, which would be in line with the Radiello® results for decane. There also seems to be a steady decrease as the days progress for alkanes which could be due to homogenization of emitted VOCs in the receiving chamber and buffer volume, VOC exfiltration, and/or VOC surface adsorption (among other factors) combined with decreased VOC emission as the paint dries. It is also possible to find terpenes, aldehydes, glycols, and organic acids just like in the empty chamber tests.

Given the fact that these families are common to S1, S2, S3, and S5, as well as the fact that the trends for those compounds are somewhat mirrored between chamber and buffer immediately from day 1 in S5, it does seem that those families are characteristic of the experimental site itself. Once again, the differing methodology between empty chamber tests and subsequent tests makes interpretations more difficult. Based on these results, it seems reasonable to hypothesize that terpenes, glycols, and aldehydes may be characteristic of the experimental site whereas alkanes may be characteristic of the paint.

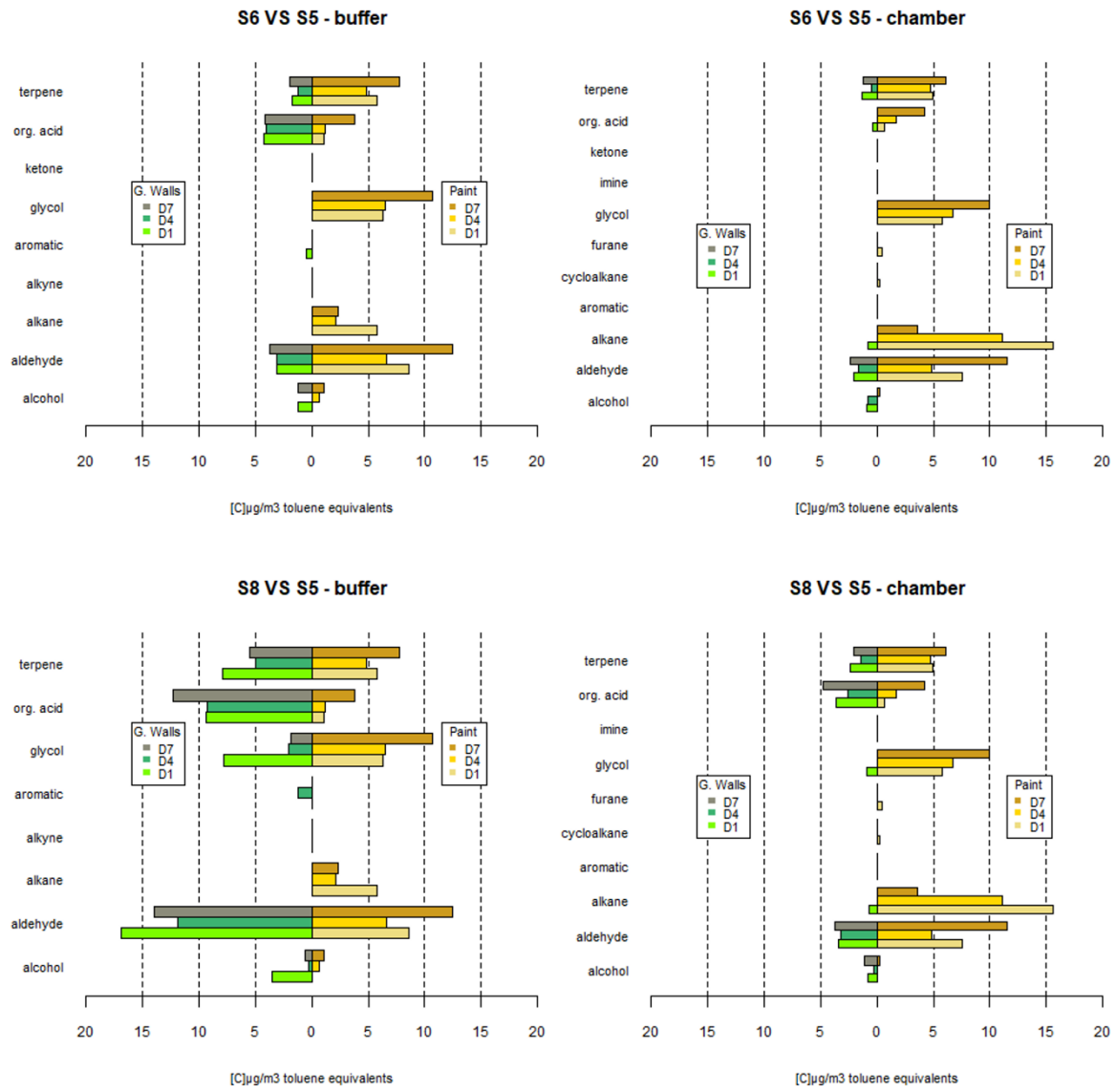

Figure 19. Comparison of green wall results and chamber results

a) S6 chamber results

The comparison of tests with green walls and the paint only test is illustrated in figure 19. It is possible to see that S6 presents very low, or even non-quantifiable concentrations, in the three main families discussed (aldehyde, terpenes, glycols) in relation to S5. Furthermore, unquantifiable/ no concentrations are seen for alkanes, except on day 1.

b) S6 buffer results

In terms of buffer results, the same tendencies are observed. On the other hand, organic acids seem more present in S6 than S5. As previously mentioned, S6 and S5 are represented by different climatic modes (S6 = winter; S5 = summer no climatization) and therefore comparing the two can be misleading.

Generally speaking the observations made here follow those made on the total area analysis of Tenax®TA results as well as those of Radiello® results.

c) S8 chamber results

The chamber results for S8 show lower values than S5 for the three main families discussed before. Organic acids however are higher in S8 than S5.

d) S8 buffer results

Unlike the chamber results, the S8 buffer results show comparable or higher concentrations for most families :

- Terpenes seem comparable between S8 and S5
- Organic acids are higher in S8 than S5
- Glycols are lower in S8 than S5 (except on day 1)
- Aromatics present quantifiable concentration(s) for S8 on day 4 only
- Alkanes are not found in quantifiable quantities for S8
- Aldehydes are higher in S8 than S5
- Alcohols are higher on day 1 for S8, and comparable on other days

The results for S8 are interesting in that they are lower than S5 in the chamber but not in the buffer. In the Radiello® results, adsorbed quantities were much higher than S5 in both the buffer and chamber. This may point to an unknown factor that leads to higher concentrations in such a way that it could be seen on Radiello® samples but not in Tenax®TA samples. This factor might play a role in such a way that the effect is not seen on the punctual Tenax®TA sampling for the chamber but is somewhat reflected in the buffer results.

Another point is that S6 results are similar between the 2 sampling methods. This implies that the hypothetical unknown factor (or factors) has to affect the sampling methods differently without doing so in S6. As mentioned for the Radiello results, the main difference between S6 and S7/S8 was the watering, plant stress, and different buffer temperature. The photoperiod could also be an interesting factor to consider. These factors will be discussed further in the later parts of this thesis.

Generally speaking, terpenes and aldehydes are major families found across all tests. Since benzaldehyde is a major representative of the aldehyde family in these results, it is important to remind that the peak corresponding to benzaldehyde was difficult to adequately qualify as it could also be attributed to various terpenes. As seen in the literature presented in part 1, the presence of terpenes is in accordance with the VOCs potentially emitted by wood based building materials such as the OSB found in the buffer zone, as well as those potentially emitted by plants and microbes.

5.3. Specific compound quantification

Certain compounds were much more often present than others and/or at higher concentrations, they will therefore be explored further. Those compounds are toluene, pentanal, hexanal, acetic acid, α-pinene, decane, benzaldehyde, phenol, nonanal and dodecane.

After closer inspection, toluene, pentanal, phenol and dodecane appear to be generally unquantifiable and won't be analyzed. The fact that toluene is generally unquantifiable is interesting as Radiello® results showed concentrations that should theoretically be quantifiable according to the calibration range used for Tenax®TA. Indeed, the minimum measurable concentration for toluene should be 0.357µg/m3 according to the following criteria :

- A minimum injected mass used for Tenax®TA calibration of 2.14ng
- A sampled volume of 6L

That being said, concentrations obtained with one method (Radiello®) may not equate to that same concentration measured by means of another method (e.g. Tenax®TA). Indeed, the discrepancy between toluene results for Tenax® and Radiello® is most likely due to the fact that Radiello® is a continuous sampling technique whereas Tenax®TA sampling is punctual as previously mentioned. This would be in line with the observations made so far comparing the similarities and discrepancies between the different methods. It is also important to remind that the calibration method for Radiello® has not been validated.

As aforementioned, Tenax®TA is not adequate for the sampling of acetic acid because of the compound's breakthrough volume of 5.6L. The results will be explored nonetheless.

Among the generally quantifiable compounds we can still find individual peaks that aren't quantifiable. They will still be shown as they can bring interesting information, especially if a specific test shows unquantifiable results whereas others do not. Because of this, some concentrations may be shown as negative which obviously doesn't reflect reality. The graphical representations are shown in annex V, in which the lower quantification limit is shown by a red dotted line.

The results presented in annex V are summarized in table 17. The green wall modes mostly present lower concentrations than S5 with paint only. As previously said, comparing S6 with S5 is not a fair comparison as the buffer temperatures in S6 are much lower than S5, meaning that building emissions for example would be lower in S6 than S5 anyway without the presence of green walls.

The exceptions are acetic acid irrespective of week or zone. The buffer zone in S8 presents quite a few higher concentrations than S5 in regards to most compounds.

Propylene glycol, the sole representative of the glycol family, presents interesting results, being absent for S6 and unquantifiable for S8 in the chamber. This may indicate an effect associated with the green wall tests. This is in accordance with Radiello® results, in which propylene glycol is absent in the chamber for green wall tests, but also in which propylene glycol is present in much higher adsorbed quantities in the buffer in green wall tests S7 and S8.

Table 17. Summary of Tenax®TA results based on their graphical representation in annex V

Comparison of green wall weeks with S5 (paint only week)				
Compound	**Buffer**		**Chamber**	
	S6	**S8**	**S6**	**S8**
Propylene glycol	Lower	Lower	Lower	Lower
Hexanal	Lower	Higher	Lower	Lower
Acetic acid	Higher	Higher	Comparable	Higher
A-pinene	Lower	Comparable	Lower	Lower
Benzaldehyde	Lower	Higher	Lower	Lower
Nonanal	Lower	Higher	Lower	Lower
Decane	Lower	Lower	Lower	Lower
Undecane	Lower	Lower	Lower	Lower

The chamber results for decane and undecane show a generally higher concentration on the first test days while it decreases to its minimum on either day 7 (S5) or day 4 (S6 & S8). In both green wall tests and empty chamber tests, decane is generally unquantifiable whereas S5 presents higher values, especially in the chamber. This reflects the observations made according to compound families. The results for alkanes seem to suggest that the green walls tests may be associated with an effect on the concentrations for that family in such a way that they are lowered. As for comparison with Radiello® results, these show that green wall tests do seem to be associated with a slight reduction in decane concentrations but this in not the case for undecane.

6. Discrepancies between sampling methods

It is generally seen that S6 (winter mode with green walls) presents the lowest concentrations/ adsorbed masses irrespective of the sampling method. Tenax®TA results present S8 as lower than most other tests in terms of concentration (chamber zone) or similar to S5 (buffer zone). This is in contrast with Radiello® results where S8 presents quite higher adsorbed quantities of compounds in relation to other test weeks.

Radiello® results show higher adsorbed quantities for S7 and S8 than all the rest. Many of the compounds that present higher quantities also happened to be found in the results without green walls. These compounds were generally benzaldehyde and various compounds with a benzene ring as well as propylene glycol and terpenes such as limonene.

Tenax®TA results show lower adsorbed quantities for S8 (chamber results) than the other tests except S6 which is the lowest. The major compounds found during green wall tests are in accordance with those of the empty chamber tests, namely benzaldehyde, propylene glycol and α-pinene. While the trend observed for S8 here is opposite to that in Radiello® results, propylene glycol showed reduction in both sampling methods in chamber results, indicating that there may be an influence of the green walls on that specific compound.

Because the types of compounds found in higher quantities in S7 and S8 were also found in empty chamber tests at lower quantities, we can hypothesize that the higher concentrations in S7 and S8 (Radiello® results) may be the result of heightened building emissions. However, there is an overlap between the types of compounds emitted by wooden building materials (such as the OSB that is found in the buffer zone) and the types of compounds emitted by plants or microbes. Because of this, it cannot be said with certainty that the results in S7 and S8 are the result of heightened building emissions, especially as there is no evident reason as to why there would be higher building emissions in S7 and S8 summer modes compared with the summer modes without green walls. That being said, we cannot exclude the possibility that higher building emissions resulting from unconsidered factors may indeed be the cause of the results seen in S7 and S8 (Radiello®) results.

Other factors of interest could be explored such as the watering as well as photoperiod during the different tests.

Effect of watering

The watering of the green walls could have had an effect. Indeed, they were watered 3 times during S6, twice during S7 and once during S8. Watering can have different effects such as :

- High moisture content on the green walls and in the chamber acting as an aqueous phase into which hydrophilic VOCs can partition (lowers measured concentrations)
- Substrate dampness causing plant stress on the long term and potentially accentuating the microbial activity of the substrate in such a way as to increase VOC emissions from the green walls (heightens measured concentrations)

Given that S6 presented the most watering events, the lower concentrations may have been partially due to the higher moisture content as compounds partition into the aqueous phase although seemingly hydrophobic compounds also show lower concentrations. Also, the green

walls had only recently been installed at S6 and therefore were healthier then than in the subsequent tests (S7 and S8). The increased stress/ substrate dampness may have lead to increased VOC emissions from the plants/ substrate/ microbes. The results of Dayane Komi Tetekpor do show a substantial increase in molds for tests with green walls, which may lead to higher MVOC levels as described in the literature presented in part 1 of this thesis. General stress could also occur from unfavorable conditions stemming from an unfavorable temperature or lack of fertilizer for example. These stresses could weaken the plants more and more as the tests advance and could also impair the phytoremediation capabilities of the green walls.

The general humidity levels could also affect the building emissions, especially in the buffer zone where the OSB is not covered. According to figure 20, chamber relative humidity was higher during S7 and S8 than S6. However in the buffer, where the OSB walls aren't covered, it was higher in S6. Because of this, the humidity itself cannot explain the higher concentrations found in S7 and S8 (Radiello® results). While finding higher concentrations in S7 and S8 is predictable given the higher buffer T° and therefore higher building emissions, the effect of temperature alone doesn't explain the much higher concentrations in S7 and S8 (summer modes), given the results for the empty chamber and paint only summer mode tests. We could also consider a potential combined effect from higher humidity and summer mode temperatures that could lead to higher building emissions in summer modes with green walls in comparison with summer modes without green walls.

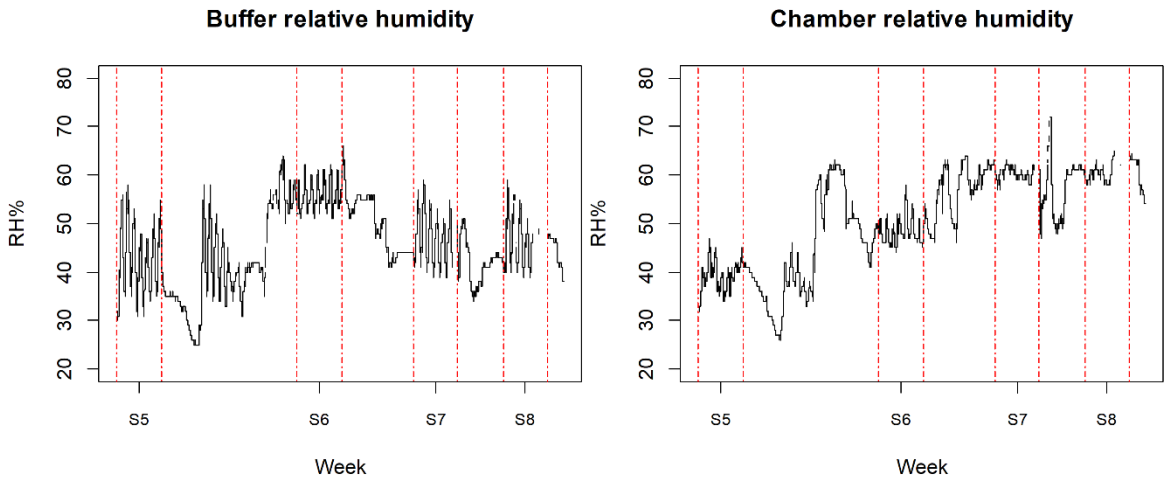

Figure 20. Relative humidity levels in S5 and green wall tests

An important point is that between the different sampling methods, we discern comparable trends for S6 but an opposing trend with S8. As previously hypothesized, this could be the result of one or more hypothetical occurrences that affect S8 in such a way that a punctual sampling method (Tenax®TA) would not reflect the concentrations measured with a continuous sampling method (Radiello®).

Photoperiod

As hypothesized in the previous part, there may have been one or more factors responsible for higher concentrations in S7 and S8 (Radiello® results). However, this doesn't explain why Tenax®TA concentrations for S8 are comparable to S6 in the chamber whereas S8 concentrations for Radiello® are much higher than S6.

One possible reason for this discrepancy may be the photoperiod. As seen in the lighting and watering of the green walls section, the Tenax®TA samples for S8 were taken towards the end of the active photoperiod of the day. Since it is known that time of day can affect stomatal uptake, the concentrations may have been lower during the Tenax®TA sampling period because of it. This implies that punctual Tenax®TA samples could be representative of the concentrations during the "daytime" period whereas Radiello® results represent the average concentrations during the week ("daytime" and "nighttime"). This could explain the higher concentrations in S8 Radiello® results whereas S8 Tenax®TA results present an opposing trend.

All of the suggestions are only hypotheses as no conclusive evidence which would allow to determine the exact cause(s) behind the irregularities can be drawn from the results. The higher sampled masses for S7 and S8 (Radiello® results) and the discrepancies between sampling methods could be caused by a mix of different factors or unknown factors.

7. Limitations

1) Lack of data

Generally speaking, the amount of data for specific sampling repetitions is low. As such, interpretation of results has been made by visual inspection only which is a major limit. Indeed, with only 2 samples per sampling day per zone at most, it is not possible to adequately verify the distribution of data in order to proceed to statistical tests to compare means between two sets of data. It may be possible to aggregate data per week as there often didn't seem to be a particular trend as far as sampling days are concerned (except for the alkane family) but this would only result in 6 samples per week which remains low.

Furthermore, the empty chamber tests were done with a different methodology to the tests with paint only and those with paint plus green walls. Because of this, they don't offer a true reference with which to confidently compare the results. That being said, interesting information can still be obtained from those tests.

In addition to that, there is only a single reference test with paint only. This test with paint only was done in summer without climatization mode. It is therefore difficult to adequately interpret the results of S6 (winter mode with green walls and paint) given the lack of reference with added VOC source only in winter mode.

Finally, there is also the problem that each test week was only tested once. Indeed, there is only a single test for each climatic sequence according to the presence of an added VOC source and/or green walls. Ideally, each test week with its specific conditions should have been repeated at least once just to evaluate how results may vary in case of a repetition of the same conditions. This would also lead to an increased amount of data usable for statistical analysis.

2) Data treatment bias

As mentioned before, only the peaks representing at least 1% of the total area in their respective chromatogram were analyzed. This leads to the aforementioned bias that can lead an identical peak among two chromatograms to be ignored in one and not the other simply because those chromatograms may have different total areas. Because of this, it is difficult to determine if certain compounds are indeed associated with specific conditions if they are only present in low quantities.

This issue could potentially be addressed by choosing a minimum area value to consider rather than a minimum percentage. This value would be an absolute value and not a relative one, meaning that every chromatogram would be affected in the same way when treating data.

Choosing which value to pick can be done retrospectively as follows :

1. Verification of total area in every chromatogram obtained during the campaign
2. Calculating the area value corresponding to 1% of the chromatogram with the lowest total area
3. Selecting only the peaks in all other chromatograms that correspond to or exceed that same value

If waiting for the experimental campaign to be over is not feasible because of the necessity to treat/ analyze data as it is acquired, then one can simply choose a value based on the first chromatograms obtained. The data treatment associated with this method can easily be accomplished with R (statistical computing and graphics software).

3) Quantification limits

Quantification is difficult for multiple reasons. The calibration range for Tenax®TA doesn't allow for the quantification of most of the data (above 50%) as the areas are too small. That being said, this problem would probably be better solved by increasing the sampled volume than by acting on the calibration range given that the latter is already established with a rather low injected mass for the minimum value of the calibration curve.

The calibration range for Radiello® analysis was mostly adequate except for the measurements in S7 and S8 which greatly exceed the upper range. The calibration could be tested with a higher upper limit. However, the calibration method has not been verified by comparison with the one described by the Radiello® providers. The results for Radiello® samples in this thesis can therefore only be compared between themselves unless the method gets validated eventually.

Finally, quantification was done in toluene equivalents and not according to the specific compounds. On top of being unable to assess the actual concentration of a compound, this may also introduce excessive variability among results for certain compounds, specifically those for which a proper specific calibration would show the GCMS detector to be less sensitive than it is for toluene. This effect can be understood according to figure 21, where it is visible that for decane the difference between two different areas would be higher if they were to be expressed in toluene equivalents given the steeper slope of toluene when compared to that of the actual compound, decane. This makes visual analysis of results more complex.

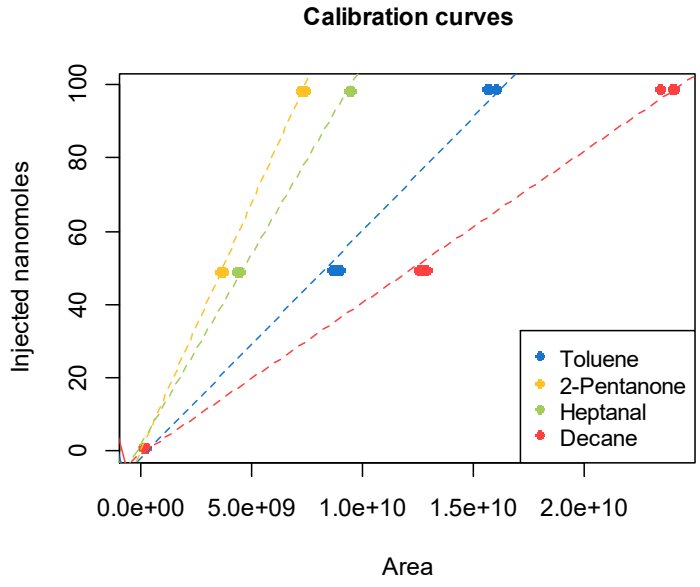

Figure 21. Comparison of different calibration curves – based on previous work unrelated to green walls (Gonçalves Prazelos, n.d.)

4) **Specific Radiello® sampling limits**

In addition to the calibration problems, there is also an issue with regards to blanks. Radiello® samples do not necessitate a blank measurement. While this is practical, some of the peaks in the sample chromatograms may not actually be from the sample but could be from some form of contamination or poorly conditioned adsorbent tube. Because no blanks were made, it is impossible to assess whether this has happened or not.

Also, Radiello® samples tend to make the TD-GCMS system, precisely the desorption trap and GC column, somewhat "dirty" in that certain peaks, namely of heavier compounds, are still found during subsequent measurements meant to verify the cleanliness of the GC column and the system. Because of this, Radiello® samples were used sparingly (only one per test week) in order to avoid having to constantly "clean" the system.

Finally, trapping flows are only known for a select number of compounds. It is then impossible to evaluate every adsorbed compound on the basis of their concentration.

5) **Specific Tenax®TA sampling limits**

As seen in the results, acetic acid was often a reoccurring compound and its concentrations were particularly high in the green wall tests. Unfortunately, the breakthrough volume for acetic acid is very low, making Tenax®TA a poor choice for accurate analysis of that compound. This is problematic as higher acetic acid emissions may be associated with the use of green walls according to the results presented in this thesis.

On another note, the punctual sampling method may overlook certain key aspects of green wall tests, namely the potential effect of the photoperiod. This could easily be fixed by planning punctual sampling during the photoperiod and outside of it as well for the sake of comparison. The fact that the photoperiod may have an effect is simply an hypothesis, it might not be a factor of interest at all.

Finally, the effect of O_3 and NO_2 on the adsorbent polymer was not considered for this thesis. This is problematic as benzaldehyde was one of the main compounds found in the analyses and it can be a degradation product of the adsorbent. However, Radiello® results also showed very high levels of benzaldehyde. O_3 and NO_2 also degrade terpenes adsorbed onto the cartridges. Because of this, the concentrations of terpenes measured by means of Tenax®TA sampling may be underestimated.

6) **Representativity with regards to real world applications**

Studies studying phytoremediation often do so by injecting an amount of pollutant into a sealed chamber where plants are housed. These containers are often small and the plants represent an unrealistic volume in them. Furthermore, the single injection is not representative of real world emissions which are continuous. Finally, these studies often evaluate phytoremediation over the course of multiple days in the sealed chamber. This means

that the pollutants are available for phytoremediation for unrealistic periods of time given that outdoor to indoor air exchange would naturally reach equivalent pollutant reduction much faster (Cummings and Waring, 2020).

In the experiments described in this thesis, the plants do not represent an unrealistic volume inside the chamber. There is also a continuous emission in the form of building emissions and semi-continuous emission in the form of the painted gypsum board as it dries. This experiment is however in sealed conditions during an entire week which may provide an unrealistically long time for interaction between pollutants and plants.

Also, as seen for Tenax®TA results, more than 50% of the individual chromatogram peaks kept for analysis could not be quantified as previously mentioned. The sampled volume was simply too low for quantification. From another perspective, the level of VOC contamination in the chamber may also be too low to be representative of an unhealthy indoor environment. Furthermore, the use of a painted gypsum board may not amount to unhealthy/representative concentrations of VOCs given the high volume of the chamber and buffer, the lower VOC concentration in the paint itself (1g/L), and the low surface area of the board. However, determining what constitutes unhealthy indoor air quality is difficult given the complexity of VOC profiles and concentrations.

That being said, many phytoremediation studies tend to use higher concentrations of contaminants (ppm range). In contrast, the experiments presented in this thesis can be of value as they offer a distinct case study with lower concentrations. Also, given that passive green wall phytoremediation is limited by the rate of pollutant diffusion as seen in the literature presented in part 1, higher chamber concentrations could theoretically be more easily treated if no factor other than the rate of diffusion is considered.

7) <u>TD-GCMS method</u>

As seen in the compound qualification results, certain difficulties were encountered when assessing what compound a specific peak can be attributed to. This was particularly difficult for the reoccurring peak at around 29.7min retention time. This peak could be attributed to benzaldehyde or various other terpenes.

This problem was also seen for the peak at around 24.2min retention time which could be attributed to multiple compounds such as xylene, furfural, 3-furaldehyde or even nonane. Such difficulties were found but to a lesser extent for the peaks at 30.1min where hexanoic acid and octanal peaks were often too close to each other.

Because of this, the TD-GCMS method could be changed by making the temperature increase faster in the hopes of obtaining a better peak separation. This could be envisioned since compounds tend to only leave the column after about 10 minutes with very few exceptions.

8) <u>Experiment complexity</u>

Many elements come into play in the experiments such as the watering of the plants, entrances and exits into the chamber during tests, and plant health among others. All of these factors can influence the results in unpredictable ways.

8. Prospectives

Because of the many limitations presented in this thesis, the experiments could be repeated to address them. The entire campaign could be repeated by ensuring that :

- NO_2 and O_3 filters are used to prevent the degradation of the adsorbent polymer and adsorbed terpenes in Tenax®TA samples
- The empty chamber tests are done with the same methodology as the subsequent tests
- The tests with paint only are done for all climatic simulations (or at least winter mode and one of the summer modes)
- The sampling methodology is fit for the purposes of the campaign (sampling volume, TD-GCMS method, calibration ranges …)
- Multiple trials are scheduled for the same conditions
- The health of the plants is maintained as best as possible
- Ensuring repeatable conditions between tests (same photoperiods at the same hours, same watering schedules, etc.…)

This however could lead to an unrealistic amount of trials that can span a very long time. The experimental campaign could therefore be shortened by only considering the worst case climatic sequence for VOC emissions for example (summer simulations). The length of each test could also be shortened since no particular trend was observed between different test days (based on visual observations of the data). Shortening the length of the test week and limiting the tests to a single climatic sequence may not be possible depending on the needs of the B.E.M.S. team.

For the purposes of the G4IW project, aluminum was placed on the walls to limit adsorption and exfiltration as much as possible even though air circulation was allowed between chamber and buffer. This unfortunately severely impacted the B.E.M.S. teams ability to conduct their research as aluminum greatly alters the thermal properties of the walls. Because the majority of phytoremediation tests seen in the literature are done in very controlled settings, the G4IW tests could conversely be repeated without aluminum to represent a more accurate situation in accordance with real life applications. This would make the project more efficient in terms of allowing other teams to collect their data in parallel.

In the same vein, tests could also be done while allowing a simulation of natural ventilation between the exterior environment and the chamber/buffer during the experiments to simulate real life applications. In all cases, the effect of the green wall has to be determined by comparison with control measurements where the green walls are not present. However, allowing for ventilation would likely impact the ability of the B.E.M.S. team to properly conduct their research.

On another note, different VOC sources could be tested. In the case of this thesis, a small painted gypsum board was used. This may not be the most pertinent choice of a VOC source given because of lack of representativity of practical cases :

a) When done painting, inhabitants usually vacate the room and optimize natural ventilation to evacuate the odors of the paint
b) The surfaces painted are much larger than the single gypsum board used

Based on these points, it may be interesting to reconsider the experiment to be more representative of conditions in actual homes. This may be done by painting a much larger surface which would most likely require a revision of the sampled volumes to avoid saturation of adsorbent tubes/ cartridges. Again, this may not be the most relevant experiment as inhabitants instinctively know to increase natural ventilation to evacuate paint emissions which means that green walls wouldn't be considered for such specific, unrepeated conditions, especially when considering that newly painted rooms are empty and green walls aren't likely to be installed in those rooms. However, it could be interesting to assess the green walls' capacity to remediate the air in painted rooms for the weeks or months following the painting. That being said, an experiment evaluating this would require very long test periods, especially when considering the need for controls for comparison, and may therefore be unrealistic.

A seemingly more pertinent experiment meant to simulate actual homes would be to test the green walls in a completely furnished room. In this case, the VOCs emitted would be typical of those found in homes in terms of composition but in concentrations as well if natural ventilation is simulated for example. Evidently, the potential capacity of the green walls to purify indoor air should be assessed by comparison with adequately designed control tests without the green walls.

Also, tests with a completely different methodology could be planned in order to study some other factors of interest. It is possible to test phytoremediation according to the photoperiod by taking punctual samples during day time conditions and during nighttime conditions for comparison. This could be interesting given the discrepancies found between Radiello® results and Tenax®TA results for S8 that may or may not be related to it. It is important to note that the photoperiod may not be a factor of interest at all or, if it is, it might only be so in conjunction with other factors such as plant stress/ higher microbial activity or building related factors leading to higher concentrations. Based on the results of the experimental campaign, it is impossible to confidently determine the cause behind the discrepancies.

Generally speaking, any future experiments would greatly benefit from a strong preplanning phase in which the methodological aspects are precisely determined well in advance in accordance with the needs of all teams involved. While the G4IW project was indeed the subject of multiple reunions prior to the start of the experimental campaign, and the methodological aspects were for the majority determined, some specifics of the methodology weren't completely finalized which left a few grey areas in the project that had to be resolved during the campaign under planning constraints. These grey areas can also be particularly problematic given that the teams aren't versed in each other's domains. Because of this, a particular issue that is unknown for one team but is known by another may not be reported because the latter team simply cannot recognize it as an issue according to their experiments. This highlights the need for effective communication and coordination between teams. It is however important to note that many potential issues simply cannot be predicted in advance, meaning that problem solving during the experimental campaign is a necessity even with precise, fully realized preplanning.

Conclusion

The results obtained from this experimental campaign are inconclusive. Indeed, it is difficult to determine the exact effect of the green walls on indoor air quality given the discrepancies between different sampling methods and the multitude of confounding factors.

According to Tenax®TA results, the tests with green walls (S6 and S8) are generally associated with favorable results, meaning a reduction of VOC concentrations inside the chamber, when compared to tests without green walls. Radiello® results on the other hand present one test week with green walls (S6 – winter mode) with favorable results but two test weeks (S7 and S8 – summer modes) with unfavorable results when compared to tests without green walls. Based on this, we can determine a common trend for S6 and an opposing trend for S8 when comparing both sampling methods. Interestingly, green walls tests seem to be associated with a favorable effect in terms of propylene glycol reduction inside the chamber irrespective of the sampling method.

Multiple hypotheses were explored in order to assess the potential cause behind the discrepancies in S8 while considering the commonality in S6 between the sampling methods. These hypotheses are for example heightened building emissions, and/or green wall emissions because of accumulated plant stress, in conjunction with a potential role of the photoperiod. However, these hypotheses are nothing but conjectures as there is no strong evidence to confidently lend credence to them. Indeed, the complexity of the experiments is such that pinpointing the exact cause behind the discrepancies is simply impossible. This highlights the necessity of maintaining rigorous and repeatable conditions between each of the test weeks in order to limit confounding factors.

Furthermore, many limitations have been brought forth such as the low number of samples, lack of statistical analysis, particular limits of the equipment, decrease in plant health, and general methodological problems such as inadequately designed controls in the case of empty chamber tests, among others. A major limitation is that comparisons were only made on the basis of visual analysis of data, meaning that trends observed may not be significant.

While the results are inconclusive, this thesis opens the door for further research. Indeed, the assessment of the methodology and limitations presented herein should ensure that future tests involving green walls in the context of the G4IW project are of higher quality in terms of data collection, data treatment, and general experimental design. Furthermore, different experimental designs could be envisioned in the hopes of obtaining a more accurate representation of actual homes such as tests with furniture as VOC sources.

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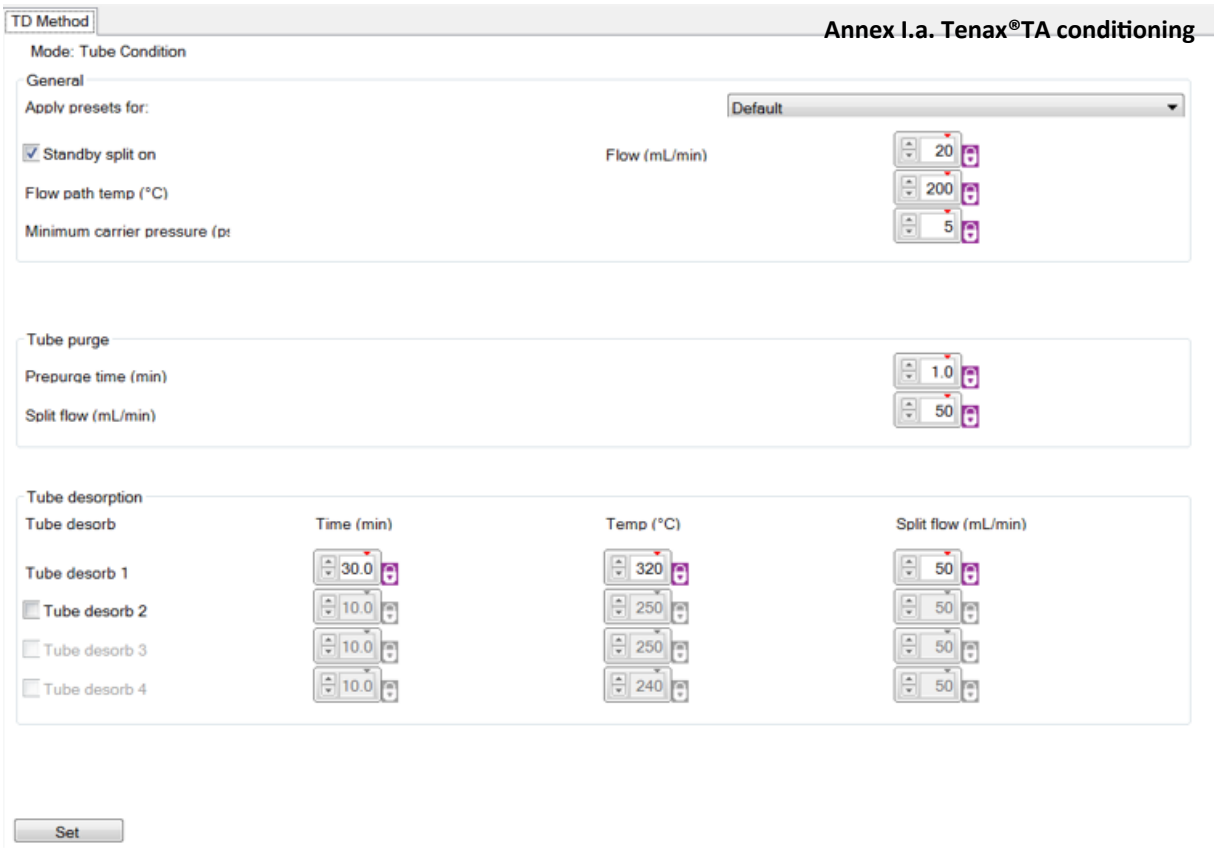
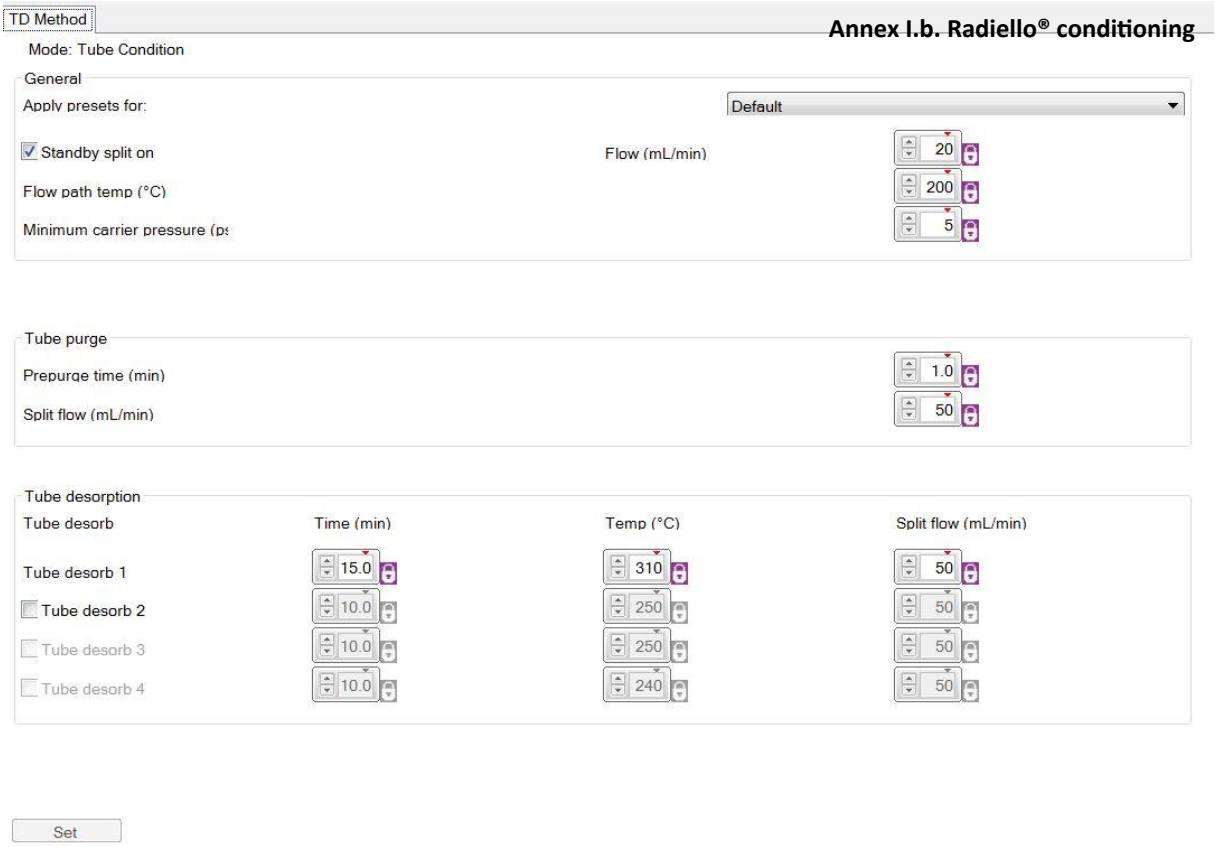
Annex I : thermal desorption programs

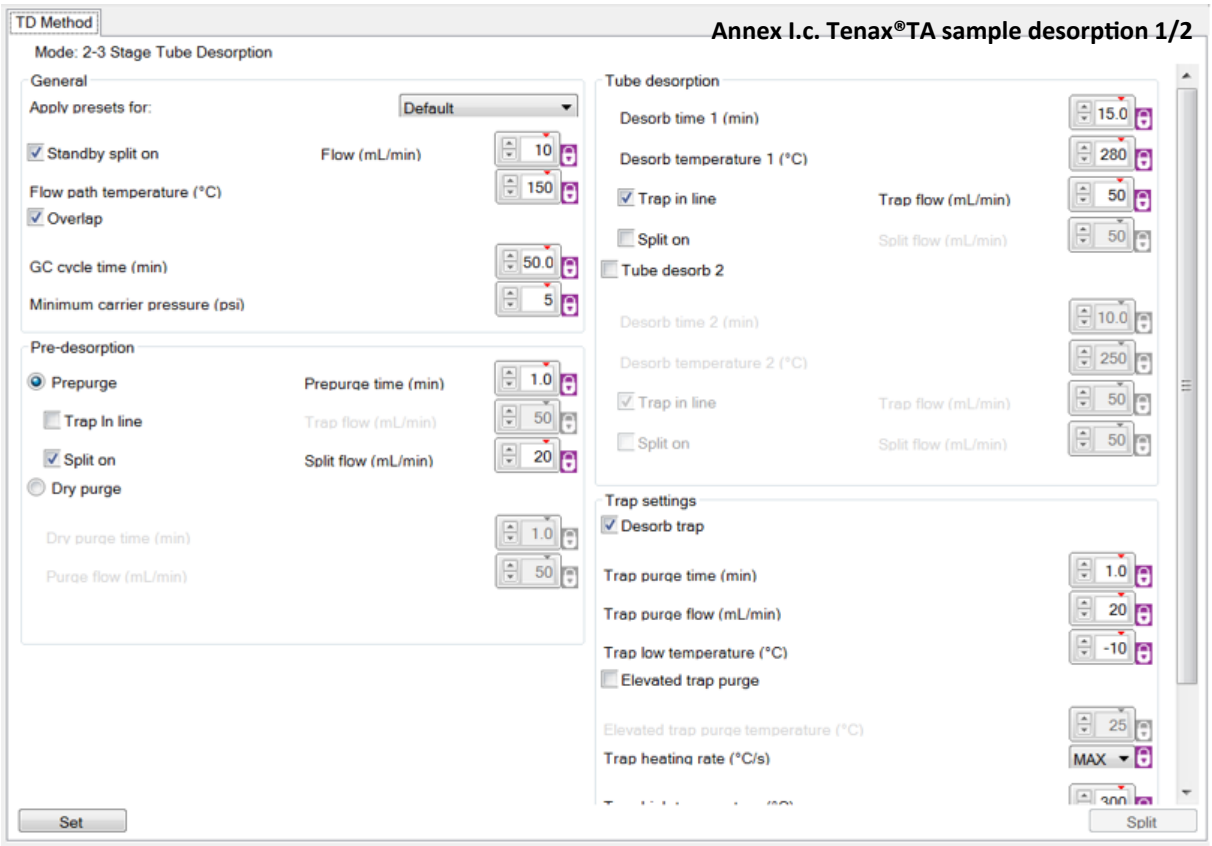
Annex I.a. Tenax®TA conditioning



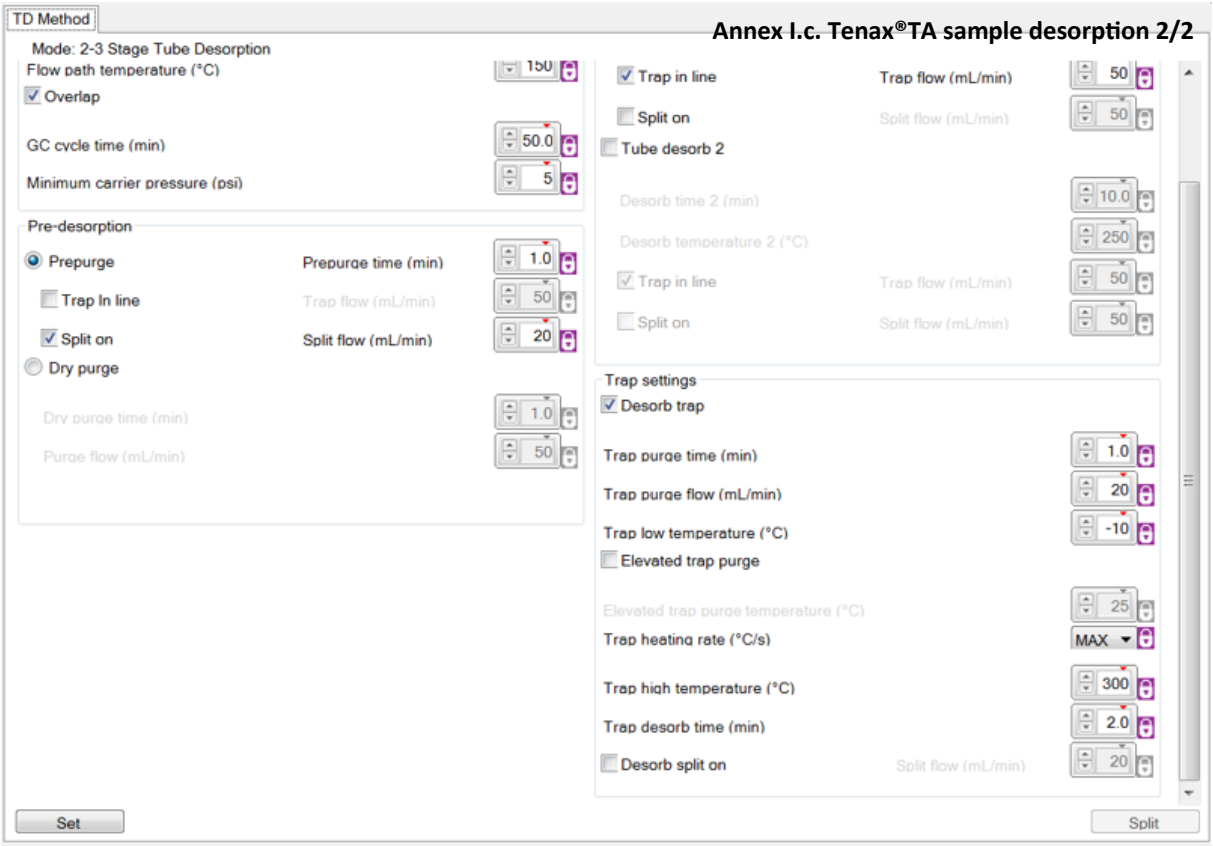
Annex I.b. Radiello® conditioning



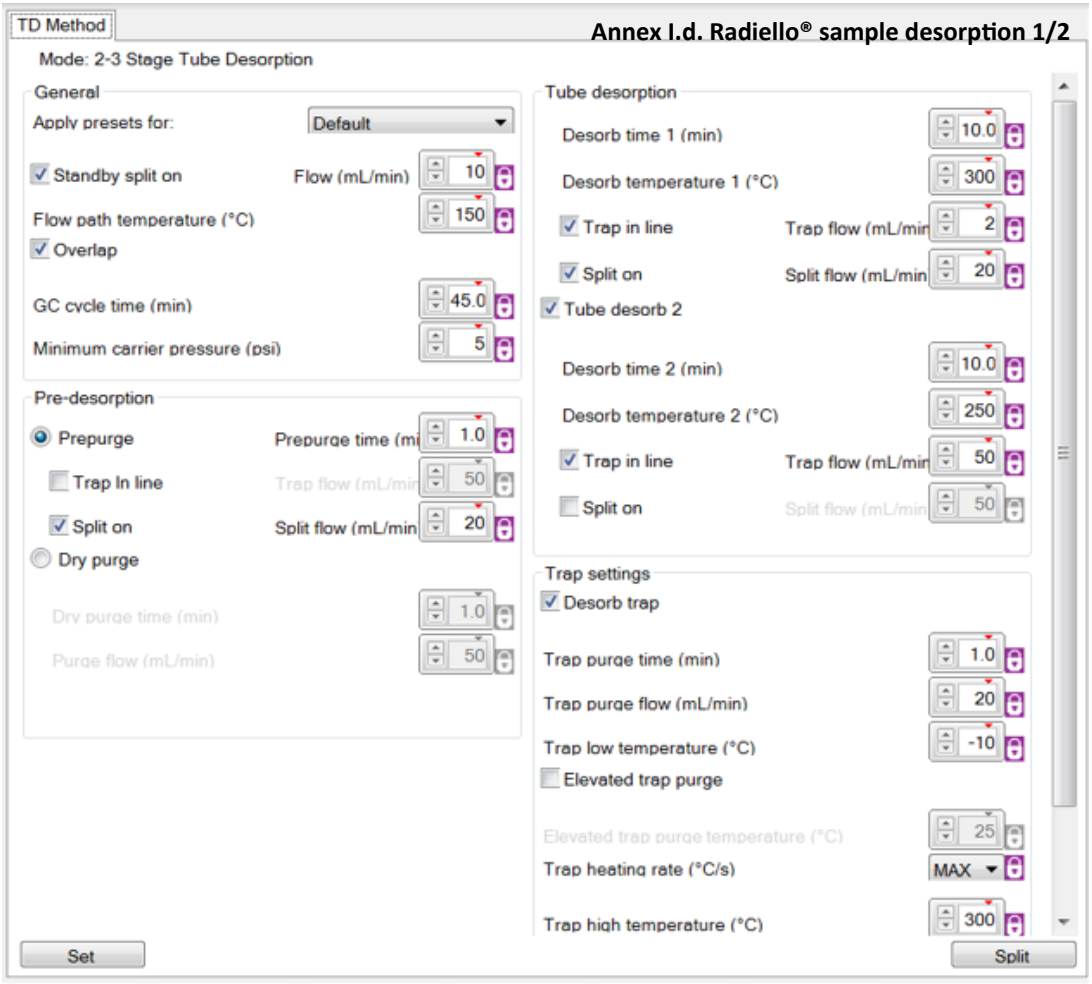
Annex I.c. Tenax®TA sample desorption 1/2



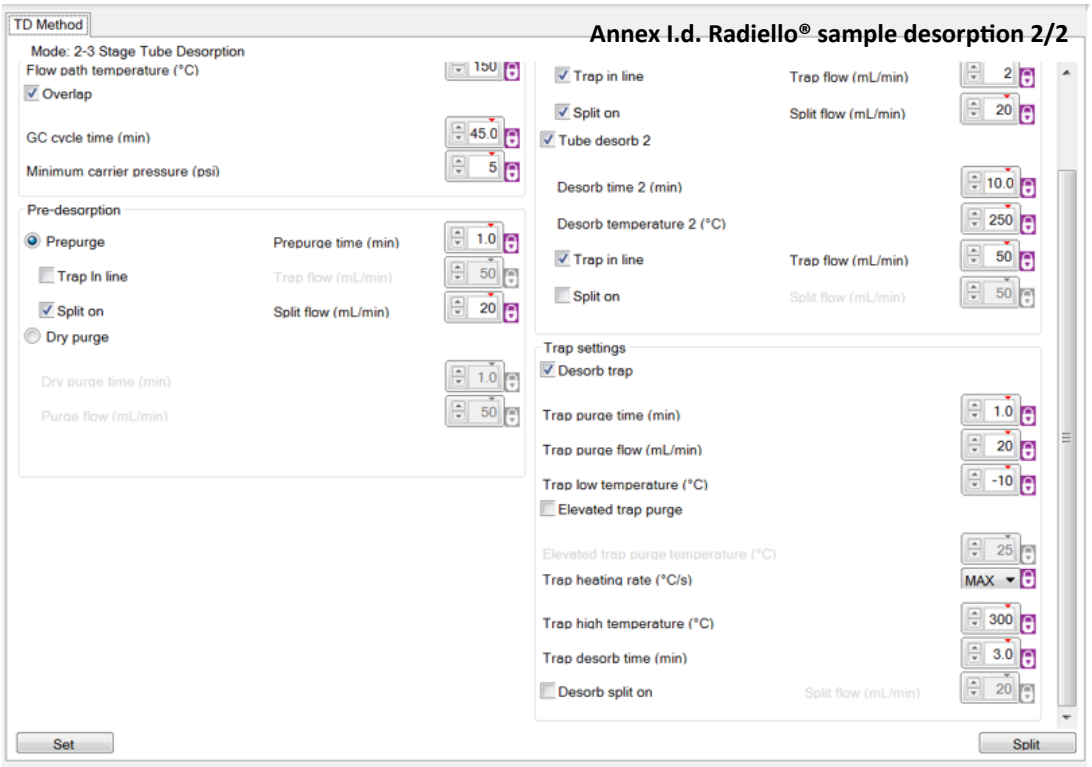
Annex I.c. Tenax®TA sample desorption 2/2



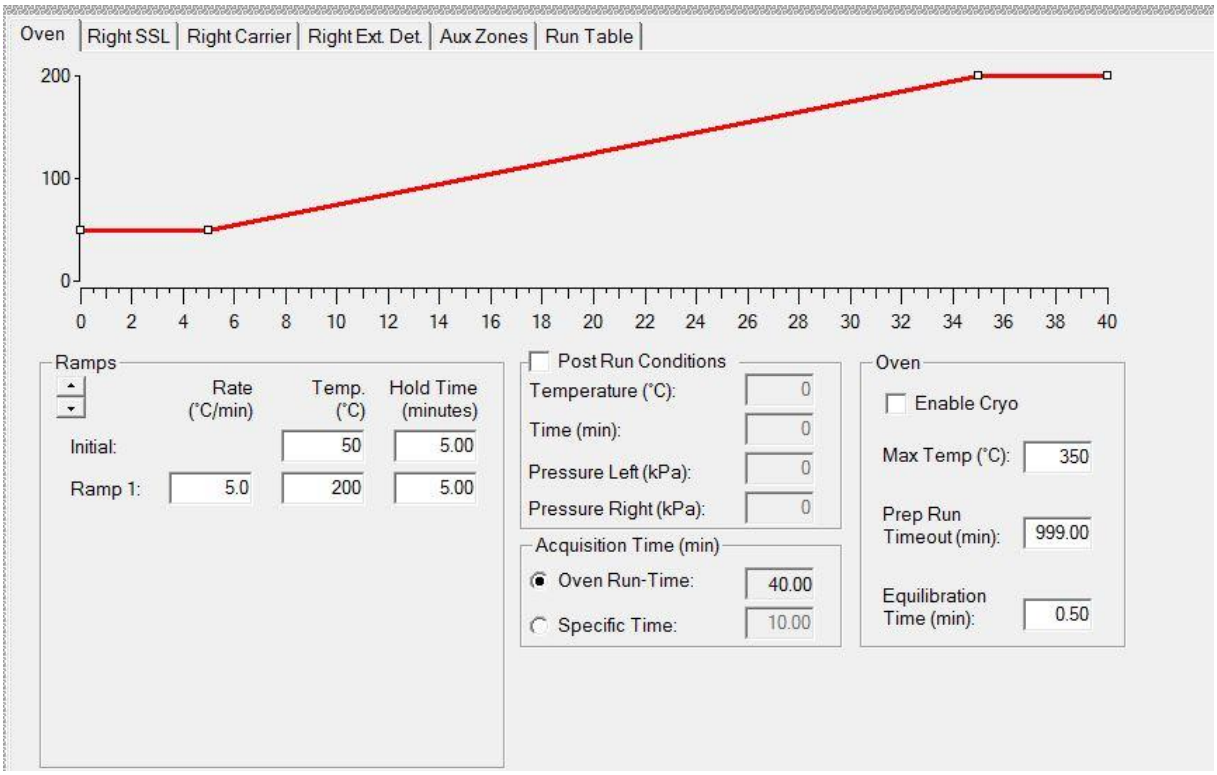
Annex I.d. Radiello® sample desorption 1/2



Annex I.d. Radiello® sample desorption 2/2



Annex II : chromatography oven temperature settings

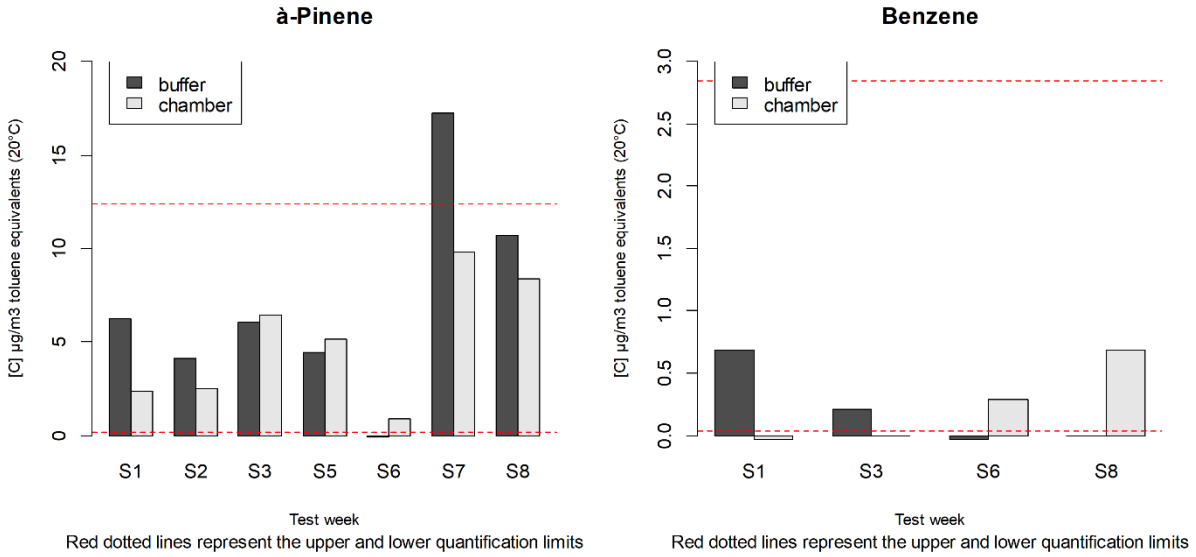


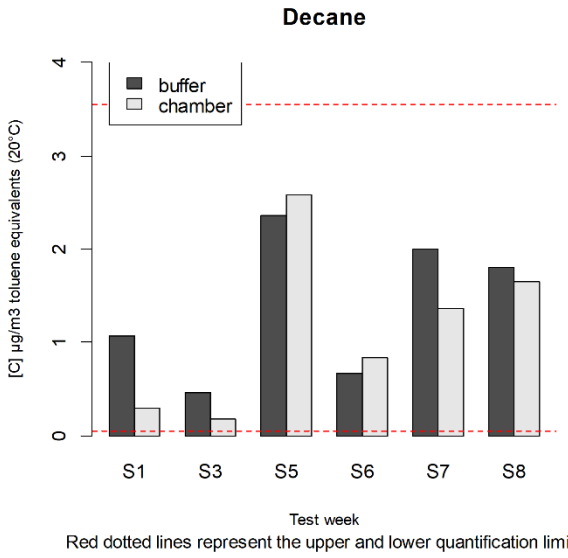
Annex III : list of the 5 highest peaks in each Radiello chromatogram[7]

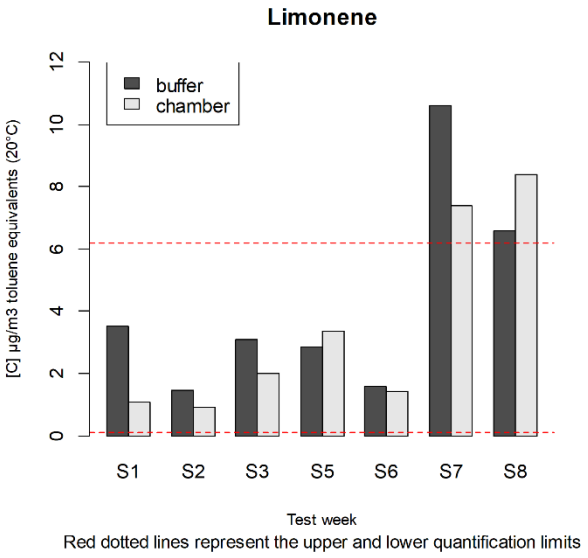
W	Compound	Buffer (ng)	Compound	Chamber (ng)
	Acetic acid	1610	Dodecane	963
	Dodecane	902	Benzene, 1-methyl-4-(1-methylethenyl)-	386
	Benzaldehyde	433	Benzaldehyde	360
	Benzene, 1-methyl-4-(1-methylethenyl)-	389	Benzene, 1-methyl-2-(1-methylethyl)-	200
S1	Propylene Glycol	381	à-Pinene	129
	Benzaldehyde	848	Benzaldehyde	941
	Propylene Glycol	603	Benzene, 1-methyl-4-(1-methylethenyl)-	710
	Benzene, 1-methyl-4-(1-methylethenyl)-	433	Propylene Glycol	614
	Styrene	412	Benzene, 1-methyl-2-(1-methylethyl)-	578
S2	Dodecane	377	Dodecane	489
	Benzaldehyde	1140	Benzaldehyde	885
	Dodecane	614	Dodecane	689
	Propylene Glycol	574	Benzene, 1-methyl-4-(1-methylethenyl)-	534
	Benzene, 1-methyl-4-(1-methylethenyl)-	566	Propylene Glycol	487
S3	Benzene, 1-methyl-2-(1-methylethyl)-	442	à-Pinene	407
	Benzaldehyde	907	Benzaldehyde	971
	Propylene Glycol	640	Propylene Glycol	783
	Decane	521	Benzene, 1-methyl-4-(1-methylethenyl)-	626
	Benzene, 1-methyl-4-(1-methylethenyl)-	455	Decane	571
S5	Benzene, 1-methyl-2-(1-methylethyl)-	452	Benzene, 1-methyl-3-(1-methylethyl)-	562
	Acetic acid	1100	Benzaldehyde	406
	dodecane	503	Acetic acid	350
	Benzene, 1-methyl-4-(1-methylethenyl)-	263	Dodecane	291
	Benzaldehyde	231	Benzene, 1-methyl-2-(1-methylethyl)-	263
S6	Limonene	195	Benzene, 1-methyl-4-(1-methylethenyl)-	257
	Benzaldehyde	4010	Benzaldehyde	2570
	Benzene, 1-methyl-4-(1-methylethenyl)-	2230	Dodecane	2010
	Benzene, 1-methyl-2-(1-methylethyl)-	1640	Benzene, 1-methyl-4-(1-methylethenyl)-	1770
	Limonene	1340	Benzene, 1-methyl-2-(1-methylethyl)-	1220
S7	Propylene Glycol	1270	Acetic acid	1180
	Benzaldehyde	3050	Benzaldehyde	2950
	Benzene, 1-methyl-4-(1-methylethenyl)-	2530	Benzene, 1-methyl-4-(1-methylethenyl)-	2070
	Benzene, 1-methyl-2-(1-methylethyl)-	2040	Acetic acid	1550
	Propylene Glycol	1680	Benzene, 1-methyl-4-(1-methylethyl)-	1510
S8	Octanal	1380	Dodecane	1110

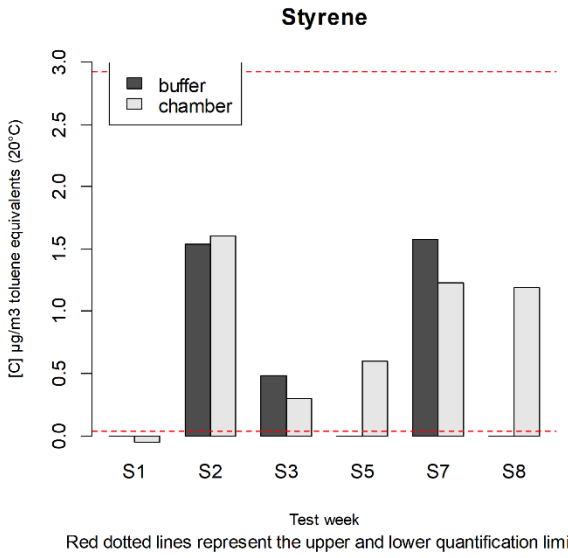
[7] Values in toluene equivalents - red values indicate that they exceed the calibration range used (min = 10.2ng ; max = 779ng)

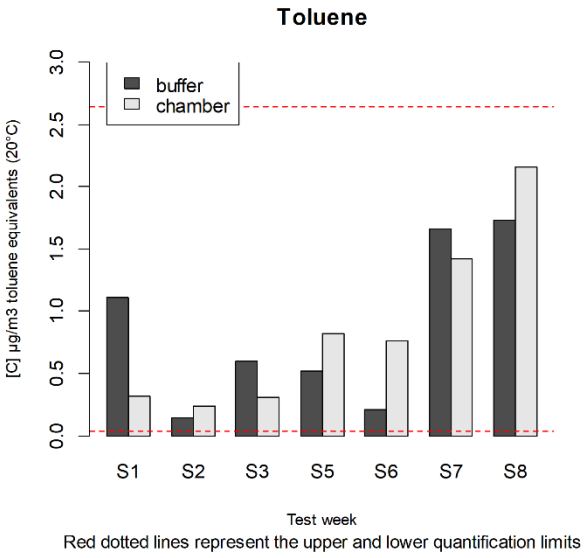
Annex IV : concentrations according to Radiello® samples

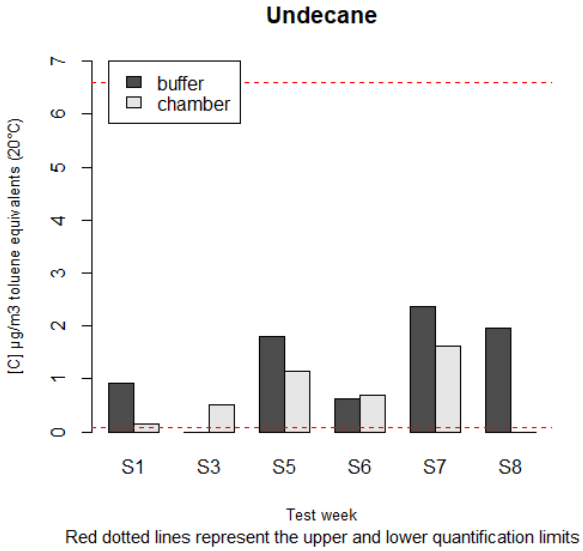






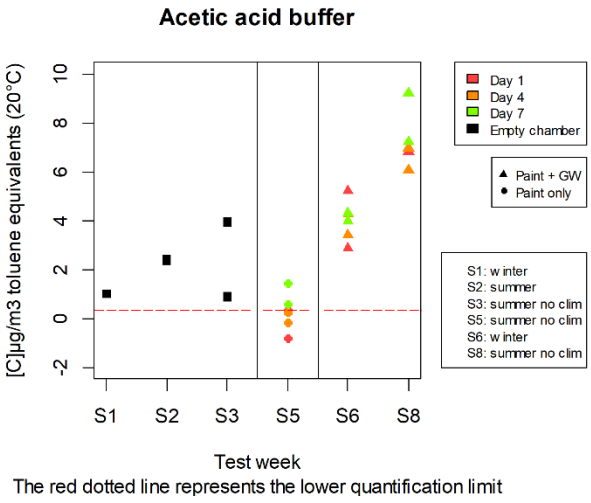




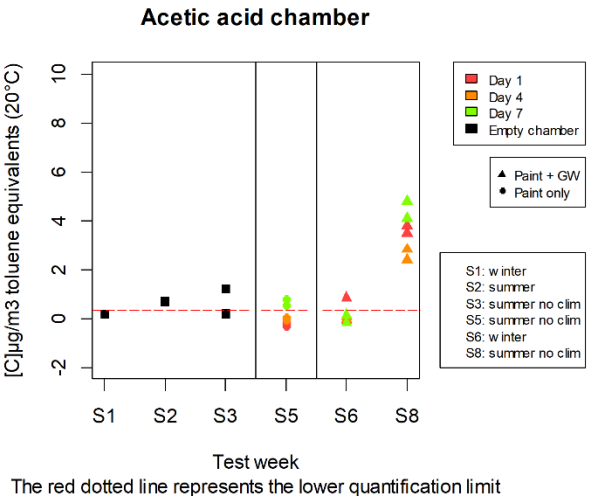


Red dotted lines represent the upper and lower quantification limits

Annex V : concentrations according to Tenax®TA samples



The red dotted line represents the lower quantification limit



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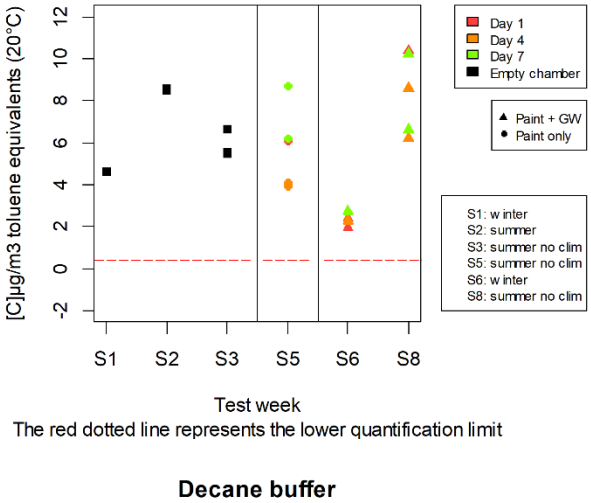

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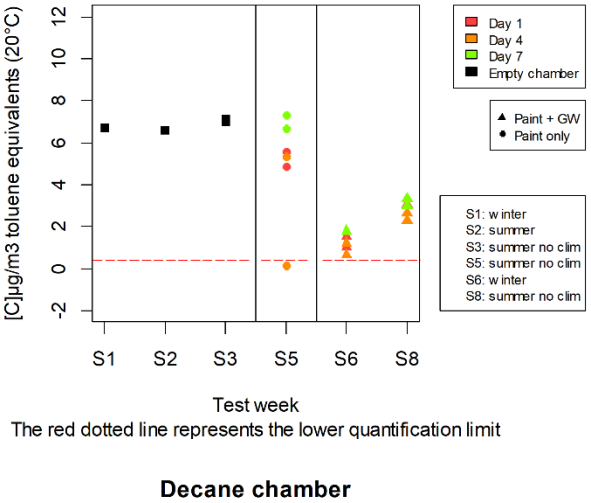

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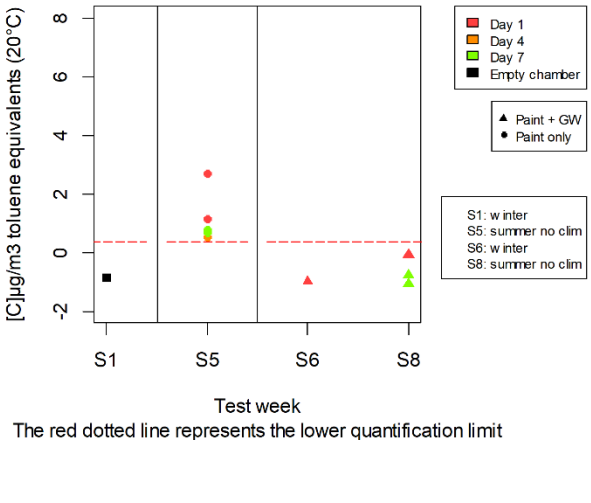

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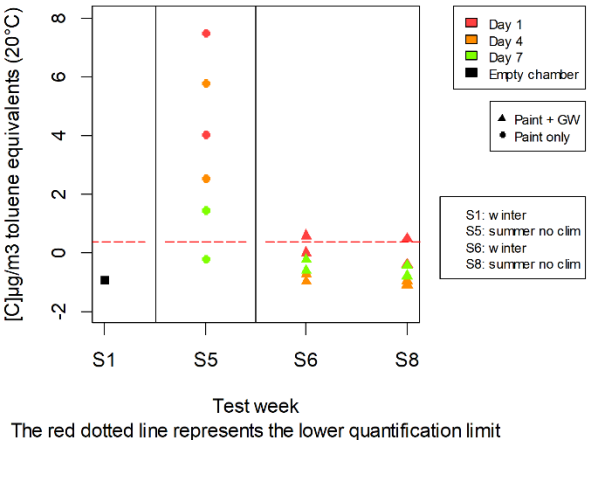
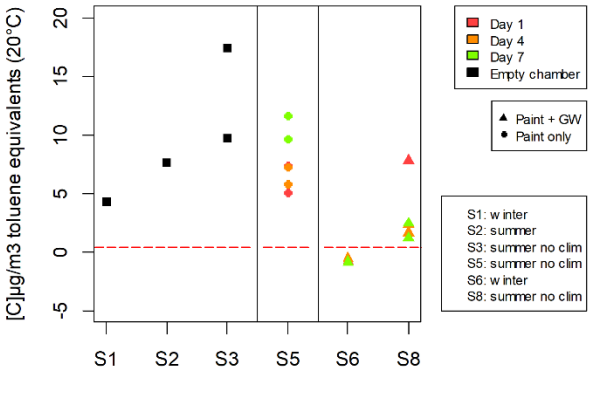


The red dotted line represents the lower quantification limit

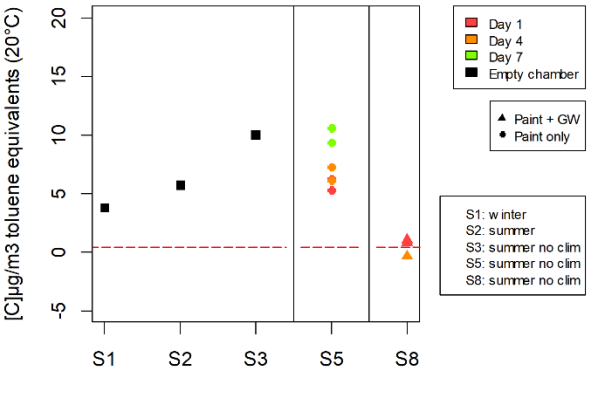
Propylene Glycol buffer



Test week

The red dotted line represents the lower quantification limit

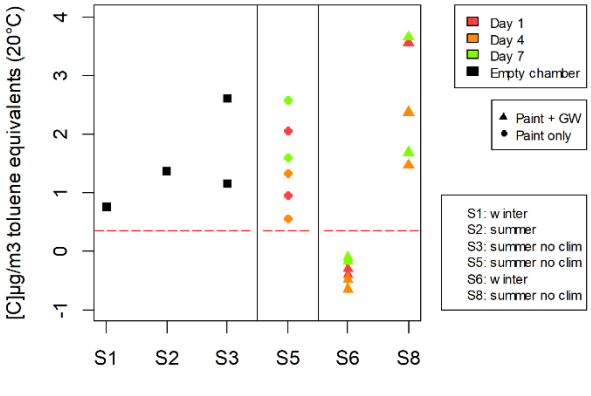
Propylene Glycol chamber



Test week

The red dotted line represents the lower quantification limit

Hexanal buffer



Test week

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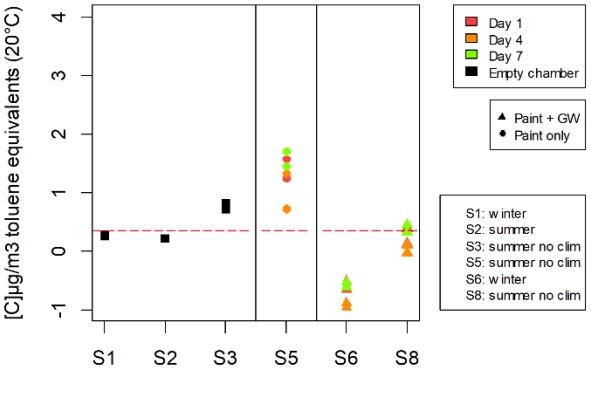
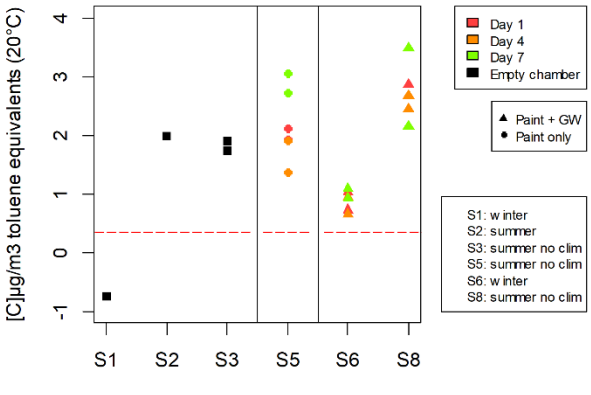
Hexanal chamber



Test week

The red dotted line represents the lower quantification limit

Nonanal buffer



Test week

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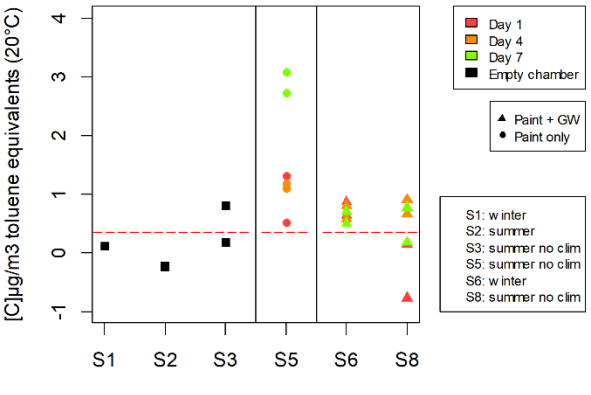
Nonanal chamber



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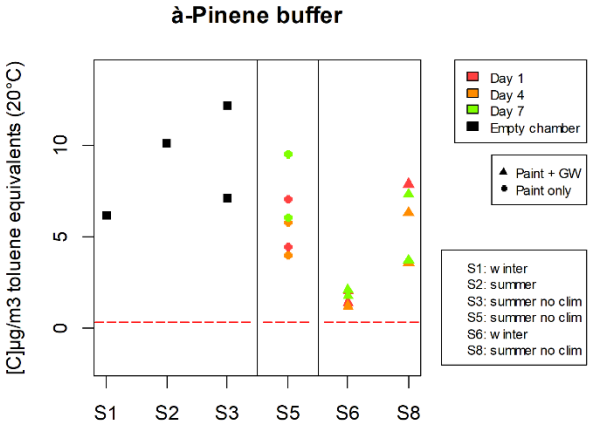

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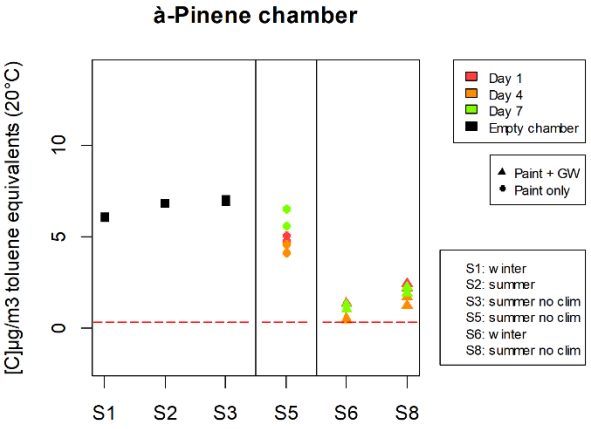

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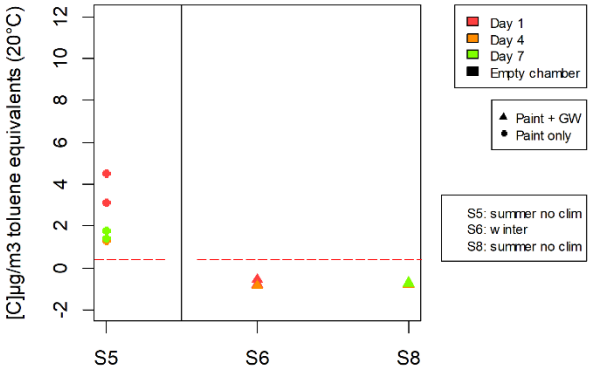

Test week

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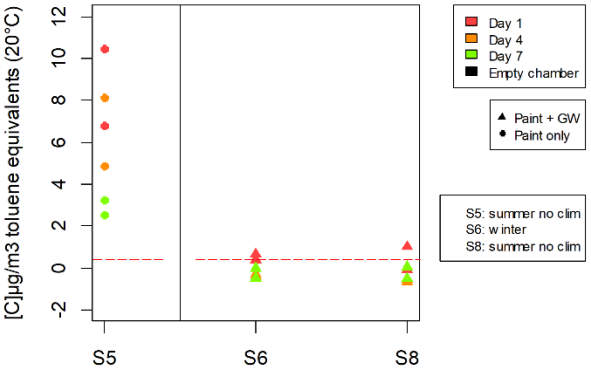

Test week

The red dotted line represents the lower quantification limit

Abstract

This Master's thesis concerns the assessment of the effect of passive green walls on indoor air quality in terms of VOCs by means of punctual (Tenax®TA) and continuous (Radiello®) sampling in the context of the “Green4Indoor Wallonia” project.

The tests were conducted in an office sized, temperature controlled chamber submitted to climatic sequences simulated in a buffer zone in order to replicate exterior temperature fluctuations in summer and winter. The composition and concentrations of VOCs inside the chamber were assessed in empty chamber tests, tests with an added VOC source (painted gypsum board), and tests with green walls plus an added VOC source, all according to the various climatic simulations. The samples were analyzed by TD-GCMS and results were assessed through visual inspection of data by means of graphical representations.

The results show that tests with green walls during winter simulations present lower VOC concentrations than tests without green walls irrespective of sampling methods. For summer simulation tests with green walls, Tenax®TA results also present lower VOC concentrations whereas Radiello® results present higher VOC concentrations when compared to tests without green walls. Given the multitude of constraints, confounding factors and problems encountered, the exact cause behind the discrepancies cannot be determined. The limitations and shortcomings of the experimental methodology were also discussed in order to propose improvements for potential future experiments involving green walls.