Doctorate (PhD) Dissertation

Kamirán Áron Hamow

Hungary, Gödöllő

2024

HUNGARIAN UNIVERSITY OF AGRICULTURE AND LIFE SCIENCES

METHOD DEVELOPMENT AND EVALUATION FOR SAMPLING, HEADSPACE GC-MS ANALYSIS AND PREDICTIVE USE OF VOLATILE ORGANIC COMPOUNDS FROM ECONOMICALLY IMPORTANT PLANTS

(MÓDSZERFEJLESZTÉS ÉS -ÉRTÉKELÉS GAZDASÁGILAG FONTOS HASZONNÖVÉNYEK LÉGTERÉBŐL SZÁRMAZÓ SZERVES ILLÉKONY VEGYÜLETEK MINTAVÉTELEZÉSÉHEZ, GC-MS ANALÍZISÉHEZ ÉS ELŐREJELZÉSI CÉLÚ FELHASZNÁLÁSÁHOZ)

PhD Dissertation

DOI: 10.54598/005360

KAMIRÁN ÁRON HAMOW

Hungary, Gödöllő

2024

Doctoral school: Plant Sciences

Discipline: Plant breeding and horticultural sciences

Head of School: *Prof. Lajos HELYES (CMHAS)*
Professor
MATE

Supervisor: *Prof. Katalin POSTA (DSc)*
Professor
MATE
Institute of Genetics and Biotechnology

.....	.....
Prof. Lajos Helyes	Prof. Katalin Posta
Approved by head of school	Approved by supervisor

Contents

List of Abbreviations

VOC(s)	Volatile organic compound(s)	ToF MS	Time of flight mass spectrometry
GC-MS	Gas chromatography coupled to mass spectrometry	GC	Gas chromatography
BVOC(s)	Biogenic volatile organic compound(s)	LED	light-emitting diode
BBVOC(s)	Biomarker biogenic volatile organic compound(s)	HS	Headspace
HUN-REN CAR	Hungarian Research Network Centre for Agricultural Research	DHS	Dynamic headspace sampling / analysis
AI	Artificial intelligence	PTFE	Teflon, Polytetrafluoroethylene
SPME	Solid phase microextraction	DVB	Divinylbenzene
FAO	Food and Agricultural Organization	MW	Molecular weight
PM	Powdery mildew	PTV	Programmable temperature vaporization
Bgt.	*Blumeria Graminis*	CIS	Cooled injection system
SPE	Solid phase extraction	PEG	Polyethylene glycol
KSH	Hungarian Central Statistical Office	EAD	Electroantennographic detection
MEP	Methylerythritol phosphate	PID	Photoionization detector
IPP	Isopentenyl diphosphate	EI	Electron impact
DMAPP	Dimethylallyl diphosphate	RI	Retention index
KEGG	Kyoto encyclopedia of genes and genomes	MS/MS	tandem mass spectrometry
GLV	Green leaf volatiles	FT-IR	Fourier-transform infrared spectroscopy
LOX	Lipoxygenase	GCxGC	two dimensional gas chromatography
PAL	Phenylalanine ammonia lyase	DAI	Days after inoculation
ROS	Reactive oxigene species	IS or ISTD	Internal standard
MeJA	Methyl jasmonate	SIM	Selective ion monitoring
SAR	Systematic acquired resistance	O.D.	Outer diameter
BSIVs	Biotic stress induced volatiles	NIST	National Institutes of Standards and Technology
HIPVs	Herbivore induced volatiles	EPA	Environmental Protection Agency
PIVs	Pathogen induced volatiles	NIH	National Institutes of Health
·OH	Hydroxyl radical	BLAST	Basic local alignment search tool
AMF	Arbuscular mycorrhizal fungi	PCA	Principal component analysis
AM	Arbuscular mycorrhizal	TIC	Total ion chromatogram
EM	Ectomycorrhizal	EIC	Extracted ion chromatogram
ABA	Abscisic acid	m/z	Mass-to-charge ratio
SA	Salicylic acid	S/N	Signal-to-noise ratio
PAS	Photoacoustic spectroscopy	BP	Boiling point
PTR-MS	Proton transfer reaction mass spectrometry	LoD	Limit of detection
GC-FID	Gas chromatography coupled to flame ionization detector	LoQ	Limit of quantification
SBSE	Stir bar sorptive extraction	OTL	1-octene-3-ol
PDMS	Polydimethylsiloxane	10-HPODE	10-hydroperoxyoctadecadienoic acid
TDU	Thermal desorption unit	SOA	Secondary organic aerosols

1. INTRODUCTION

Plants produce a wide range of volatile organic compounds (VOCs) during their metabolic processes. Almost any part of the plant—roots, stems, leaves, flowers, and fruits—is capable of producing, storing, and releasing these compounds (Owen et al. 2002; Köllner et al. 2004; Laothawornkitkul et al. 2009; Crespo et al. 2012; Colquhoun et al. 2013). Numerous studies have already focused on identifying plant scent compounds (Dicke and Loreto, 2010; Spinelli et al. 2011). The emission of these compounds is influenced by the plant's age and phenological stage (Loreto and Schnitzler, 2010), as well as the presence of abiotic and biotic stressors**.** The wide spectrum of VOCs produced by the plants can be excreted in significant amounts during physical damage, pest injury, or pathogen infection. These VOCs are released even hours or days after the stress event (Dudareva et al. 2013). Fungal diseases are accompanied by the immediate release of fungal VOCs when they colonize a substrate-rich medium, such as cereal grains (Magan and Evans 2000). The analysis of the volatile headspace of plants can point to a yet visually undetectable infection, and the pathogen may even be identified selectively (Dudareva et al. 2013). Numerous research groups have already dealt with the detection of plant infections, separation from healthy plants, and analysis of volatile compounds (Schuh et al. 1997; Loreto et al. 2006; Derendorp et al. 2010; Jansen et al. 2010a; Jansen et al. 2010b; Elad et al. 2016; Kasal-Slavik et al. 2017).

E-nose Laboratory has been working on "Analysis of Natural Odor Patterns and Their Agricultural Applications" since 2017 in Martonvásár, Hungary, at the HUN-REN Centre for Agricultural Research (CAR). The main goal of our research was to develop a new type of artificial sensory system that can determine the complex odor compositions of agricultural plants and allow for early detection of pests and pathogens in agricultural crops based on changes in their scent composition. For this reason, a baseline task was to collect VOCs and analyze them by gas chromatography coupled to mass spectrometry (GC-MS) measurements from healthy and infected or diseased plants. In addition, establish biomarker biogenic volatile organic compounds (BBVOC) of the different adverse states at various plant growth and infection stages to build a database of related VOC patterns. The purpose of the database included analysis by machine learning and AI-based statistics, thus enabling the development of prediction algorithms so stable biomarkers can be targeted by other techniques.

There are many methods for extracting and collecting volatile compounds from plants. Previously, destructive solvent extractions were widespread, but nowadays, non-destructive sampling techniques are more popular. One type of scent collection is the so-called static method, in which

equilibrium is established between the sample and the volatile compounds in the airspace above it, and then sampling takes place. The other type is the dynamic method, in which the vapor phase is continuously renewed and equilibrium is not established. Among the static sampling techniques, SPME (solid-phase microextraction) (Arthur and Pawliszyn, 1990) is commonly used, while among the dynamic methods, open or closed system volatile collection is the most widely used (Vuts et al. 2018). With the aforementioned techniques, our group had the opportunity to collect various plant volatile compounds and detect and monitor changes in the plant's volatile profile. A non-invasive sampling and analysis approach where samples can be stored and reanalyzed if needed with cost effectiveness and field portability for sampling, the pull-type open-loop DHS VOC collection followed by SPE and GC-MS analysis, was chosen. The choice for this approach and its adaptation, implementation, refinement, and testing exhibit unique challenges since, despite its widespread use by various fields in science, little do we know about performance parameters affecting the accuracy of such methods, also detailed and comprehensive know-how descriptions are gaps in scientific literature. After adaptation and testing application of approach and workflow for sampling and analysis of different plant-pathogen and/or other diseased states followed by characterization of the volatile fingerprint and its components as well as their abundance. From this complex dataset it is possible to establish candidates for Biomarker Biogenic Volatile Organic Compounds (BBVOCs), select the most promising combinations, and study the identified biomarkers and their emission characteristics. Early detection of infections and pests can be crucial for effective, environmentally friendly defense, precision agricultural techniques, early disease detection, and also aid in patho- and chemotyping. Pathogen-derived BVOCs (Biogenic Volatile Organic Compounds) can substantially and dynamically modify the VOC profile in and above a crop field or even on a larger scale and may also function as biomarkers for the detection of or forecasting of early infections (Li et al. 2019). However, surprisingly little is known at present about the composition and quantity of BVOC emissions specifically from crop fields (Guenther, 2013; Bachy et al. 2016 and 2020), which is in contrast with their comparatively great abundance. Therefore, it is of high priority that their precise composition, temporal and geographical distribution, and fluxes are characterized and understood. To measure and characterize this process and its significance, the wheat-powdery mildew interaction was tested and presented here (aside from the many other pathogens and plant species sampled, analyzed, and tested during the project) in this thesis since wheat is the most important cereal in the temperate climate, with a global production of ca. 750 million tons harvested on more than 200 million hectares (FAO 2020). Powdery mildew (PM) disease, caused by the fungus *Blumeria graminis* (DC.) Speer f.sp. *tritici* Marchal (*Bgt*, syn. *Erysiphe graminis* DC. f.sp. *tritici* Marchal), is one of the most widespread

foliar diseases of wheat globally. It occurs practically everywhere wheat is grown, and thus may release biomarker and other BVOCs from millions of hectares worldwide (Basandrai and Basandrai, 2018). This pathogen can cause significant yield losses, especially where nitrogen fertilizers are routinely applied (Last, 1953; Rowaished, 1980; Tompkins et al. 1992). Though annual variations occur regionally depending on weather and other conditions (Murray, 2009), yield reductions without protective measures may amount, in extreme cases, to 40–50% (Oerke, 2006; Savary et al. 2019), while grain quality is also affected (Gao et al. 2018). This is an obligate biotrophic pathogen, *i.e.*, it grows only on the leaves of living plants and has a relatively minimalistic interaction with the host (Liang et al. 2018). As a result, fungal BVOCs will essentially be emitted from an active infection site, contrary to other pathogens, which may induce additional emissions during their subsequent necrotrophic or saprophytic stages (Pusztahelyi et al. 2017). Importantly, VOC emission from wheat (Bachy et al. 2020) appears to be weak and simple in profile compared to other crops (Gomez et al. 2019). This relatively "noise-poor" volatile background provides a yet unnoticed advantage and represents an excellent experimental system to screen for specific BVOCs that may be involved in and signal the progression of *Bgt* or other fungal pathogen infection in wheat and other cereals (Hamow et al. 2021).

2. OBJECTIVES AND AIMS

During my PhD work I have set the following aims:

1. **Selecting a** non-invasive static/dynamic **sampling and analysis approach based on pilot experiments,** where samples can be stored and reanalyzed, **for differentiation between healthy and adversely affected economically important plants** in agri- and horticulture.
2. **Implement an open-loop-pull-type-dynamic headspace VOC collection followed by SPE (solid-phase extraction) elution and GC-MS analysis (open-loop-pull-type-DHS-SPE-GC-MS) approach as a method, as well as to test and critically evaluate method performance, and if possible refine the methodological approach**
   - Performance parameters of the GC-MS analysis method for qualitative and quantitative purposes
   - Adsorbent SPE elution recovery without/with internal standard correction and testing the effects of mixtures for VOC-s used for calibration
   - Characterization of sorbent breakthrough and desorption effects by recovery experiments, in case of continuous and periodic (intermittent) DHS-VOC sampling to mitigate possible breakthrough and adsorption/desorption effects
   - Evaluate sorbent trap capacity and competition of VOC-s for the volatile traps binding sites during continuous DHS sampling
3. **Application of the pull-type-DHS-SPE-GC-MS method**
   - From healthy and fungal pathogen (emphasis on *Blumeria Graminis* f. sp. *tritici* wheat powdery mildew) affected wheat headspaces characterization of potential robust volatile biomarker biogen molecules (BBVOC) as indicators of infection at early and advanced states
   - Survey of robustness of BBVOC-s and monitoring of their emissions and their testing in mixed pathogen background

3. LITERATURE REVIEW

3.1 The origin, genetics, distribution, and economic significance of wheat and its disease powdery mildew (PM) caused by fungal pathogen *Blumeria graminis* f. sp. *tritici*

Common wheat, or bread wheat (*Triticum aestivum* L.), belongs to the grass family (*Poaceae*) and the genus *Triticum*. It originates from Southwest Asia, the so-called "Fertile Crescent," which includes present-day Southwest Iran, North Iraq, Southeast Turkey, Syria, Jordan, and Israel (Lev-Yadun et al. 2000). Based on their chromosome numbers, wheat species can be classified into three groups (Kihara, 1924): Diploid series with n=7; genome: A; B, D, G; Tetraploid series with n=14; genome: AB or AG; Hexaploid series with n=21; genome: ABD or ABG. The hexaploid *T. aestivum* likely evolved after the cultivation of diploid and tetraploid wheats that are assumed to have originated from Northwest Iran or Northeast Turkey. Based on their growth habit, wheat can be categorized into two main types: winter and spring. Winter wheat varieties can be grown in areas where winter weather conditions provide adequate cold treatment for vernalization, but the temperature is not too low to cause damage to the plants. Winter wheat generally has higher yield and greater crop stability than spring wheat due to its longer vegetative phase, resulting in better tilling and the accumulation of more assimilates in the grain. Spring genotypes of wheat can be economically grown in areas where winter is too cold for winter wheat or (in subtropical and Mediterranean climates) where the "winter" is too warm for meeting the cold requirements of winter wheat varieties (Kiss, 2016).

Wheat is an important commodity crop that provides food to about 30% of the world's population and accounts for over 20% of human-consumed calories (Arzani and Ashrah, 2017). Over the last decade, global wheat production has shown an increasing trend except for a slight decrease during the 2018/2019 growing season. It is worth noting that the global human population is expected to exceed the 9 billion by 2050 increasing the global demand for food. Current wheat yield gains are estimated at around 0.5 to 1% per annum, below the 2.4% required to meet the global demand for this commodity. Consequently, wheat production should increase by up to 70% to meet the projected global demand for wheat products by 2050. The average yield of wheat has been stagnant by up to 40% in recent years, which shows that the current output and productivity rate are not sufficient to ensure future food security. The shortage of arable land, the tension on water resources, and climate change limit the potential to expand production areas to increase output. Furthermore, the low productivity of wheat is also attributed to several biotic and abiotic factors that reduce its yield potential. Therefore, new-generation wheat cultivars need to be developed with enhanced tolerance/resistance to a plethora of stresses, *e.g.*, resistance to diseases, pests, soil alkalinity and salinity, and nitrogen use efficiency to enhance yield potential (Bapela et al. 2023).

On a global scale, wheat is cultivated on nearly 240 million hectares, playing a fundamental role in both food supply and livestock feed. In Hungary, the annual sown area of winter wheat approaches 1.0-1.2 million hectares, constituting a significant portion of the agricultural land under cultivation. Depending on the yield, we produce approximately 5-6 million tons of goods annually (Láng and Bedő, 2006). Hungary is particularly susceptible to extreme weather events, increasing the vulnerability of agricultural production. The main objectives of wheat breeders are to enhance yield security, resistance to pathogens and pests (biotic stress tolerance), improve crop quality, and increase plant tolerance to abiotic stresses. Generally, economically and safely cultivable varieties are those selected based on multi-year field trials conducted under the environmental conditions of a given area. For the latest data, you can refer to the Hungarian Central Statistical Office (KSH) that reported wheat cultivation in Hungary took place on 1,053,575 hectares, resulting in a total yield of 5,933,625 tons, averaging 5.63 tons per hectare for the year 2023.

Diseases such as powdery mildew (PM), caused by the fungal pathogen *Blumeria graminis* f. sp. *tritici*, is a leaf disease that occurs worldwide annually, and have contributed to significant yield losses (Bapela et al. 2023). In Hungary, its epidemic spread was first observed in 1961 (Podhradszky and Csuti 1962), and since then, it appears on Hungarian wheat fields every year. The *Blumeria* genus demonstrates monophyletic characteristics, encompassing solely the species "*Blumeria graminis*." This species further delineates into eight forma speciales, targeting various grasses and cereal crops such as wheat, barley, oats, and rye. Notably, *B. graminis* f. sp. *dicocci* (affecting tetraploid durum wheat) and *B. graminis* f. sp. *triticale* (hybrid of wheat and rye mildew) can infect wheat, extending the host range. The challenge arises as breeding for powdery mildew (PM) resistance in wheat lacks specificity across these *formae speciales*, and their prevalence in different cultivars and regions remains largely unexplored. Consequently, enhancing the development of PM-resistant cultivars hinges on a nuanced comprehension of mildew populations and the dynamic interplay between adapted and non-adapted *formae speciales*. This knowledge could pave the way for improved strategies in identifying novel genetic sources of resistance against PM. The sluggish progress in cultivar resistance development can be attributed to multiple factors, including the complexities in PM screening, inadequate understanding of the genetic underpinnings of disease resistance, and the polygenic nature of resistance, heavily influenced by environmental conditions (Bapela et al. 2023). Analysis of volatile compounds, particularly identification and monitoring of biomarker and other BVOCs may serve as a tool to aid breeders in screening for PM resistance (Hamow et al. 2021).

Figure 1. Early symptoms of powdery mildew (*Blumeria graminis*) on wheat leaf (photo: Puskás, K.)

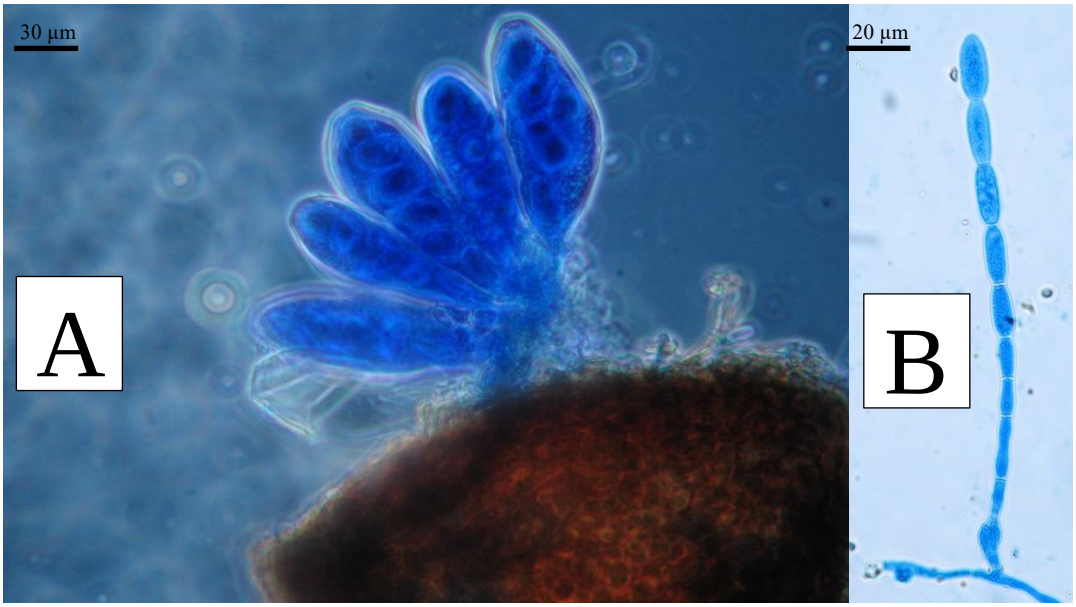


Figure 2. A: asci released from chasmothecium, each contains eight ascospores of *Blumeria graminis*; **B:** formation of conidiospore chain on a conidiophore (photos: Komáromi, J.)

The characteristic of the pathogen-host relationship is true parasitism, where the fungus does not destroy the attacked plant cell. It absorbs nutrients from the plant's epidermal cells through the cell membrane, inhibiting plant growth, resulting in small spikes, tiny, shriveled, and premature ripening grains. The average crop loss in typical years is 5-8%, but in cases of severe infection, it can reach up to 40% (Griffey et al. 1993, Komáromi, 2016). The name "powdery mildew fungi" comes from the powdery coating resembling flour on the surface of infected plants, which is actually the sporulating mycelium of the fungus as presented on **Figure 1.**

Within the *Ascomycota* phylum, they belong to the *Pezizomycotina* subphylum, the *Leotiomycetes* class, and the *Erysiphales* order. Powdery mildew fungi can infect more than 10,000 host plant species (Braun and Cook 2012, Komáromi, 2016). They are obligate biotrophic parasites, meaning they can only feed and grow on living plant tissues. Both conidia and ascospores, the latter developed in the sexual reproductive structure, play a role in infection. They attach to the host's surface using an appressorium, penetrate through the epidermal cell walls, and absorb nutrients from the cells using haustoria. The sexual fruiting body was initially called cleistothecium but later renamed as chasmothecium (Braun et al. 2002, Komáromi, 2016). Ascospores opening from the chasmothecium can be observed on **Figure 2. (A)** while conidiospores on a conidiospore on **(B)**.

3.2 Description of plant and plant-related volatile organic compounds (VOCs): diversity, functions, and biosynthesis

Volatile organic compounds (VOCs) are a mixture of low molecular-weight compounds originating from different types of organisms (Maffei et al. 2011). Under biotic (insects, beneficial fungi, pathogenic fungi, bacteria) and abiotic (heat, drought, UV radiation, etc.) stresses, plants often release complex VOC bouquets. Plant VOCs are essential in communication between plants and other organisms (Dudareva et al. 2006), which has been demonstrated in the laboratory and in agricultural systems (Kessler and Baldwin, 2001; Baldwin et al. 2002; Turlings and Erb, 2018). Volatiles emitted from microorganisms such as bacteria and fungi have been investigated less than VOCs emitted from plants (Effmert et al. 2012; Junker and Tholl, 2013; Weisskopf, 2013; Penuelas et al. 2014).

Plants and their associated microorganisms produce an extensive range of VOCs, which serve as critical mediators of various physiological processes, signaling mechanisms, and ecological interactions. Plants exchange inorganic compounds with their environment (CO_2, O_2) during photosynthesis and respiration, but most of them are also capable of emitting volatile organic compounds (VOCs) through various organs, such as flowers, fruits, or leaves. The physicochemical constraints of volatility limit VOC components to small-molecule, mainly lipophilic compounds belonging to the terpenes and non-terpene aliphatic compounds (including nitrogen- and sulfur-containing compounds), phenylpropanoids, and benzoids (Duc et al. 2022). Many VOCs produced by plants have been widely used in the industry as flavorings and fragrances, with research in this area dating back in the food and perfume industries (Bicchi et al. 2004). Despite the fact that their significance in plant physiology and plant ecology began to be investigated only in the last 10-15 years, research has shed light on the role of VOCs in interactions between plants and other organisms, as well as under biotic and abiotic stresses (Dudareva et al. 2004). Plants produce a wide variety of compounds, ranging from simple molecules like ethene

and methanol to complex molecules such as terpenes and various alkaloids. Over 100,000 chemical components produced by plants are known, and among them, at least 1700 are volatile compounds that play essential roles in growth, communication, defense, and survival (Baldwin et al. 2006). The study of volatile substances was initially limited to fragrance compounds emitted by flowers, but the focus has shifted to the study of volatile organic compounds produced by other vegetative tissues nowadays (Dicke and Loreto, 2010). The most well-known volatiles are those emitted by flowers to attract pollinators (Pichersky and Gershenzon, 2002). Several plant species store mixtures of VOCs in specialized secretory structures such as glandular trichomes or resin canals (McGarvey and Croteau, 1995; Gershenzon et al. 2000). These compounds are released when tissues are damaged, which may act as repellents for pests (although it can also act as attractant for some parasitoids) or inhibiting microbial growth (Langenheim, 1994). Furthermore, recent research indicates that the consumption of plant tissues generally induces the *de novo* biosynthesis and emission of VOCs, including six-carbon green leaf volatiles (*e.g.*, cis-hex-3-enal), methyl salicylate, methyl jasmonate, indole, terpenes, etc. These volatile compounds can play a direct protective role (Andersen et al. 1994; De Moraes et al. 2001) or serve as indirect defense mechanisms by attracting natural enemies of herbivores to prey upon them or parasitoids that parasitize them (Turlings et al. 1995; Kessler and Baldwin, 2001; Dicke and Hilker, 2003; Rasmann et al. 2005). Finally, chemical signals sent by damaged plants not only affect herbivores but also serve as warning signals to neighboring plants, inducing defensive responses in them (Arimura et al. 2000; Engelberth et al. 2004).

3.2.1 Chemical groups of plant VOCs

3.2.1.1 Terpenoids

Terpenoids are a prominent group of plant VOCs, characterized by their isoprene-based structures. Examples include monoterpenes (*e.g.*, limonene) and sesquiterpenes (*e.g.*, β-caryophyllene) with diverse physiological roles, such as defense and allelopathy. Terpenoids are synthesized via the methylerythritol phosphate (MEP) pathway in plastids. For instance, isopentenyl diphosphate (IPP) and dimethylallyl diphosphate (DMAPP) serve as building blocks for terpenoid synthesis (Gershenzon and Dudareva, 2007). Terpenoid biosynthesis KEGG (Kyoto Encyclopedia of Genes and Genomes) map presented as **Annex 9.2 Figure S1**.

3.2.1.2 Green leaf volatiles (GLVs)

GLVs are C6 compounds, including (Z)-3-hexenal and (E)-2-hexenal. These VOCs are involved in plant defense, wound signaling, and indirect defense through herbivore attraction. GLVs are derived from fatty acids through the lipoxygenase (LOX) pathway. LOX enzymes catalyze the conversion of linolenic acid to GLVs upon plant tissue damage (Scala et al. 2013).

3.2.1.3 Phenylpropanoids

Phenylpropanoids encompass compounds like benzaldehyde or eugenol. They contribute to plant defenses against herbivores, pathogens and play a role in attracting pollinators. Phenylpropanoids are synthesized via the phenylalanine ammonia lyase (PAL) pathway. PAL catalyzes the conversion of phenylalanine to cinnamic acid, a precursor for various phenolic compounds (Dixon et al. 2009). Related biosynthesis KEGG map presented in **Annex 9.3 Figure S2**.

3.3 Abiotic stress-induced volatiles in plants

Plants frequently encounter environmental stressors such as drought, heat, and salinity, which significantly impact their growth and survival. Plants respond to changes in light, temperature, or other abiotic stressors, such as floods and droughts, with emissions of volatile organic compounds (Ebel et al. 1995; Holzinger et al. 2000; Kreuzwieser et al. 2000). Abiotic stress-induced volatiles, including isoprenes, terpenes, and green leaf volatiles, have emerged as vital players in plant responses to these challenges (Peñuelas and Staudt, 2010). Drought stress induces the emission of isoprene, a volatile compound linked to stress tolerance. Isoprene helps mitigate oxidative damage, stabilize cellular membranes, and maintain photosynthetic efficiency during drought conditions (Vickers et al. 2009). Terpenes, especially monoterpenes and sesquiterpenes, are induced by heat stress. These compounds modulate heat stress responses by regulating stomatal conductance and influencing plant-microbe interactions (Llusià and Peñuelas, 2000). However, the precise physiological role of these terpenes remains not fully understood. It is hypothesized that volatile terpenes enhance the heat tolerance of photosynthetic tissues by incorporating themselves into thylakoid membranes and stabilizing them under elevated temperatures (Loreto et al. 1998; Sharkey and Yeh, 2001; Sharkey et al. 2001). There is also growing evidence suggesting that terpene fragrance compounds boost antioxidant activity in plants by neutralizing reactive oxygen species (ROS) (Loreto and Velikova, 2001; Loreto et al. 2001).

Green leaf volatiles (GLVs) such as (Z)-3-hexenal and (E)-2-hexenal, play a crucial role in plant responses to various stresses, including heat. These volatiles act as signaling molecules, triggering defense mechanisms and enhancing stress tolerance (Dixon et al. 2009). Salinity stress induces the release of methyl jasmonate (MeJA), which, in turn, triggers the production of specific volatiles. MeJA-mediated volatiles are involved in ion homeostasis, enhancing salt tolerance in plants (Song et al. 2017). The biosynthesis and emission of abiotic stress-induced volatiles are tightly regulated. Stress-responsive genes, such as those encoding terpene synthases and lipoxygenases, are activated under adverse conditions, leading to volatile production (Sharkey et al. 2013). Signaling pathways involving jasmonic acid and abscisic acid play pivotal roles in mediating these responses. Abiotic stress-induced volatiles have ecological implications, influencing plant

interactions with herbivores, pollinators, and neighboring plants. These volatiles mediate plant-plant communication, enhance indirect defenses, and facilitate ecological adaptations in natural ecosystems (Blande et al. 2014). Another important plant hormone derived volatile is methyl salicylate (MeSA) and it functions as a signaling molecule in plant defense mechanisms by inducing systematic acquired resistance (SAR) if MeSA used as a priming agent, enabling plants to respond more effectively to subsequent threats against biotic (pathogen attack) and for abiotic stress (Gondor et al. 2022).

3.4 Biotic stress-induced volatiles in plants

Plants are in a perpetual struggle against biotic stressors such as herbivores, pathogens, and parasites. As part of their sophisticated defense arsenal, plants produce and release biotic stress-induced volatiles (BSIVs) that play crucial roles in signaling, defense, and ecological interactions. Herbivore feeding activates the release of herbivore induced plant volatiles (HIPVs), from damaged plant tissues (Dicke et al. 2009). These volatiles serve as signals to neighboring plants, warning them of impending herbivore attacks (Arimura et al. 2005). HIPVs also attract natural enemies of herbivores, such as parasitoids and predators, creating a cascade of indirect defenses (Turlings and Erb, 2018). This phenomenon, known as "indirect defense," has profound ecological implications in plant-insect interactions (Dicke and Baldwin, 2010). Pathogen-Induced Volatiles (PIVs) are emitted by plants as a response to pathogen attacks by releasing specific volatiles, as part of their defense mechanisms (Kishimoto et al. 2005). These volatiles can inhibit pathogen growth or attract beneficial microorganisms (Ryu et al. 2003). PIVs play a role in priming uninfected parts of the plant, inducing systemic resistance against pathogens (Hossain et al. 2011). Plants often simultaneously emit HIPVs and PIVs in response to multiple stressors (War et al. 2011). These combined signals can enhance the plant's defense mechanisms and influence nearby plant communities and the interplay between HIPVs and PIVs can create intricate ecological networks involving herbivores, pathogens, and their respective natural enemies (D'Alessandro and Turlings, 2005). Understanding this complexity is crucial for managing pest populations in agricultural and natural systems.

3.5 Original physiological roles of plant VOCs and their significance in agroecosystems

Volatile organic compounds (VOCs) are organic chemicals that readily vaporize into the air and play a pivotal role in the functioning of agroecosystems. This scientific text explores the diverse roles of VOCs in agriculture, from plant defenses to ecological interactions, and highlights their relevance in crop management and sustainability. Agroecosystems, which encompass agricultural fields, orchards, and managed landscapes, are intricate environments where various biotic and abiotic factors interact. Among the many chemical compounds produced and released by plants,

VOCs stand out as key players in mediating these interactions. Plants emit a wide array of VOCs, including terpenoids, green leaf volatiles, and phenolic compounds. These emissions serve physiological roles and multiple purposes in agroecosystems. Examples include but not confined to **(I.) Plant Defense mechanisms -** Plants release VOCs as part of their defense mechanisms against herbivores and pathogens. For instance, the emission of terpenoids can deter herbivores by acting as repellents or attracting predators of herbivorous insects (Dicke et al. 1990). Moreover, green leaf volatiles, such as cis-3-hexenal, can be released upon herbivore feeding and serve as signals for neighboring plants to activate their own defense responses (Arimura et al. 2000).

(II.) Communication and signaling - VOCs like floral scents play a pivotal role in attracting pollinators and in intraspecific and interspecific communication within agroecosystems (Knudsen et al. 2006). These compounds enhance pollination and reproductive success in plants (Raguso, 2008). For example, the release of (E)-β-caryophyllene by maize plants has been shown to attract parasitoid wasps, which parasitize the eggs of herbivorous insects, thereby enhancing biological pest control (Rasmann et al. 2005).

(III.) Influence on crop health and productivity - The presence of VOCs in agroecosystems can have profound effects on crop health and productivity such as **Indirect defense against pests** - Many plant VOCs are integral components of defense against herbivores and pathogens. For instance, (E)-β-caryophyllene functions as attractant for natural enemies of herbivores (Arimura et al. 2009).

Indirectly, VOCs contribute to crop protection by attracting natural enemies of herbivores. Studies have shown that the presence of certain VOC-emitting plants in agroecosystems can increase the abundance and effectiveness of natural enemies, reducing the need for chemical pesticides (Landis et al. 2000). **Allelopathy and weed management** - Some VOCs, such as terpenoids and phenolic compounds, serve as allelopathic chemicals. They inhibit the growth of neighboring plants, providing a competitive advantage (Weir et al. 2004). In addition to their role in pest management, VOCs can influence weed-crop interactions. Some plant-derived VOCs exhibit allelopathic effects, inhibiting the growth of competing weed species (Bertin et al. 2003). This phenomenon has implications for weed management strategies in agriculture.

(IV.) Environmental impacts and sustainability - Understanding the ecological roles of VOCs in agroecosystems can inform sustainable agricultural practices. Reduced reliance on synthetic pesticides and herbicides can result in decreased environmental contamination and promote biodiversity (Isman, 2006). VOC-mediated communication between plants and their associated organisms can also enhance crop resilience and reduce yield losses (Kessler and Baldwin, 2001). Low-molecular-weight terpenes, including isoprene (C5), monoterpenes (C10), and

sesquiterpenes (C15), are emitted in substantial quantities by woody plants and have a notable impact on atmospheric chemistry. They contribute to the formation of ozone and secondary organic aerosols when combined with anthropogenic pollutants (Hoffmann et al. 1997; Kesselmeier and Staudt, 1999; Atkinson, 2000). Additionally, terpenoid emissions influence the levels of free radicals (·OH) and the residence time of methane in the atmosphere (Thompson, 1992; Sharkey and Yeh, 2001;). Considering the above volatile organic compounds (VOCs) are essential components of agroecosystems, influencing plant defenses, ecological interactions, and overall crop health and productivity. Recognizing the multifaceted roles of VOCs in agriculture can lead to more sustainable and environmentally friendly farming practices.

3.6 Microbial derived VOCs

Microbial VOCs are released by microorganisms such as bacteria and beneficial and pathogenic fungi (Korpi et al. 2009; Thorn and Greenman, 2012). Volatile organic compound profiles can be substantially altered by pathogen-derived VOCs, and can therefore function as biomarkers for detection, differentiation, and characterization or even forecast of early infections (Li et al. 2019; Hamow et al. 2021). More than 100 bacteria and fungi produce soil microbial VOCs (Effmert et al. 2012), and approximately 250 fungal VOCs have been described (Morath et al. 2012; Roze et al. 2012). Plants can perceive microbial VOCs from a distance and prime plant responses to microorganisms (Bailly and Weisskopf, 2012; Effmert et al. 2012; Bitas et al. 2013; Schmidt et al. 2015). Microbial VOCs can potentially mediate plant–microbe interactions (Moisan et al. 2020a; Moisan et al. 2020b; Xu et al. 2021). Microbial VOCs can diffuse through the soil environment and potentially affect plant growth and defense (Piechulla et al. 2017; Tyagi et al. 2018). Bacterial VOCs can increase plant growth and trigger systemic resistance and also influence motility and antibiotic resistance in other bacteria (Ryu et al. 2003; Ryu et al. 2004a and 2004b; Lee et al. 2012; D'Alessandro et al. 2014; Park et al. 2015). Similarly, VOCs emitted by pathogenic and beneficial microorganisms can promote plant growth (Velásquez et al. 2020b), and microbial volatiles can improve plant tolerance and sustain plant growth (Liu and Zhang, 2015; Jalali et al. 2017; Camarena-Pozos et al. 2019, Duc et al. 2022).

3.7 Volatile compounds as biomarkers of infection and diseases

The emergence of diseases and increased pest infestations significantly reduce food security and impact human health. Diagnosis of plant diseases relies on molecular biomarkers (pathogen-specific nucleic acids). However, laboratory-based molecular tests (*e.g.*, polymerase chain reaction) are complex, not accessible in open fields, not remotely controllable, and detection is only possible after the appearance of symptoms (Aksenov et al. 2013). Early identification of plant pathogens required faster and non-invasive methods to improve intervention timing and disease

spread prevention, thereby enhancing treatment effectiveness. Plant volatiles are increasingly being considered as unique diagnostic markers for plant diseases. Plants produce a wide spectrum of volatile organic compounds (VOCs) which can be excreted in significant amounts during physical damage, pest injury or pathogen infection. These VOCs are released even hours or days after the stress event (Dudareva et al. 2013). Research shows that the emission rate and composition of VOCs from infected plants differ from those of healthy control plants (Shualev et al. 1997; Jansen et al. 2009; Jansen et al. 2010a and 2010b; Jansen et al. 2011). While it can be challenging to establish a correlation between a specific VOC and disease status, there is growing evidence that a VOC panel with a specific composition can serve as an effective diagnostic tool. Collective analysis of plant volatile profiles creates a multidimensional dataset, known as a "fingerprint," which can be effectively used to differentiate between biotic and abiotic plant stresses with high confidence (Blasioli et al. 2014; Fang and Ramasamy, 2015; Khater et al. 2017). For example, three marker compounds, namely trans-hex-2-enal, 5-ethylfuran-2(5H)-one, and 2-phenylethanol, were found to be abundant in potato and tomato leaves infected with late blight (*Phytophthora infestans*) (Laothawornkitkul et al. 2010). Furthermore, higher concentrations of 4-ethyl guaiacol and 4-ethyl phenol were characteristic of crown rot (*Phytophthora cactorum*) in strawberries (Jelen et al. 2005). Additional studies have found significant quantities of lipogenase products and methyl salicylate in the scent samples of tomatoes infected by *Botrytis cinerea* (Blasioli et al. 2014). Plant diseases cause severe economic losses in agriculture worldwide. Monitoring plant health and early detection of pathogens are essential for reducing the spread of infection and developing effective coping strategies. VOC-based approaches, following initial research, enable rapid, cost-effective, and reliable pathogen detection, even before the appearance of symptoms, and can identify the simultaneous presence of multiple pathogens based on VOC profiles (Martinelli et al. 2014).

3.8 Challenges in aboveground and belowground VOC differentiation, plant belowground VOC and effects on fungal pathogens, fungal VOCs and its effect to plant host

Challenges in the differentiation of volatile organic compounds (VOCs) in both aboveground and belowground environments, as well as the impact of belowground plant VOCs on fungal pathogens and vice versa, present significant hurdles (Schulz and Dickschat, 2007; Das et al. 2012; Junker and Tholl, 2013). Distinguishing belowground VOCs from aboveground ones is particularly arduous due to the heterogeneous nature of soil environments, leading to technical constraints in VOC collection (Tholl et al. 2021). Extensive research has been conducted on VOC-mediated interactions between plants and various organisms, including both above and belowground plant-insect and plant-plant interactions, since the pioneering work of Baldwin and Schultz in 1983

(Bruce et al. 2005; Baldwin et al. 2006; Kegge and Pierik, 2010; Clavijo McCormick et al. 2012; Effah et al. 2019; Effah et al. 2022). However, our understanding of the roles played by VOCs produced by soilborne fungal pathogens and beneficial fungi, such as mycorrhizae, in influencing plant performance remains limited. Furthermore, the effects of exposure to fungal VOCs on plant resistance or tolerance to herbivory, both above and belowground, have yet to be fully explored (Duc et al. 2022). Specific methodologies, sampling techniques, and experiments needed for differentiation are discussed in section 3.10.3.

Plant belowground VOCs and their effects on fungal pathogens are gaining importance in the context of reducing chemical usage in plant protection. The analysis of VOC production patterns in root tissues is becoming increasingly crucial due to their potential roles in belowground biotic interactions, particularly with fungal pathogens. The number of identified root VOCs has surged in recent years. While only a limited number of root volatiles were known in various plant species such as maize, barley, bean, and *Arabidopsis thaliana* in 2015, hundreds more have been reported since then (Schenkel et al. 2015; Cordovez et al. 2017; Schenkel et al. 2018; Moisan et al. 2019). Research on the functions of root volatiles, particularly in invasive and noninvasive conditions, has predominantly focused on model plants like *A. thaliana* (Casarrubia et al. 2016; Cordovez et al. 2017; Schenkel et al. 2018; Moisan et al. 2019), but numerous other plant species have also been investigated. Root VOCs from various plant families, including *Solanaceae, Brassicaceae*, and cucurbits, as well as non-cultivated plants, have been studied for their antifungal activity or ability to enhance plant defense against pathogens and herbivores (Duc et al. 2022). These root VOCs have been grouped into 15 biosynthetic origins/chemical classes in **Figure 3.** and **Annex 9.4 Table S1**. Volatile organic compounds are classified into different chemical groups depending on plant species, genotype, sex, development stage (**Table 1.** and **Annex 9.4 Table S1**) (Schenkel et al. 2015; Delory et al. 2016a; Delory et al. 2016b; Kihika et al. 2017; Kindlovits et al. 2018; Murungi et al. 2018; Xie et al. 2022). One of the most common groups is terpenoids, which include the sesquiterpenes (E)-β-caryophyllene, daucadiene, (E)-α-bergamotene, humulene, (E)-β-farnesene, and three putative petasitene isomers (petasitene 1–3) and the monoterpenes α-pinene and β-myrcene (Gfeller et al. 2019; Gulati et al. 2020). Other major groups of root volatiles include aldehydes, alcohols, n-alkanes, and ketones. Following strong mechanical injury in barley plants at each developmental stage, the four main volatile aldehydes were characterized and included hexanal, (E)-hex-2-enal, (E)-non-2-enal, and (E,Z)-nona-2,6-dienal (Delory et al. 2016a). The volatile organic compounds released by roots vary depending on the biotic stress agent that is causing damage to the plant. Tomato roots infected by *Fusarium oxysporum* emit VOCs such as benzonitrile, benzothiazol, dimethyl trisulfide, and formic acid, which have antifungal activities,

and a terpene-like compound, which activates antagonistic response; whereas healthy tomato plants release n-alkanes, beclomethasone dipropionate, p-cymene, decanal, and 3-carene, which are compounds without antimicrobial activity or special role (Gulati et al. 2020). Effects of endophytic fungi on plant hosts and their VOC production can have an effect on other microorganizms and may even serve as biocontrol agents against pathogens by mycofumigation (Kaddes et al. 2019a).

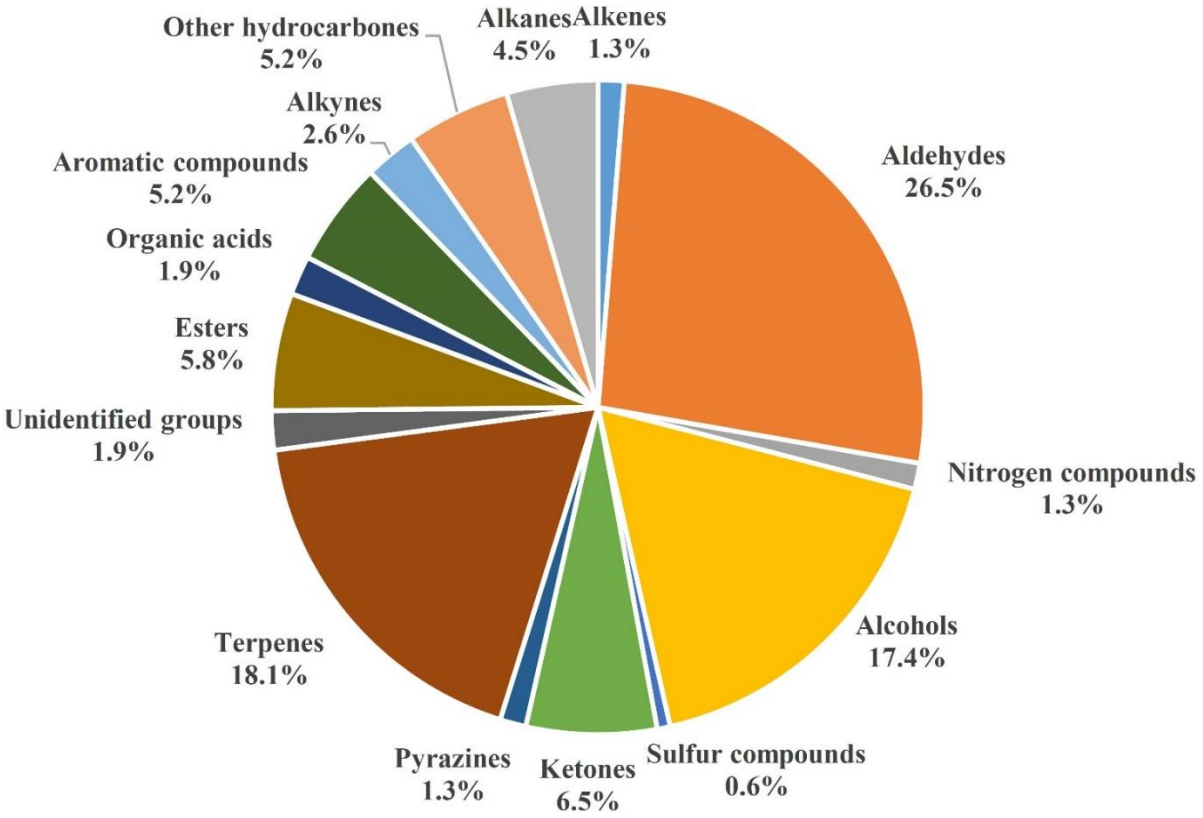


Figure 3. Diversity of plant root VOCs, 155 volatile compounds from different plants collected from 2016 to 2022 (Duc et al. 2022).

Antimicrobial VOCs produced by natural hosts, though typically present at low levels, exhibit significant antagonistic activity. Furthermore, certain VOCs released by beneficial microorganisms such as *Pseudomonas putida* BP25 have shown promise in eco-friendly disease management in agriculture (Sheoran et al. 2015). For instance, pyrazine derivatives produced by *P. putida* BP25 exhibit inhibitory activity against various pathogens and pests (Kihika et al. 2017; Murungi et al. 2018). Additionally, monoterpenes like (+)-limonene and 1-octen-3-ol have been found to inhibit the growth of fungal pathogens (Simas et al. 2017; Herrero-Garcia et al. 2011). Understanding the roles of root volatiles in regulating belowground microbiomes and their effects on microbial communities is a key area of research. Despite the potential of belowground volatiles in controlling fungal diseases, further investigations are required to harness their applications in sustainable agriculture (Sharifi et al. 2022).

The impact of fungal pathogen-derived volatile organic compounds (VOCs) on plants (detailed in **Table 2.**), varies depending on the type of pathogen and its mode of nutrient acquisition, whether through biotrophic or necrotrophic means (Schenkel et al. 2015; Gulati et al. 2020). These VOCs, characterized for numerous fungal species (Fiers et al. 2013; Casarrubia et al. 2016; Werner et al. 2016; Cordovez et al. 2017; Cordovez et al. 2018; Martín-Sánchez et al. 2020; Moisan et al. 2020), exhibit low chemical diversity and likely serve as info-chemicals to attract or repel interacting organisms (Gulati et al. 2020). Some of these compounds, including 1-octen-3-ol and 2-phenylethanol, classified as phytotoxic, hinder plant growth (Werner et al. 2016). For example, 1-octen-3-ol inhibits root growth and cotyledon bleaching in *A. thaliana* seedlings and impairs seed germination (Splivallo et al. 2007; Lee et al. 2014). Additionally, VOCs from fungi like *Serratia plymuthica* and *F. culmorum* affect maize growth by limiting micronutrient availability in roots (Martín-Sánchez et al. 2020). Fungi like *F. acuminatum* hinder tomato growth, while others reduce leaf surface area and root length in barley (Fiers et al. 2013; Gulati et al. 2020). Despite their negative impact, certain fungal VOCs promote plant growth, modulating root architecture and increasing biomass (Cordovez et al. 2017; Moisan et al. 2019; Moisan et al. 2020). These VOCs, including alcohols, pyrones, phenols, sesquiterpenes, ketones, and aldehydes, influence plant growth and architecture (Casarrubia et al. 2016; Cordovez et al. 2018; Fincheira and Quiroz, 2018; Moisan et al. 2019; Duc et al. 2022). Moreover, they induce host defense mechanisms, altering ion flow and pH gradient to inhibit fungal growth (Kaddes et al. 2019b). Some, like naphthalene and monoterpenes, exhibit antibacterial effects in tomatoes (Gulati et al. 2020). Infection with fungal pathogens alters plant VOC emissions, enhancing chemical protection and deterring further fungal colonization (Schulz-Bohm et al. 2017; Gulati et al. 2020). Soilborne fungi-derived VOCs also confer resistance to above- and below-ground herbivores like cabbage root fly and cabbage white butterfly, negatively impacting their development and performance (Cordovez et al. 2017; Moisan et al. 2019; Moisan et al. 2020b). These VOCs modify root architecture, affecting plant chemistry and morphology, and can promote glucosinolate accumulation, deterring leaf caterpillar performance (Aziz et al. 2016). Additionally, they influence nematode development and behavior, inhibiting egg hatch and slowing development (Terra et al. 2018; Moisan et al. 2021). Thus, fungal VOCs not only impact plant growth but also aid in attracting disease antagonists or natural enemies of pests for defense (Duc et al. 2022).

3.9 Volatile organic compounds in mycorrhizal symbiosis

The intricate symbiotic relationship between plants and arbuscular mycorrhizal fungi (AMF) is a fundamental aspect of soil ecosystems and agricultural practices, characterized by a mutual exchange of resources. The AMF, mainly belonging to the *Glomeromycotina phylum*, forms

symbiotic associations with the majority of vascular and agricultural plants, leading to improved nutrient and water uptake for the plant (Smith and Read, 2008). This symbiosis is initiated through a precisely regulated molecular crosstalk and influenced by nutrient availability (Choi et al. 2018). Compounds such as strigolactones, released by host roots in response to inorganic phosphorus starvation, play a crucial role in the molecular signaling between fungi and plants, inducing AM spore germination, hyphae production, and branching (Ho-Plágaro and García-Garrido, 2022). Additionally, various plant compounds, including flavonoids and polyamines, actively influence hyphal elongation or branching, shaping the intricate nature of mycorrhizal fungal symbiosis (Bécard et al. 1992; Akiyama et al. 2005). The establishment of AMF involves the formation of arbuscles within the roots, facilitating the exchange of nutrients and photosynthates (Nadal and Paszkowski, 2013). AMF through extensive extraradical hyphal networks present in soil influences other organisms, root physiology, and root exudation patterns (Duc et al. 2022). While substantial progress has been made in understanding the molecular regulation of AM symbiosis, there is limited information on the role of VOCs during mycorrhization (Ho-Plágaro and García-Garrido, 2022). Sun et al. (2015) demonstrated that germinating spores of the AMF *Gigaspora margarita* emit unidentified volatiles, influencing lateral root density and number in non-host plants like *A. thaliana* and *Lotus japonicus*. VOCs released by fungi also modulate host root orientation, altering the branch angle of lateral roots, thereby increasing the likelihood of AM hyphae contacting roots in the rhizosphere (Sun et al. 2015). Auxins, known regulators of lateral root branch angles, can be triggered by VOCs. The gene LjCCD7, a vital component of the strigolactone synthesis pathway, is stimulated by fungal VOC signals, contributing to mycorrhizal VOCs' crucial role in increasing strigolactone biosynthesis and root proliferation (Sun et al. 2015). Another prevalent mycorrhiza–plant interaction is ectomycorrhizal (EM) symbiosis, involving various *ascomycetes* and *basidiomycetes* forming symbioses with around 6000 tree species (Brundrett, 2002; Van Der Heijden et al. 2015). In EM, volatile compounds, including terpenoids, alcohols, aldehydes, and ketones, are produced during the pre-symbiotic stage and influence the interaction between host plants and fungi (Menotta et al. 2004). Terpenoids like thujopsene released by the EM fungus *Tricholoma vaccinum* enhance lateral root formation and root hair length, facilitating EM establishment (Abdulsalam et al. 2021). The mycorrhizosphere effect, significantly increasing soil biological activity, is observed in both AM and EM symbioses, influencing root exudates and contributing to changes in soil microbial communities (Linderman, 1988; Schellenbaum et al. 1991). Mycorrhizal colonization significantly impacts plant hormonal homeostasis, with ethylene, influenced by mycorrhizal colonization, functioning as a phytohormone modulating volatile biosynthesis (Chen et al. 2020).

Table 1. Plant root VOCs and its properties (Duc et al. 2022).

Plant	VOC compounds	Properties	References
Carex arenaria	γ-capro; γ-deca; γ-nonalactone	attract benefit bacteria from bulk soil	Schulz-Bohm et al. 2017
Cucumis metuliferus (CM3)	Creosol	attract and kill *M. incognita*	Xie et al. 2022
Poplar	salicylaldehyde	play a role as a nematicide	Lackus et al. 2018
Cucumis metuliferus (CM3)	Benzene, (methoxymethyl)	repel *M. incognita*	Xie et al. 2022
Pepper	Thymol	repel root-knot, cyst, and stubby root nematodes	Kihika et al. 2017
Centeaurae stoebe ; tomato	(E)-β-caryophyllene; daucadiene; (E)-α-bergamotene; humulene; E-β-farnesene; petasitene 1-3; β-myrcene	effect on the germination and greowth of different sympatric neighbours	Gfeller et al. 2019; Gulati et al. 2020
Centeaurae stoebe ; tomato; spinach; pepper; poplar	α-pinene		Kihika et al. 2017; Murungi et al, 2018; Lackus et al. 2018; Gfeller et al. 2019; Gulati et al. 2020
Cucumber line Xintaimici; tomato; spinach; pepper	Tridecane	attract second stage larvae (J2) of *M. incognita*	Simas et al. 2017; Kihika et al. 2017; Murungi et al. 2018
Tomato; pepper	p-cymene		Kihika et al. 2017; Gulati et al. 2020
Tomato	Sabinene		Murungi et al, 2018
Tomato; spinach; pepper	Limonene; 2-(methoxy)-3-(1-methylpropil)pyrazine		Kihika et al. 2017; Murungi et al. 2018;
Tomato; spinach	2-isopropyl-3-methoxypyrazine		Murungi et al. 2018;
Cucumis metuliferus (CM3)	2-Penten-1-ol; (Z-)		
Cucumber line Xintaimici; tomato; pepper	Methyl salicylate		Kihika et al. 2017; Murungi et al. 2018; Xie et al. 2022
Cucumis metuliferus (CM3)	1-Nonyne	improvement plant resistance of to *M. incognita*	Xie et al. 2022
Carex arenaria	Benzonitrile		Schulz-Bohm et al. 2017
Carex arenaria	Benzofuran		Schulz-Bohm et al. 2017
Not given	Limonene	inhibited the fungal mycelial growth and spore germination of *Botrytis cinerea*	Simas et al. 2017
Barley	methyl pro-2-enoate and methyl propanoate	supressed the mycelial growth and prohibited spore germination of *Fusarium culmorum* and *C. sativus*	Kaddes et al. 2019b
Tomato	benzonitrile; benzothiazol; dimethyl trisulfide	antifungal activity to *Fusarium oxysporum*	Gulati et al. 2020

Table 2. Fungal VOCs and its effect to plant host (Duc et al. 2022).

Plant host/fungi	VOC compounds	Properties	References
Maize/ *Serratia plymuthica; Fusarium culmorum*	Not given	Iimited the availability of micronutrients such as Fe, Zn, Cu, and Mo in the root	Martín-Sánchez et al. 2020
Tomato/ *Fusarium oxysporum*	branched alcane, dodecane, eicosane, docosane, naphthalene, beclomethasone dipropionate	Prohibited plant growth and curtailed shoot length and root parameters, as well as lessened root surface and biomass	Gulati et al. 2020
Brassica rapa/ R. solani, *Fusarium oxysporum* f.sp. *raphani*	3-octanol, 3-octanone	Diminished the root growth rate of *Brassica rapa* seedlings	Moisan et al. 2021
A. thaliana/ R. solani	1-octen-3-ol, 2-phenylethanol, 3-methyl-1-butanol, 1- hexanol, 3-octanol, 3-octanone, trans-2-octenal	Inhibited plant growth	Werner et al. 2016; Cordovez et al. 2017
A. thaliana/ R. solani	Unidentified	Plant growth promoted by altering root architecture and enhancing root biomass; reduced aboveground resistance to the herbivore *Mamestra brassicae*	Cordovez et al. 2017
Brassica rapa/ R. solani, *Fusarium oxysporum*, *Ulocladium atrum* and *Phoma leveillei*	Not given	Stimulated root and plant growth, flowering, accelerating plant bolting, bud and flower production, improved reproductive success; enhanced plant resistant to cabbage root fly *Delia radicum* and large cabbage white butterfly *Pieris brassicae*	Moisan et al. 2020a
Brassica rapa / F. oxysporum	Not given	Inhibited root-knot nematode *M. incognita* egg hatching and development of cyst nematode *Heterodera schachtii*	Terra et al. 2018; Moisan et al. 2021
Arabidopsis/ *Penicillium aurantiogriseum*	Not given	modify root metabolism and architecture, and improve nutrient and water use efficiencies	García-Gómez P. et al. 2020
-/ Fusarium culmorum	α-Terpinene, β-Phellandrene, 3-Carene, and Camphene	Reduced swimming and swarming motility bacteria, *Collimonas pratensis* Ter291 and *Serratia plymuthica* PRI-2C	Schmidt et al. 2016
Tricholoma vaccinum (EM fungi)	Produced monoterpene limonene, sesquiterpene β-barbatene	Antimicrobial activity	Abdulsalam et al. 2021
Tilia americana/Tuber borchii (EM fungi)	Produced 29 volatiles including alcohols, aldehydes, and ketones	These VOCs may facilitate ectomycorrhizal fungi establishment	Menotta et al. 2004
Populus/Laccaria bicolor (EM fungi)	Released sequiterpene thujopsene	Increased Populus lateral root formation and root hair length in the pre-symbiotic phase, facilitating ectomycorrhizal fungi establishment	Ditengou et al. 2015
Tricholoma vaccinum (EM fungi)	Emitted geosmin	Improved sporulation and spore germination in AMF. This volatile may also be important in ectomycorrhizal fungi establishment	Abdulsalam et al. 2021
Rhizophagus irregulari (AMF)	Produced unknown volatiles	Directly suppressed growth and extension of fungal pathogens, *F. oxysporum, F. graminearum, Verticillium dahlia, Rhizoctonia solani*	Zhang et al. 2018
Gigaspora margarita (AMF)	Emitted unknown volaties	Increased density and number of lateral roots of A. thaliana (non-host plant for AMF) and *Lotus japonicus*	Sun et al. 2015

Table 2. continued - Fungal VOCs and its effect to plant host (Duc et al. 2022)

Plant host/fungi	**VOC compounds**	**Properties**	**References**
-/ AM genus Glomus	Not given	Improved biotic stress tolerance in an array of plants attacked by herbivores	Dowarah et al. 2021
Medicago truncatula/Rhizophagus irregularis	Specifically released limonene	This volatile may help plant recognize the symbiotic mycorrhizal fungi	Dreher et al. 2019
Tomato /*R. irregularis*	Increased methyl salicylate	Attracted the aphid parasitoid *Aphidius ervi*	Volpe et al. 2018
Asclepias curassavica /*Funneliformis mosseae*	Increased 3-hexenyl acetate, hexyl acetate, methyl salicylate	modified plant attractiveness to insect behavior	Meier and Hunter, 2019
Grapevine/*F. mosseae*	Increased benzaldehyde, geraniol, 2–hexenal, 3–hexenal	Improved plant defenses against pathogen/herbivore attack	Velásquez et al. 2020b
Elymus nutans/ F. mosseae	Increased D-Limonene, p-Xylene, 1,3-Diethylbenzene		Zhang et al. 2022
Grapevine/ *F.. mosseae*	C13–norisoprenoid *β*–ionone decline	Improved plant resistance to water stress	Ju et al. 2018
Medicago sativa /*Rhizophagus irregularis*	Volatization of inorganic Asenic	Decreased As toxicity in the host plant	Li et al. 2021

AMF, arbuscular mycorrhizal fungi; EM fungi, ectomycorrhizal fungi

The salicylic acid (SA) signaling pathway, activated by mycorrhization, modifies root exudate profiles, influencing soil microbiomes (Martínez-Medina et al. 2017a and 2017b). Pons et al. (2020) revealed that phytohormones, including cytokinin, auxin, gibberellin, and ethylene, are produced by the AM fungus *Rhizophagus irregularis*. Similarly, the EM fungus *Tricholoma vaccinum* emits ethylene and excretes ABA (abscisic acid), SA, jasmonates, and indole-3-acetic acid (Abdulsalam et al. 2021). Root VOC emissions, influenced by the mycorrhizosphere effect and mycorrhiza-induced changes in phytohormone homeostasis during colonization, have broad-spectrum and long-term fungistatic efficacy (Zhang et al. 2018). Mycorrhizae-induced plant volatiles play a crucial role in responding to abiotic and biotic stresses. Mycorrhizae exert significant influence on the concentrations and composition of root VOCs in various plant species, including *Sorghum bicolor, Medicago truncatula,* and *Vitis vinifera* (Sun and Tang, 2013; Dreher et al. 2019; Velásquez et al. 2020a). Mycorrhiza-induced volatiles, such as methyl salicylate, benzaldehyde, geraniol, and terpenoids, play a crucial role in modulating plant defenses. These volatiles increase under stress conditions, affecting aphid attraction and enhancing resistance against fungal pathogens (Raskin, 1992; Tang et al. 2015; Velásquez et al. 2020b). Terpenoids, vital in above- and belowground tritrophic interactions, serve as attractants for parasitoids and predators of herbivorous insects (Palma et al. 2012; Penuelas et al. 2014).

In conclusion, the symbiotic relationship between plants and mycorrhizal fungi involves intricate molecular signaling, nutrient dynamics, and the release of specific VOCs. It significantly impacts the rhizosphere microbiome, alters root exudates, contributes to plant resilience against abiotic and biotic stresses, playing a crucial role in shaping ecological interactions and overall ecosystem health. Nevertheless, mechanisms associated with fluxes of volatile terpenoids with different roles in mycorrhizal symbiosis remain unknown (Duc et al. 2022).

3.10 Options for collecting and analyzing volatile compounds

The growing scientific interest in the fields of biochemistry, plant physiology, ecology, and atmospheric chemistry has led to the development of systems for the sampling and analysis of volatile compounds (Millar and Sims, 1998; Tholl et al. 2006; Tholl et al. 2021). In the past decade, the analysis of volatile compounds has advanced significantly, thanks to relatively inexpensive and sensitive compact instruments, especially those coupled with gas chromatography-mass spectrometry (GC-MS). Advanced headspace analysis techniques provide more representative volatile compound profiles compared to traditional solvent extraction or steam distillation methods. In addition to manual headspace sampling methods, high-resolution, online, automated VOC analysis systems have become essential for monitoring rapidly changing volatile compound profiles in response to plant growth or stress. The demand for real-time measurements has increased interest in non-chromatographic methods, most commonly based on techniques like chemiluminescence, photoacoustic spectroscopy (PAS), or mass spectrometry (*e.g.*, proton transfer reaction (PTR-MS)). The latest technological advancements and applications in VOC sampling and analysis are represented by miniaturized air sampling devices, sub-surface sampling of VOCs, VOC-based phenotyping, and fast, portable VOC sensors. The advantages and disadvantages of these techniques compared to previous methods have been summarized and compared by Tholl et al. (2021), as illustrated in **Table 3.** VOCs are collected either from detached plant parts or, preferably, *in situ* from a well-defined plant area, avoiding additional VOC emissions caused by damage. Depending on the type of plant being studied, the rate of VOC emission can vary significantly, which determines the type of instrument needed to achieve the appropriate sampling efficiency and sensitivity. While trace amounts of trapped volatile compounds are sufficient for analytical purposes, larger quantities are required for NMR studies or biological investigations. Additionally, a decision must be made regarding whether to create a "snapshot" in terms of quality (static sampling) or to investigate quantitative, developmental, or stress-induced changes in VOC emissions with appropriate temporal resolution (dynamic sampling).

Table 3. Advantages / disadvantages of VOC sampling and detection methods (Tholl et al. 2021)

Method/ Application	**Advantages**	**Disadvantages**
Static Sampling *GC-MS, GC-FID SPME, SBSE, PDMS tubes*	- Small sampling devices - Sensitive - Cost-effective - No organic solvent use	- Separation of sampling and analysis in time - Single sample analysis due to thermal desorption (SPME) - Limited quantitative analysis - Adsorbent preference for analytes - SBSE, PDMS tube: Requires specialized desorption unit
Dynamic Sampling GC-MS, GC-FID Pull/push–pull systems adsorbent traps (TDU - thermal desorption or SPE like solvent desorbtion by elution)	- Controlled VOC sampling and preconcentration - Qualitative and quantitative analysis - Applicable in both above and below-ground environments - Repeatable sample analysis - Suitable for miniature devices (needle trap, dynamic SPME)	- Separation of sampling and analysis in time - Additional equipment required for sampling (pumps, flow meters, partial or complete packaging of plant parts, carbon filters for ambient air purification) - Adsorbent preference for analytes - Use of organic solvents
Real-Time PTR-MS	- Real-time, untargeted monitoring of VOC emissions - Qualitative and quantitative analysis - High resolution with low detection limits (PTR-ToF-MS) - Applicable for VOC phenotyping, combined with simultaneous physiological measurements	- Expensive - More challenging for field use - Limited ability to distinguish certain isomers; additional GC-MS analysis may be needed - Requires special cuvette system and controlled conditions for phenotyping
Portable Miniaturized GC- *detection by iontrap MS or DMS (Dynamic VOC sampling and endrichment on sorbent)*	- *In situ* VOC fingerprinting in the field - Portable device - Fast operational time - Combined examination of the plant and its microenvironment	- Limited separation and resolution due to reduced GC column length (compared to non-portable, benchtop instruments) - Requires a specialized mass spectral library for compound identification
Electronic Nose	- *In situ* VOC observation in outdoor conditions - Portable device - Fast operational time	- Low sensitivity and limited chemical specificity - Inability to identify unknown components - Signal stability distortions, shifts due to environmental interferences, and complicated data processing
Smartphone-Based VOC Sensors	- *In situ* VOC fingerprinting in the field - Wireless connection and on-site data analysis - Fast operational time, small, highly cost-effective, user-friendly - Better specificity and fewer environmental interferences compared to electronic noses	- Preconcentration step required - Unable to identify unknown components - Real-time monitoring not yet available

DMS – Differential Ion Mobility Spectrometry; FID – Flame Ionization Detector/Detection; GC – Gas Chromatography; PTR-MS – Proton Transfer Reaction-Mass Spectrometry; SPME – Solid Phase Microextraction; SBSE – Stir Bar Sorptive Extraction; PDMS – Dimethyl Polysiloxane; ToF – Time-of-Flight Analyzer; VOCs – Volatile Organic Compounds.

3.10.1 Sampling VOCs with static headspace analysis methods

During static headspace analysis, the plant or a part of it is placed in a closed chamber, and the emitted volatile compounds are captured by an adsorbent material. The air surrounding the plant remains "static," meaning there is no circulation within the chamber/system. The odorants accumulate on the adsorbent or a direct sampling of the headspace with a gastight syringe and injection of the gas sample can be utilized without capturing pollutants from the flowing air, which could interfere with the detection of less significant VOCs. Therefore, this method is even more advantageous for studying plants with low VOC emissions. Despite recent developments in solid-phase microextraction (SPME), static headspace analysis has its drawbacks. In the motionless environment, moisture accumulates along with heat, especially if sampling is conducted under illumination (there are some exceptions like LED illumination), which can disrupt normal physiological processes and affect the emission of volatile compounds. Since not all emitted odorants are trapped during a single sampling event, it is challenging to determine the temporal changes in emissions. In summary, static headspace analysis is suitable for qualitative VOC analysis and comprehensive profiling of VOCs in various plant species at a specific moment rather than for quantitative assessment of variable VOC emissions.

3.10.1.1 Solid-Phase Microextraction (SPME)

A significant innovation in static headspace analysis is the introduction of solid-phase microextraction (SPME), which offers a fast and simple way to collect volatile compounds in the ppbv (parts per billion by volume) range. The core of SPME is the extraction fiber, often a small glass rod coated with a film or a similarly sized sorbent material affixed to the end of the glass. The fiber is situated within a modified syringe needle, which is inserted through the gas-tight septum of a sample container used for vapor analysis and extended into the sample space. After an appropriate extraction time (several minutes to half an hour), the fiber is retracted into the sheath and subjected to thermal desorption for subsequent gas chromatographic analysis. SPME fibers can typically be used around a hundred times. Since thermal desorption from the SPME fiber eliminates the need for solvents that might contain contaminants, it is a solvent-free method. However, desorption involves the entire sample, therefore the injection cannot be repeated from a single collected sample. The quantity of compound adsorbed onto the SPME fiber depends not only on its thickness but also on the analyte's distribution coefficient, which generally increases with molecular weight and boiling point. Quantitative determination in SPME is usually possible with internal or external calibration. To achieve reproducible quantitative results, it is essential to establish equilibrium between the fiber and the analyte, where the amount of analyte desorbed from the fiber is proportional to the compound's quantity in the sample. The time required to

establish this equilibrium depends on the analyte's volatility, polarity, and the sorbent's properties. If an autosampler with very punctual and reproducible event timing executes SPME based VOC sampling, waiting for the total equilibrium can be skipped to increase throughput and reduce analysis time. However this requires a total validation and ongoing quality control samples and procedures during analysis to establish reliable quantitation (appropriate standard calibration mixtures are essential). However, for analytes with significantly different distribution coefficients, quantitative analysis using the SPME technique can be cumbersome or unfeasible. SPME has been applied in various studies related to food, air, soil, and water samples, and there is an increasing number of publications on its use in biological research as well (Flamini et al. 2002; Shen et al. 2004; Rohloff and Bones, 2005; Tomova et al. 2005).

3.10.1.2 Direct headspace sampling

Direct vapor analysis is an alternative for trapping VOCs is direct vapor analysis, in which the entire vapor phase is transferred into a gas-tight syringe and directly injected into a gas chromatograph. This process can be automated with commercially available automatic vapor headspace samplers. However, this method requires relatively high VOC concentrations in the sample space for effective application. Therefore, it is only usable when adequate sensitivity is achieved and only the most abundant VOC-s with high concentration in the gas sample are likely to be detected and quantitated.

3.10.2 Possibilities of Dynamic Headspace Analysis (DHS)

Dynamic headspace analysis (DHS) is one of the most commonly used techniques for studying plant volatile compounds. In this sampling method, a continuous airflow circulates through the sample container, acting as a carrier gas, thereby increasing the absolute amount of the vapor phase. While the analytes are adsorbed onto the adsorbent, the carrier gas circulates around or leaves the sample container, promoting the trapping of numerous volatile compounds, resulting in more efficient detection. In the case of open dynamic headspace systems, some problems similar to those observed in static headspace analysis may arise, such as increasing temperature and humidity or the release of accumulated hazardous VOCs into the environment due to the airflow. To avoid the disruptive effects of potential contaminants, it is crucial to ensure that the incoming air is clean, often by filtering it, for example, through activated carbon. In dynamic headspace analysis, volatile compounds are usually trapped on an adsorbent and enriched before GC analysis. It is a good idea to apply Teflon (PTFE) tubes and connections before airflow reaches the adsorbent(s) - for closed-loop systems wherever it is possible PTFE should be used - to avoid phthalates (used for flexibility increment of polimers) as a contamination originating from the systems plastic (silicone tubing for example) parts. Adsorbent materials are available in a wide

variety, and many studies provide comprehensive information on their selection and application (Raguso and Pellmyr, 1998). **Table 4.** summarizes the most commonly used adsorbents, including carbon-based materials and organic polymers, with information on thermal stability, affinity, and related studies. The adsorbent material is typically packed into thin glass or metal tubes, separated by glass wool or Teflon (PTFE) plugs or metal grids. During sampling, the air containing VOCs passes through the adsorbent bed at a precisely controlled flow rate. The captured compounds can be eluted from the adsorbent with a suitable clean solvent or a low-boiling-point solvent mixture, essentially performing solid-phase extraction (SPE). The elution solvent must contain a specified amount of standard compound (*e.g.*, 1-bromodecane or 1-bromododecane ideally since bromine ever so rarely appears in samples collected from headspaces of plants, fungi or ecosystems) for semi-quantitative analysis. Adsorbent materials suitable for thermal desorption, which exhibit high thermal stability (*e.g.*, Tenax, carbon molecular sieves, or activated carbon), can be used to avoid solvent extraction. During thermal desorption, VOCs are desorbed from the adsorbent under high-temperature conditions and are typically focused using cryofocusing before GC separation begins (see chapter 3.10.4). Compared to solvent extraction, thermal desorption provides increased desorption efficiency, and sample dilution does not occur. These factors contribute to enhanced analytical sensitivity. Additional benefits include reduced manual sample preparation time and the absence of contaminants that may be present in organic solvents. However, this method also has its limitations. Repeated sample injection is not feasible, and artifacts, thermal decomposition of thermally unstable compounds, or reactions of the trapping medium may occur (**Table 4.).** The primary issue with any trapping material is the incomplete adsorption of VOCs. Carbon-based adsorbents are highly specific and may only capture certain VOCs. When sampling complex VOC mixtures, careful consideration and the use of multiple adsorbent materials may be required for qualitative and quantitative representativeness of the measurement. This problem is addressed through "multi-bed adsorption," where adsorbents with different retention capabilities are placed in sequence. This allows the incoming air to first pass through an adsorbent capable of capturing highly volatile VOCs (*e.g.*, Carbograph and Carbotrap C). A comprehensive overview of the theory and practical application of multi-bed traps is provided by Ciccioli (2002). Multi-bed traps are commercially available (*e.g.,* Carbotrap/Carbosieve SIII beds, Markes International, Pontyclun, UK) or can be assembled manually (Schnitzler et al. 2004). In "push/pull" type DHS sampling, the studied plants can be non-invasively sampled, making it possible to repeat the sampling from the same plant at all stages of disease in the case of infected plants (Jansen et al. 2011). Consequently, dynamic headspace trapping is a frequently used method in chemical ecology (Conchou et al. 2017), especially when combined with SPE and liquid injection, as the

resulting liquid sample can be suitable for various GC-based analyses. However, during dynamic sampling, the desorption of adsorbed volatile organic compounds may occur over time due to the continuous suction effect, and desorption is primarily affected by flow rate and residence time, in addition to temperature for a specific adsorbent (Mirzaie et al. 2021). Furthermore, when solvent elution is used to transfer the adsorbed VOCs into the liquid phase, the efficiency of the applied SPE procedure(s) must also be characterized.

Table 4. Comparison of sorbents used for plant VOC trapping (Mátyus, 2023).

Adsorbents	Type	Particle Size (mesh)	Specific Surface Area (m2 g-1)	Max. Temp. (°C)	Approximate Range of Capturable Compounds (Boiling point)	Adsorption Properties	By-products, Pollutants
Porapak Q Super Q (very high purity version)	Ethyl-vinyl-benzene-divinyl-benzene	80/100	500-600	250	C5 - C12 bp: 50°C-200°C	High affinity for lipophilic substances to moderately polar organic compounds, for medium molecular weight compounds. Applicable to a wide range of VOCs, including oxygenated compounds. Low affinity for polar and/or low molecular weight compounds (H2O). Frequently used in VOC analysis.	Aromatic ketones, alcohols
AePorapak N	Divinyl-benzene - vinyl-pyrrolidone	80/100	250-350	190	C5 - C8 bp: 50°C-150°C	Specifically applicable to volatile nitriles and volatile alcohols.	No data/reference
Tenax TA	Poly-(2,6-diphenyl-p-phenylene-oxide)	60/80	35	350	C7 - C26 bp: 100°C-400°C	High affinity for lipophilic substances to moderately polar organic compounds, for medium molecular weight compounds. Not suitable for very volatile organic compounds. Low affinity for polar and/or low molecular weight compounds (H2O). Preferred for terpenes and frequently used in VOC analysis.	The degradation of benzaldehyde, acetophenone, and higher molecular weight aldehydes occurs under the influence of sunlight, with interference from ozone, e.g., with terpenes
Chromosorb 102	Styrene-divinylbenzene copolymer	60/80	350	250	bp: 50°C-200°C	Applicable to a wide range of VOCs, including oxygenated compounds.	No data/reference
Carbotrap	Graphitized carbon	20/40	100	>400	C5 - C12	Applicable to a wide range of VOCs; ketones, aldehydes, alcohols (bp>75°C), apolar compounds.	Decomposition of terpenes (a-pinene, b-pinene) due to thermal desorption [62].
Carbosieve SIII / Carboxen 100	Carbon molecular sieve	60/80	820	1200	>400	bp: -60°C-80°C	Suitable for small hydrocarbons. Not suitable for reactive hydrocarbons (1,3-butadiene, isoprene).
Activated Carbon		>1000	>400	C5 to C16	Less effective than Tenax for trapping aromatic aldehydes on CSLA traps	Rarely used for thermal desorption	Oxidation of terpenes (ocimene) on the adsorbent's active surface
PDMS	Polydimethylsiloxane	Not specified	<300	Volatile and less volatile compounds, depending on the layer thickness / fiber coating	Mainly non-polar adsorbent for non-polar volatile substances	Used as an SPME fiber coating	Inadequately conditioned adsorbent
PDMS /DVB	Polydimethylsiloxane / Divinylbenzene	Not specified	<300	MW 50-300	Bipolar adsorbent for polar volatile compounds	Used as an SPME fiber coating	Inadequately conditioned adsorbent
PDMS / Carboxen	Polydimethylsiloxane / Carboxen	Not specified	<300	MW 30-225	Bipolar adsorbent for trace amounts of volatile compounds	Recommended for low molecular weight substances (MW<90)	Inadequately conditioned adsorbent
CW/DVB	Carbowax / Divinylbenzene	Not specified	<300	MW 40-275	Polar adsorbent for polar alcohols and polar analytes	Inadequately conditioned adsorbent	

3.10.2.1 Closed-loop dynamic headspace analysis

The closed-loop extraction system has made the sampling of VOC emissions caused by pests/herbivores more efficient (Boland et al. 1984; Dudareva et al. 2004), as demonstrated for Lima beans and detached flowers (Koch et al. 1999). In these systems, air circulates through a closed chamber during the collection of odor compounds. The simple closed-loop extraction system was developed by Boland and Donath (1984), consisting of a 1-3 liter glass desiccator or other borosilicate/teflon-walled vapor space enclosure connected to a circulating pump. Plants or plant parts are placed in the glass chamber, and air continuously circulates through a stainless steel odor trap, allowing for quantitative trapping of emitted VOCs (Donath and Boland, 1995). Since the closed-loop air circulation minimizes the adsorption of contaminants compared to open systems (see dynamic headspace analysis systems), closed-cycle sampling is suitable for collecting odor samples from plants or other matrices with low VOC emissions. Another advantage is that the sampling unit can be easily set up in a controlled climate chamber, allowing for simultaneous sampling of multiple different plants, making it suitable for non-targeted, scanning studies. However, results from closed-cycle systems should be compared with open systems to exclude the influence of compounds that may be important due to the absence of fresh air, such as ethylene, which does not bind to adsorbent traps and can accumulate in the chamber. The relative humidity may also increase during the sampling cycle(s) without occasional venting.

3.10.2.2 'Pull' and 'push-pull' dynamic headspace analysis systems

In contrast to the closed-loop sampler, in 'pull' and 'push-pull' systems, continuously flowing air enters from the outside, passes through the sample chamber, and then exits the system through an adsorbent trap connected to a vacuum pump (Handley and Adlard, 2005). The simplest form of a pull system is when the adsorbent trap is placed directly next to the plant or plant part without being separated from the environment (Burger et al. 1988; Kaiser, 1991; Halitschke et al. 2000). It is easy to set up, inexpensive, and portable, allowing for simultaneous sampling from multiple chambers (Lockwood, 2001). Its application in open fields was demonstrated by Kessler and Baldwin (2001). This system works well for plants that emit significant amounts of VOCs. However, there is a relatively high risk that environmental pollutants may also adsorb and interfere with the detection of compounds originating from the sample during GC analysis (Marriott et al. 2001). Isolating leaves or flower parts of plants that emit a small amount of odor from the environment with a glass bell jar or oven bag can reduce the disruptive effects of these contaminants (Ragunathan et al. 1999). The schematic structure of the pull-type DHS approach we used is illustrated in **Figure 4.** Dudareva et al. (2004), as well as Raguso and Pellmyr (1998) reported similar devices in the context of vapor analysis of *Antirrhinum majus* and *Clarkia breweri*

flowers. In most of the systems mentioned above, environmental factors can be easily controlled by programming the parameters of the climate chamber and manually adjusting airflow and humidity (Jakobsen, 1997). In case of push-pull DHS sampling the air will be pumped and regulated by flowmeters from both sides (inlet/outlet) of the headspace to be sampled. Airflow is pumped towards the inlet thus pushing the flow into the headspace to be sampled while another pump and flow meter will generate a pull effect by suction from the headspace outlet. Of course push-pull systems cost almost twice as much since pumps and flow meters are the most expensive parts of these systems. A schematic representation of a push-pull system provided in **Figure 5.**

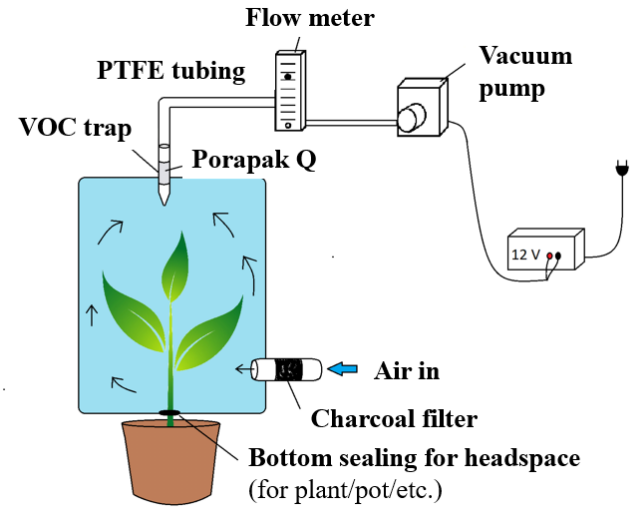


Figure 4. Schematic representation of an open-loop pull-type dynamic headspace sampling

3.10.3 Methodology on belowground research of volatile organic compounds

The sampling of belowground volatile organic compounds (VOCs) poses unique challenges due to their release as a blend of compounds that become diluted in the plant's surrounding environment. Despite recent advancements in techniques for sampling aboveground VOCs, sampling belowground volatiles is more complex due to the nonhomogeneous trapping environment (van Dam et al. 2016; Tholl et al. 2021; Sharifi et al. 2022). While methodologies for sampling aboveground VOCs have seen progress, there is a pressing need to invest in advanced methodology and instrumentation to effectively capture and fully analyze belowground VOCs (Sharifi et al. 2022). Presently, most research on root VOCs utilizes ground root material, which allows for the analysis of the total profile of volatiles in root tissue, albeit with the limitation that it may detect chemicals not induced by major root damage (Gfeller et al. 2019; Tholl et al. 2021). Understanding the complexities of belowground VOCs, which comprise a mixture of volatiles from various sources including plant roots, bacteria, fungi, parasites, herbivores, and predators, presents a significant challenge (Delory et al. 2016a; van Dam et al. 2016). Distinguishing the origins of VOCs is essential when assessing their effects on trophic interactions, particularly in the

context of fungal VOCs influencing plant-root-insect interactions. Additionally, belowground VOCs are influenced not only by environmental dilution but also by microbial activity, further complicating their analysis (Raza et al. 2016; Bier et al. 2017; Schenkel et al. 2018; Abis et al. 2020; Gutiérrez-Santa et al. 2020). Given these challenges, there is a need for sampling methods capable of collecting targeted belowground VOCs in the face of a nonhomogeneous environment and must address the complexities of belowground VOCs and overcome the technical limitations posed by their sampling environment (van Dam et al. 2016; Tholl et al. 2021; Duc et al. 2022). **Table 5.** reviews sampling approaches and their advantages and drawbacks to collect belowground VOCs in the soil matrix (Gfeller et al. 2019; van Doan et al. 2021; Tholl et al. 2021).

Table 5. Advantages and disadvantages of dynamic and passive methods to collect volatile organic compounds (VOCs) in belowground environments (Duc et al. 2022).

Method to collect belowground VOCs	**Advantages**	**Disadvantages**	**After sampling/pre-analysis process**
Dynamic sampling (Tholl et al. 2021) Gas chromatography–mass spectrometry (GC-MS), Pull/push–pull systems (Adsorbent traps, Trapping Super-Q)	Separate sampling and analysis times Controlled collection and pre-concentration of VOCs Quantitative and qualitative analyses Repeatable sample analysis Application of miniature devices (*e.g.*, Super-Q trap)	High Cost More challenging to apply in the field or other places Sampling requires equipment (pumps, flow meters, charcoal filters, VOC traps) Use of organic solvents in solvent elution and liquid injection	Method collects volatile mixtures, need to future step to distinguish original VOCs Trap>>elute traps with solvents for liquid injection or use thermal desorption of traps>>GC-MS or Gas Chromatography–Time-of-Flight Mass Spectrometry (GCxGC-Tof MS) analysis
Passive sampling (Tholl et al. 2021) GC-MS, SPME, Polytetrafluoroethylene (PTFE) tubing	Low cost Miniature sampling devices, sensitive, cost effective No consumption of organic solvents, clear spectrum of VOCs without solvent background interference Sampling is a snapshot of the VOC current state rather than for a time interval	Separate sampling and analysis times One-time only sample analysis due to thermal desorption (SPME) Limited quantitative analysis Adsorbent preference for analytes	Method collects volatile mixtures>> directly measure with thermal desorption of fibers or tubing>>GC-MS or GCxGC-Tof MS analysis

Sampling is either static type by SPME as described in section 3.10.1 or dynamic type by push/pull systems discussed under section 3.10.2 (Duc et al. 2022). Dynamic methods collect all belowground VOCs (emitted from roots, soilborne organisms, and soil matrix), by using clean-air flow through the belowground system, with VOCs trapped by a Super-Q filter **(Figure 5.)** (Hiltpold et al. 2011; van Doan et al. 2021). Other sorbent materials are also frequently used to

trap VOCs and are summarized by Tholl et al. (2006); Tenax TA and Carbopack B are used even in passive methods to sample belowground VOCs (Martín-Sánchez et al. 2020). Of possible passive sampling methods, a less complex system is one in which an SPME fiber inserted into a gap of a pot and exposed to belowground VOCs at room temperature (**Figure 4.**). The fiber is immediately analyzed by GC-MS. However, using SPME is at best a semi-quantitative approach, and depending on VOC composition, different SPME fibers should be tested because of differences in fiber affinity for classes of VOC compounds. In addition, extraction times and temperatures are important and need to be optimized. High temperatures and long extraction times may cause desorption of VOCs that have relatively low fiber affinity or low boiling point.

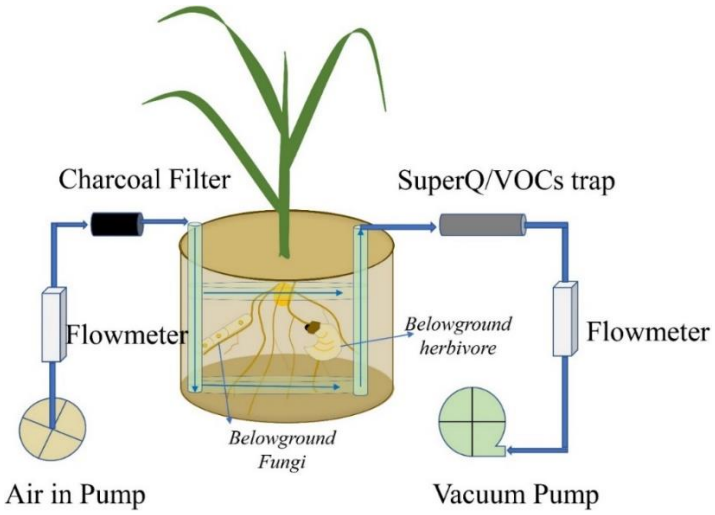


Figure 5. VOC emissions from roots, soilborne organisms, and soil matrix are collected by a push–pull system. The VOCs are trapped by a Super-Q trap (Duc et al. 2022).

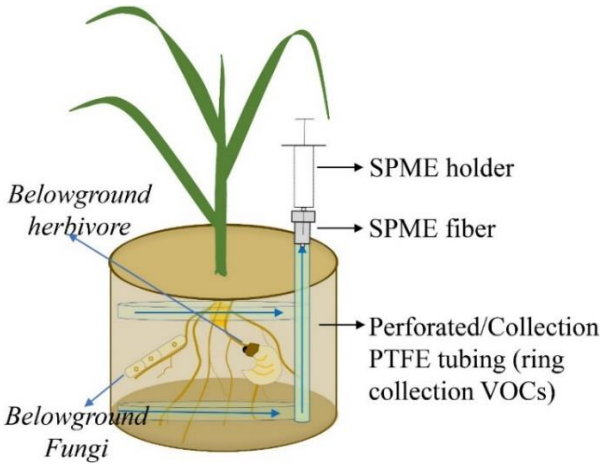


Figure 6. Volatile organic compound (VOC) emissions from roots, soilborne organisms, and soil matrix are collected by a passive system. VOCs are trapped by a solid phase micro extraction (SPME) fiber. Polytetrafluoroethylene (PTFE).

3.10.4 Gas chromatographic separation and detection possibilities for the measurement of plant volatile organic compounds (VOCs)

The analysis of plant VOCs adsorbed on different adsorbent materials using a configured GC technique is a routine task. There is a wealth of literature available describing measurement protocols and the latest technical innovations (Ragunathan et al. 1999; Lockwood, 2001; Marriott et al. 2001; Dewulf and Van Langenhove, 2002; Merfort, 2002; Handley and Adlard, 2005; Materić et al. 2015), only a small excerpt of which I present here. The GC measurement equipment includes a controlled temperature heating chamber capable of rapidly heating from room temperature to 300 °C. The column, which can be either capillary or packed, is located here. In VOC analysis, a capillary column is used, which is a thin glass capillary coated with a polyimide layer, typically 30-60 meters long. The film layer inside the column is the stationary phase, suitable for separating compounds based on their physical and chemical properties. One end of the gas chromatographic column is connected to the inlet (usually a split/splitless or programmable temperature vaporizer - PTV-type inlet or CIS inlet which is a special PTV type inlet that can be either heated or even cryocooled and it is manufactured and sold mostly by Gerstel company), and the other end is connected to the detector. The samples are introduced through the heated (or in case of special CIS inlets even cold injection is possible) inlet and then transported through the separation column by the carrier gas (usually helium). Each VOC interacts differently with the stationary phase and partitions to varying degrees between the stationary and mobile phases (carrier gas). Increasing the temperature changes the partition coefficient, and eventually, all compounds enter the mobile phase and are swept into the detector through the "transfer line" (a heated region connecting the GC and MS). Separation is based on differences in boiling points and polarities. Therefore, different VOCs leave the column at different times and can be identified and quantified using mass spectrometry or other types of detectors (Materić et al. 2015).

During VOC GC analysis, samples are either injected into the heated injector as solvent extracts or removed from the SPME fiber or other adsorbent material through thermal desorption in a special thermal desorption unit (TDU) that is mounted on a CIS type inlet - by heating the thermal desorption tube to 250-300 °C. In the two-phase thermal desorber, materials detached by heat are focused in a cryo trap (done in CIS type inlet serving below the thermal desorber apparatus as a cryo trap for focusing) before being transferred to the GC column for separation by heating up the CIS inlet in a programmable even multi stepped, and if needed a very fast (up to 12°C/s) thermal gradient after cryo trapping phase considered to be finished. Recent technological developments allow for the coupling of online systems with automated thermal desorption. Furthermore, an interesting method description has emerged for the direct thermal desorption of fragrance compounds from inflorescences, where the inflorescences were placed in quartz microfiber filters

and then placed in a modified GC injector (Jürgens and Dötterl, 2004). It is important to note that care must be taken to prevent thermal degradation of some components when sudden high temperatures are applied. For analytical purposes, packed or silica gel capillary columns with different stationary phases are generally used for the separation of VOC compounds, where the stationary phase is mostly consists of dimethyl polysiloxanes (PDMS) (*e.g.*, DB-1, DB-5, CPSil 5), and more polar polyethylene glycol polymers (PEG) (*e.g.*, Carbowax® 20M, DB-Wax, and HP-20M). Numbers indicate in the names of the columns the percentage of phenyl groups besides PDMS. Five percent phenyl containing columns are a good general choice, they are called semi-standard non-polar type columns providing good retention and separation capabilities with the exeption for the most polar and low boiling point compounds of interests, for those intermediate (up to 50% phenyl even) or PEG based columns that are called polar ones are the most suitable, however these columns do not tolerate such high temperatures as non-polar or semi-standard non polar phases would do. After separation, the volatile compounds can be analyzed with various detectors.

• Flame Ionization Detectors (FID) are often used for quantitative analysis because of their wide linear range, stable response, and detection limits in the picogram to nanogram range. Additionally, chemical ecologists frequently use FID detectors in combination with electroantennographic detection (EAD) to measure antennal responses to pheromones or other VOCs in biosensor gas chromatographs (GC-EAD).

• The Photoionization Detector (PID) is another type of detector commonly used to detect volatile terpenes. It is more sensitive in the presence of reactive double bonds than FID, but it requires thorough calibration for quantitative determinations.

• Mass spectrometers (MS) are the most common detectors used in routine plant VOC GC analysis. In most standard benchtop GC-MS instruments, compounds leaving the column are ionized by electron impact (EI) ionization, leading to the formation of positively charged molecular ions or fragments, which are separated based on their mass-to-charge ratio (m/z) with a quadrupole mass analyzer unit with unit resolution, as well as ion trap analyzers, but high-resolution mass analyzers can also be used (*e.g.*, Orbitrap). Time-of-flight (TOF) mass analyzers are also used, characterized by high resolution and mass accuracy. In scanning mode, a total ion chromatogram is obtained, providing information on compound retention times and mass spectra. The mass spectrum consists of a characteristic fragmentation ion pattern for each component, and these spectra can be matched to reference libraries, such as the Wiley and NIST or Fiehn MS databases, as well as other databases containing retention index (RI) data (*e.g.*, the NIST 17th edition already includes Kováts RI data). Retention index calculations are crucial factors for unknown and even targeted analysis,

since independent (*e.g.*, from applied heat program and other settings) retention index can be calculated for unknown component based on for example n-alkane based retention index for a certain column phase type (*e.g.*, different for 1 % phenyl containing phases (non-polar), 5% phenyl phases (semi-standard-non-polar) and for polar phases like wax columns). Kovats index (Kováts, 1958) can be calculated by measuring n-alkane series and the retention time of the unknown compound and the n-alkane retention times eluting before and after unknown peak by using the equation:

$$RI=100*[n+(N-n)*(t_r(unknown)-t_{r(n)})/(t_{r(N)}-t_{r(n)})]$$

where **RI** - retention index calculated for unknown compound; **n** - carbon number of lower boiling point (BP) alkane (*e.g.*, decane n=10); **N** - carbon number of higher BP alkane (*e.g.*, undecane N=11); $\mathbf{t_r(unknown)}$ - retention time (RT) in minutes for unknown peak; $\mathbf{t_r(n)}$ - RT of lower BP alkane eluting before t_r(unknown) and $\mathbf{t_r(N)}$ - RT for higher BP alkane eluting after it. However, identification based solely on retention index or mass spectrum is not reliable and can often lead to misidentifications. Therefore, in addition to using multiple libraries, it is advisable to consider preliminary or tentative identifications based on the best-matching mass spectra and the closest RI value in the absence of reference material. In the ideal approach to identification, Kováts indices are determined on two different polarity columns, taking advantage of orthogonal selectivity, and the deconvoluted mass spectrum of the compound is compared or matched with a spectral database and/or a certified standard. Since plant volatile mixtures may contain numerous chemically different compounds, including isomers, a simple GC-MS analysis may not be suitable for the identification of all compounds. Tandem mass spectrometry (MS/MS) allows the separation of individual compounds within complex GC peaks and achieves lower detection limits (Ragunathan et al. 1999; Granero et al. 2004). In MS/MS measurements, the ion selected by the first mass analyzer (the parent ion or, *e.g.*, a fragment produced by EI ionization) undergoes further fragmentation in a collision cell during collision with a neutral gas (the most common ion activation method, although there are many others). After fragmentation, the resulting fragment ions are analyzed in the second mass analyzer, providing additional structural information and better signal-to-noise chromatograms. Additionally, GC-MS analysis can be complemented with Fourier-transform infrared spectroscopy (FT-IR). This spectroscopic method was developed for distinguishing closely related isomers with highly similar EI mass spectra (Marriott et al. 2003).

- FT-IR provides information about the original molecule's structure and produces a unique spectrum even for very similar isomers. The limitations of using GC-FT-IR include cumbersome quantification and time-consuming evaluation, although the Sadler database continuously provides high-quality data (Sadler Division of Bio-Rad, Philadelphia, PA, USA).

- If it is impossible to efficiently separate a complex odor mixture on a single column, two-dimensional capillary gas chromatography (GC×GC) can be used. **Figure 7.** serves as an example and display of such a system. In this approach, compounds are separated in the first column, and selected fractions (heart-cut) are transferred to the second column. This results in a four-dimensional data set (1st dimension being retention time on the first column, 2nd dimension being retention time on the second column, 3rd dimension is peak intensity, and the 4th dimension is the mass spectrum itself). This approach is used for the determination of the enantiomeric composition of monoterpene hydrocarbons in the tissues of Norway spruce (*Picea abies*) by combining a conventional GC column with a chiral column (Borg-Karlson et al. 1993). Recently, a comprehensive GC×GC system was developed, which, by combining columns of different polarities, increased the total separation space significantly. This method is particularly useful for the analysis of essential oils, as it improves peak resolution and enhances the qualitative and quantitative determination of odor compounds (Di et al. 2004; Marriott et al., 2004). Identification using comprehensive GC×GC can be effective in studying chemical fingerprints and achieving the best available selectivity with the advanced deconvolution capabilities of TOF mass analyzers and two-dimensional separation. Its worth mentioning that even if the TOF MS coupled to the GCxGC system is a unit mass resolution one and not a real high resolution TOF, for GCxGC fast analyzers are required due to the very small peak widths that are results of cryomodulation and refocusing to collect enough data points from narrow Gaussian peaks to accurately characterize them (12 data points, ideally 20 is required above 5% peak height for accurate quantitation).
- Proton transfer reaction mass spectrometry (PTR-MS) is an analysis technique to measure VOCs directly at a certain time, for example, to understand the mechanisms of belowground VOCs in ecosystems like Danner et al. (2012) demonstrated. Directly measured VOCs were released from root herbivore damage in cuvettes on the top of the soil at the stem and root interface. Acton et al. (2018) measured VOCs by using airflow generated in a root glass chamber filled with a potting substrate. All belowground VOCs emitted to the environment in a certain time can be measured by PTR-MS (Majchrzak et al. 2018; Tholl et al. 2021; Sharifi et al. 2022). The PTR-MS method also has disadvantages because it characterizes only the mass-to-charge ratio (m/z) of VOCs and not their exact molecular identity. In addition, one molecular formula may represent different structures, which cannot be discriminated by PTR-MS. Some small-chain alkanes are also not detected by the technique. Therefore, the PTR-MS method is generally used simultaneously with GC-MS to determine the chemical identities of volatiles from the m/z data (Sharifi et al. 2022).

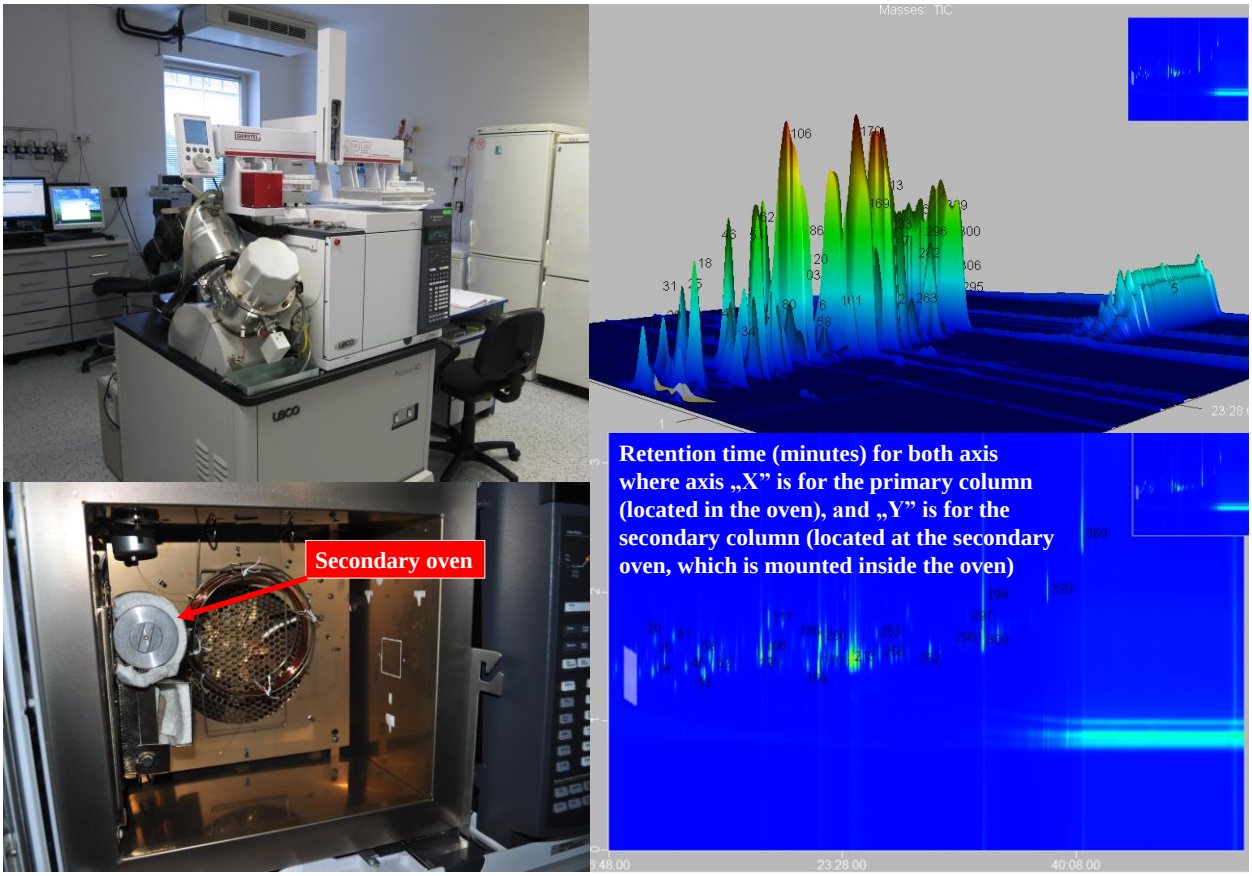


Figure 7. GCxGC-TOF-MS system, of Leco Corp. Pegasus 4D model, and representations of 2D-GC separation by contour and 3D maps

3.10.5 Evaluation of methods used for VOC sampling and analysis

While various techniques exist for selecting the most appropriate method for a specific issue, comparing results from different methods is challenging due to potential variations in odor profiles depending on the measurement method. Unfortunately, few studies have compared methods. Key factors affecting odor compound collection in the sample chamber include environmental conditions like light intensity, temperature, and relative humidity, which directly impact plant odor metabolism, photosynthesis, and transpiration. Regulating airflow is crucial for controlling temperature, humidity, and achieving optimal gas exchange. Different adsorbents and desorption methods can lead to varying qualitative and quantitative results. Significant differences in VOC pattern of *C. breweri* flowers when using different adsorbents and solvents. Higher flow rates during GC analysis can result in increased background noise. Sampling time must be optimized considering circadian rhythms, with plant responses to chewing or damage potentially lasting hours or days depending on the species and plant part. Longer sampling times may be necessary for plants with low VOC emissions. Increasing the quantity of analyzed plant material, reducing surrounding air volume, and adjusting flow rates can enhance odor compound detectability, but this may lead to increased evaporation and airborne contaminants (Duc et al. 2022).

4. MATERIALS AND METHODS

4.1 Materials and methods regarding a pilot experiments for surveying different plant-pathogen/pest setups and methods for VOC collection

4.1.1 Plant species and their cultivation

For our experiments, we used different crops, such as wheat and barley, corn, tomato, and button mushroom, however I will only present those experiments where I significantly contributed and at least partially evaluated the data from our work with Radványi et al. (2019). The types of plants and their cultivation conditions are summarized in **Table 6.**

Table 6. Plant species, respective genotypes and cultivation conditions for the pilot experiment for VOC sampling and analysis

Plant Species	Variety	Growth Conditions
Wheat (*Triticum aestivum*)	Carstens V	18-20°C, long-day
Barley (*Hordeum vulgare*)	Harrington (BC 52), Mv Initium (BC 5), KH Hunor (BC 168)	25°C, long-day
Tomato (*Solanum lycopersicum*)	Uno Rosso	25°C, Natural Light

4.1.2 VOC collection methods in the pilot experiment

Two types of sampling techniques were used in our measurements. We used SPME sampling for corn, tomato, and button mushroom samples, however I will only address tomato samples for SPME due to reasons mentioned above. During sampling, we placed the samples in a closed space (generating headspace by either PTFE bags or borosilicate apparatus) and waited at least 60 minutes to achieve equilibrium between the sample and the air above it before the start of sampling. Sampling time varied depending on the size of the plant, the sampling temperature, and the amount of air above the sample. We used a so-called "volatile collection" sampling system (essentially an open-loop pull-type DHS) to collect VOCs from wheat and barley samples. We attached filters filled with activated carbon to the lower air inlet of the covers and connected VOC collection tubes filled with 50 mg of 80-100 mesh Porapak Q adsorbent **(Figure 8.)** to the upper air outlet. Odor collection was carried out for 24 hours with a flow rate of one L/minute. The execution of the sampling approach and conditions are summarized in **Table 7.**

Table 7. Plant Species, Sampling approach type and conditions

Species	Sampling Type	Sampling Conditions	Sampling Duration	Tempe-rature
Wheat (*Triticum aestivum*)	Volatile collection	50mg Porapak Q	24 hours	25-30°C
Barley (*Hordeum vulgare*)	Volatile Collection	50 mg Porapak Q	24 hours	25-30°C
Tomato (*Solanum lycopersicum*)	SPME	50/30 µm DVB/CAR/PDMS	30 minutes	25-30°C

4.1.3 Pests and pathogens and sampling time

During our experiments, we examined control (healthy) and infected samples. Sampling was performed at specific days after the infection, plant species infectious agents and sampling time are summarized in **Table 8.**

Table 8. Summary of plant species, infectious agents and sampling times

Plant	Infectious agent	Sampling time
Wheat	*Blumeria graminis f. sp. Tritici* type 51	At the onset of symptoms (7 days after inoculation - DAI) and in advanced disease stage (14 DAI); n=8
Barley	*Pyrenophora teres f. teres*	Harrington: 7 DAI (n=1 for control, wounding and inoculated), and 20 DAI (n=2 for control and inoculated); Mv Initium: 8 DAI (n=1) KH Hunor: 23 and 37 DAI (n=2)
Tomato	*Botrytis cinerea* (B0510)	In the visibly advanced stage of the disease

4.1.4 Structure determination and relative quantitation by GC-MS for pilot experiments

In all cases, our measurements were carried out using a gas chromatograph coupled to a mass spectrometer (GC-MS). For the analysis of plant volatiles, we used an Agilent 6890 GC and 5973 MS, and for the analysis of button mushrooms, we used an Agilent 6890 GC and 5975 C MS coupled analytical system (Agilent Technologies, Santa Clara, CA, USA). During our measurements, we used an Agilent HP-5 MS (5% phenyl)-methylpolysiloxane) Ultra Inert 30 m x 0.25 mm x 0.25 µm capillary column for the separation of volatile components. After SPME sampling, the sampling fiber was placed directly into the GC injector (heated up to 250 °C), where the components were desorbed and then introduced onto the column. For plant analysis, the carrier gas was helium 6.0 (1 mL/min constant flow). After volatile collection sampling, we eluted the adsorbed VOC compounds with 300 µl of chromatography-grade *n*-hexane (VWR, Radnor, Pennsylvania, USA). The samples were stored in a freezer at -20°C until analysis in borosilicate GC injection vials with inert glass inserts sealed by PTFE septum vial caps. For analysis, 1 µl was

injected into the gas chromatograph (injector temperature: 270°C) in splitless mode. Different heating programs were developed for each plant sample to achieve optimal separation. Detection by mass spectrometry was used with electron impact positive ionization (EI+) with the standardized 70 eV energy. The ion source was heated up to 230 °C, and the quadrupole temperature was 150°C. The mass spectrometer was operated in scan mode to record 33–500 m/z. The Agilent Mass Hunter Qualitative Analysis B.08.00 program was utilized to evaluate the data, and the identification of the components was performed using the NIST 2017 MS Search mass spectral library. For identification, English common names were used, so we can easily search for them in the literature and databases (Radványi et al. 2019).

4.2 Experiments regarding open-loop-pull-type-DHS VOC collection and SPE type sample preparation

All samples and calibrations mentioned under sections 4.2 and 4.4 were analyzed by the method described in section 4.3 and evaluated according to the principles presented in section 4.4.3. Before each experimental measurement, the VOC traps were washed twice with 800 µl of *n*-hexane and dried and purged with nitrogen flow prior to any additioning (like spiking experiments) or VOC collection. It's important to note that the experiments were conducted on frequently used VOC traps, so the performance characteristics determined during the experiments specifically apply to regenerated adsorbents (not brand new odor traps that would provide the most optimal conditions) to test the traps under everyday experimental conditions. After VOC trapping and elution of adsorbents to produce a liquid sample (essentially a solid phase extraction, SPE), the volatile traps were washed twice with 800 µl (per solvent type) of methanol, a 3:1 (v/v%) mixture of methanol:chloroform, dichloromethane, and *n*-hexane, and then rinsed under a gentle nitrogen flow. This was done to ensure that any possible contamination was eliminated, allowing the sorbent tubes to be reused later. In every experiment, external solvent-based calibration was used, applying linear regression with a weight of 1/x, where $R2 > 0.99$, and other criteria as set by SANTE/11312/2021 (Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis). Unless indicated otherwise, this was applicable for the 0.1–2.5 µg/ml (aka ng/µl, injected on column amount) concentration range using at least three points for quantitation in the case of all experiments below. External solvent-based calibration points were produced from the appropriate submixes, the complete mixture, or other reference mixtures by diluting them with n-hexane directly into GC injection vials to be injected later into the GC-MS system and method described in Section 4.3 (Mátyus 2023). Following any addition/spiking directly onto the VOC traps, the sorbent tubes were purged with a nitrogen flow

rate of 0.4 L/min for 5 seconds to evaporate any residual solvent. Subsequently, the sorbents were eluted (after addition and/or sampling) with 300 µl of *n*-hexane, during which the solvent was moved up and down the sorbent bed three times using a 1 ml pipette, and the solution containing the adsorbed compounds was transferred to a borosilicate injection vial under positive pressure. The samples obtained in 4.2 were placed in borosilicate injection vials (using a 250 µl restrictor if necessary), sealed with PTFE-lined screw caps, and analyzed immediately or stored at -20°C until analysis was possible.

4.2.1 Reference solutions and mixtures, general handling of VOC traps

Solvents, such as *n*-hexane (Pestinorm Supratrace GC grade), methanol, ethanol, dichloromethane, chloroform (at least HPLC grade), as well as desilanized glass wool (GC-grade) and activated charcoal were purchased from VWR International (VWR, Radnor, Pennsylvania, USA). The reference materials were obtained from the Merck-Sigma group (Darmstadt, Germany), and (5Z)-octa-1,5-dien-3-ol was purchased from Toronto Research Chemicals (Toronto, Canada). The Porapak Q adsorbent for VOC trapping was supplied by Waters Corp. (Milford, Massachusetts, USA). From the available reference materials, 1 mg/ml stock solutions were prepared in borosilicate PTFE-capped screw-top centrifuge tubes, which were stored at -20°C. Considering the retention indices of the components and their solubility properties, 9 submix reference solution mixtures (hereinafter referred to as submixes) were prepared at a concentration of 100 µg/ml. A tenth mixture included a homologous series of *n*-alkanes (C7-30), also at a concentration of 100 µg/ml. The **annex 9.6 Table S3** provides the details about the individual components of the reference mixtures, their identifiers, properties, the retention times measured in our GC-MS methodology described in section 4.2 and 4.3, 4.4.3, and their calculated and literature-based n-alkane based semi-standard non-polar retention indices and respective quantitative ions (Mátyus, 2023).

4.2.2 Spiking of reference mixture solutions to VOC traps directly for assessing SPE elution of components and effect of mixtures from porapak Q adsorbent by *n*-hexane with calculation of recovery (%)

4.2.2.1 Spiking of submixes and their recovery (%) without and with internal standard

From the prepared submixes listed in section 4.2.1 and **Annex 9.6 Table S3**, 30 µl were added with Hamilton syringe to the Porapak Q-filled sorbents **(Figure 6.)** with five repetitions**,** and then the sorbent tubes were purged as described in section 4.2 with a nitrogen to evaporate any residual solvent. Subsequently, the sorbents were eluted after addittioning and/or sampling with 300 µl of *n*-hexane as described in section 4.2, (theoretically 10 µg/ml eluate concentration after spiking from the prepared submixes). A volume of 100 µl were taken from the eluted samples and

combined with 900 µl of hexane for dilution by a factor of 10 so final diluted eluate obtained corresponded to 1 µg/ml (1 ng/µl -1 ng theoretical concentration injected on column) for injection into the GC as presented in section 4.3. In the second experimental round, the above experiment was repeated (submix 6 was prepared without 1-bromodecane and submix 8 was prepared again without 1-bromododecane for the second experimental round to exclude internal standard candidates), so 30 µl from submixes of 100 µg /ml and for elution volume correction by adding the internal standard 1-bromodecane (after elution of the sorbent into a vial, before any dilution steps, 2 µl was added to the eluate from an 500 µg/ml concentration solution of 1-bromodecane in n-hexane using a Hamilton syringe that is a 1000 ng absolute added value to each eluate, therefore only eluate volume may affect the measured peak area for the internal standard in theory, so elution volumes, thus concentrations measured can be corrected yielding more accurate results). After the dilution of the IS spiked eluate (dilution factor of 10 again) the resulting diluted eluates theoretical concentration was 1 µg/ml containing 100 ng absolute value 1-bromodecane. For calibration diluting the individual submixes (submixes 1-9) and *n*-alkane series mix (submix 10) with *n*-hexane directly into injection vials were applied. Recoveries assessed against the external calibration mentioned under section 4.2, and response of 1-bromododecane was used as an internal standard (IS) for obtaining correction factor for each individual samples elution volume (300 µl in theory, variable volumes ranging from 200-100 µl mostly eluted from traps depending on VOC trap condition and swelling of adsorbent packing and glass wool stoppings inside the individual traps).

4.2.2.2 Evaluation of recovery for complete mixture constituted from submixes

In the third experimental round we wanted to examine the effects on the recovery if the nine VOC submixes were combined into a mixture solution with a concentration of 10 µg/ml, which contained all previously analyzed odor compounds (except the homologous series of alkanes of submix 10.). This is referred to as the complete mixture. I investigated recovery, as described under section 4.2.2.1, but in this case with an addition of 30 µl from the complete mixture (10 µg/ml) directly onto the adsorbent traps, followed by elution with 300 µl n-hexane. Eluates were spiked by adding 2 µl from 50 µg/ml concentration of 1-bromodecane in *n*-hexane as an internal standard (100 ng absolute value added). The resulting eluate was not diluted further, (theoretical concentration of components in the eluate at 1 µg/ml, thus 1 ng injection on column). A comparison of recovery results (n=5 with internal standard correction) from section 4.2.2.1, and from the complete mixture (n=2, with internal standard correction) were made.

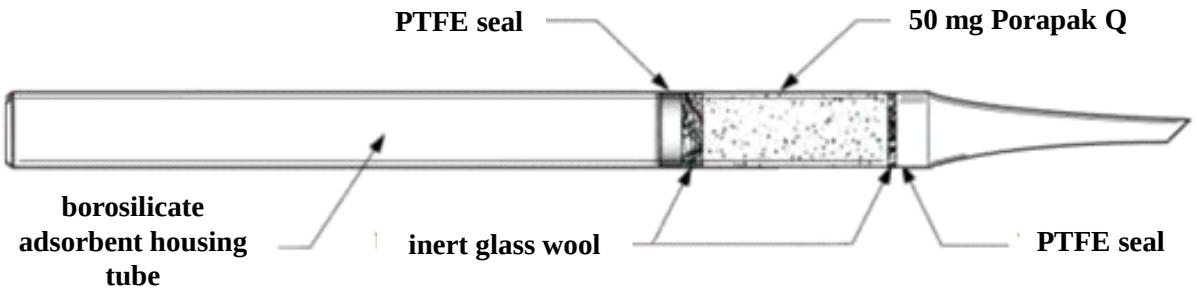


Figure 8. Schematic representation of the VOC trap sorbent filled with 50 mg Porapak Q sorbent developed and applied for DHS sampling

4.2.3 Investigation of recovery in case of continuous and periodic open-loop-pull-type-DHS sampling followed by SPE elution

As described in Section 4.2.2.2, we spiked the complete mixture (10 µg/ml obtained from pooling submix 1–9 without 1-bromodecane and 1-bromododecane) and, in a separate experiment, also with submix 10 of the n-alkanes (10 µg/ml) in n-hexane by adding 30 µl of them onto the VOC traps for 8 repetitions in each case (concentration level of 1 µg/ml with respect to the elution volume). However, after spiking, the 3-3 spiked VOC traps have been inserted and used to the pull-type dynamic headspace sampling system (continuous and periodic DHS) before start of the sampling duration. The confined vapor space was created using glass chambers, and at the bottom of these chambers, we placed tubes filled with activated charcoal to reduce VOC background from external air. The adsorbent traps were connected to the outlet holes at the top of the chambers using PTFE tubing, followed by a silicone tube (after the VOC trap) that connected to a flow meter and a pump. Three VOC traps spiked as described above were inserted for continuous open-loop-pull-type DHS sampling, where air flowed through the sample chamber at a rate of 0.8 L/min at 26°C for 6 hours. As far as I know, in collaboration with my masters student at the time, namely Réka Mátyus, we were the first to devise and conduct what we refer to as cyclic/periodic pull-type DHS sampling with the prototype odor collector apparatus (named "nose-e," as presented in Figure 9.), developed under the e-nose project by our research group at CAR. An innovative feature of it, compared to commercially available portable VOC collection apparatuses, was its programmability to automatically switch “on” or “off” and repeat different programmed cycles. This was done to reduce expected losses due to desorption by not constantly pulling airflow from the sampled headspace but rather periodically. To achieve this, we reduced the total flow volume compared to continuous sampling by 66.66% during the sampling by operating the nose-e for 5 minutes (flow on) and then allowing it to rest for 10 minutes (flow off), repeating this sequence for the entire 6-hour duration. Three adsorbents spiked as described in 4.2.2.2 were inserted into the periodic open-loop-pull-type DHS setup, as well as a blank sample (for both DHS methods), where no compounds were added to the sorbents and connected to the DHS systems.

The remaining two adsorbents spiked were eluted to obtain direct eluates as described under 4.2.2.2. After the sampling time ended for both DHS approaches, we performed elution as described in Section 4.2.2, and I applied the internal standard correction with 1-bromodecane here as well. For quantitative comparison evaluation of recovery% resulting from direct spiking (n = 2), periodic (n = 3), and continuous DHS (n = 3), sample eluates obtained and quantitated against external calibration according to Section 4.2 (Mátyus, 2023).

4.2.4 Competitive binding site investigation of odor components adsorbed on the sorbent during open-loop-pull-type DHS sampling followed by SPE elution

The experiment aimed to compare the odor profiles of two different types of fruit separately and when they were present in the same airspace to investigate competition for adsorbent binding sites. Commercially available fruits of tomatoes and pears were homogenized using a Russell Hobbs 23180–56 NutriBoost blender and chopper. Five grams from each homogenized fruit matrix were weighted into 50-ml centrifuge tubes. The sampling was carried out for 6 hours at a flow rate of 0.8 L/min at 26–27 °C. Tomato and pear fruits were chosen because they exhibited both different and common components; their quantities were present at a similar magnitude in a presurvey we conducted. Four empty centrifuge tubes were placed in one headspace chamber for creating blank samples. Three headspace chambers contained only tomato (two 50-ml tubes with tomato and two empty ones put inside the sampling chamber), three contained only pear (two 50-ml tubes with pear and two empty ones), and three HS chambers contained both tomato and pear (two 50-ml tubes filled with tomato and two with pear). A picture of the experimental setup is shown in **Figure 9**. We concluded this experiment in the GC-MS laboratory, where high background levels were expected and examined from blank samples collected to further push and test sorbent capacity towards its limit, since usually indoors a high background noise is to be expected in blanks, which is one of the biggest drawbacks for DHS techniques, especially in open-loop-pull systems. Elution from the sorbents was carried out according to section 4.2.2.2, with IS correction, and relative quantitation was done against the response of nonane, described under section 4.2 (Mátyus, 2023).

4.3 GC-MS VOC analysis method for liquid injection of eluates and samples obtained by open-loop-pull-type-DHS VOC collection and SPE elution sample preparation

Measurements of liquid samples were carried out by GC-MS on an Agilent (Agilent Technologies Inc., Santa Clara, California, USA) 7890B GC coupled to a 5977B MS system. The instrument was equipped with a Gerstel MPS CTC type autosampler and a CIS4 inlet with septumless head installed (Gerstel GmbH, Mülheim a. d. Ruhr, Germany).

Figure 9. Picture of the open-loop-pull-type DHS sampling system during the competitive binding site investigation, as described in Section 4.2.4

Injection volume was 1 µL in splitless mode, septum purge flow was 3 mL/min, and purge flow was 50 mL/min starting at 3 min. Before each run, the CIS4 inlet was cooled with liquid CO_2 to 20 °C and the temperature equilibrated for 0.5 min. The injector temperature program was the following to minimize compound degradation during column transfer: 20 °C held for 0.25 min (initial time), then with a rate of 12 °C/s, the CIS4 inlet was heated up to 270 °C with a hold time of 6 min.

Separation was carried out on a J&W HP-5MS UI 30 m x 0.25 mm x 0.25 µm semi-standard, non-polar type capillary column (Agilent). Helium 6.0 (SIAD Macchine Impianti S.p.A., Bergamo, Italy) was used as a carrier gas with a flow rate of 1 mL/min (36.26 cm/s) in constant flow mode. The oven temperature program was set as follows: 40 °C, hold for 3.5 min, increase by 7 °C/min to 140 °C, then by 20 °C/min to 280 °C, and hold for 2 min. As a post-run function, the column was flushed by heating it up to 325 °C with a column flow of 1.5 mL/min for 2 min before returning to initial conditions. The total analysis time from injection to injection was 36 minutes. For MS detection, EI ionization was used with a standard 70 eV energy, and the MS was tuned and calibrated by perfluorotributylamine according to the manufacturer's instructions.
A gain factor of two was applied for the scan and SIM events to maintain optimal sensitivity for both. The auxiliary heater was set to 250 °C, the MS source to 250 °C, and the MS quad to 150 °C. Mass spectra were collected in the Scan & SIM combined acquisition mode; the cut time was 5.2 min. For identification, the scan event was set to monitor *m*/*z* 35–600 with a scan speed of 9 scans per second and a 0.1 *m*/*z* step size. In the SIM event, *m*/*z* 93 was monitored with a dwell

time of 20 ms during the whole run, which is a characteristic fragment for most terpenoids. For the quantitation and confirmation of identified important and abundant fungus-related alcohols and a ketone *m*/z 57, 70, 72, 93, and 99 were acquired in SIM mode with a 20 ms dwell time during 10.05 to 11 min (Hamow et al. 2021).

4.4 Application of open-loop-pull-type-DHS for non-invasive dynamic sampling followed by untargeted quantitative GC-MS measurement in relation to wheat PM infection

All methods and materials described under this section were published in Hamow et al. (2021).

4.4.1 Plant material and inoculation treatment

4.4.1.1 Greenhouse experiments

Seeds (20-30 pieces) of the susceptible bread wheat cultivar 'Carsten V' (c and Donner 2000) were sown each into 1-liter clay pots containing garden soil and 1 cm of sand layer on the top. The bread wheat cultivar 'Carsten V' was used in all but one experiments because it does not contain any known *Pm* resistance genes to powdery mildew (Nover, 1958; Vida et al. 2002) and therefore it is expected to be susceptible to all *Bgt.* pathotypes. Plants were grown in an automated greenhouse (Global Glasshouse Ltd., Szentes, Hungary) at a humidity of 60-90% with illumination at 12 h photoperiods using Groxpress 600W E40 lamps at 2050 K color temperature (Sylvania, Budapest, Hungary). To simulate environmental temperature variations, three independent experiments were carried out in January-February of 2018 (28 days) and in February-March of 2019 (31 days) and 2020 (29 days). Temperature was continuously recorded in 10 min intervals inside as well as outside the greenhouse compartment (**Annex 9.8 Figure S4.**). The inoculum originated from a single colony and was maintained on 'Carsten V' plants under isolated circumstances (**Annex 9.9 Supplementary Method**). Inoculation was applied by manually shaking conidiospores of *Bgt.* pathotypes 51 and 71 (Frauenstein et al. 1979) onto single leaves of 7-days-old test plants (stages 11-12 at the Zadoks scale, Zadoks et al. 1974) in a closed box. Control plants without inoculation and blank control pots with identical soil composition but without plants were simultaneously included in the experiments. Each treatment consisted of four biological replicates, except for blank controls, which consisted of two individual pots. The experiments were executed three times (in 2018 with *Bgt.* pathotype 51 as well as in 2019 and 2020 with pathotypes 51 and 71): in each experiment two repetitions of four pots per treatment were sampled simultaneously, except for plants inoculated with pathotype 71 which were represented by two individual pots (detailed setup in **Annex 9.9 Supplementary Method**).

4.4.1.2 Growth chamber experiment

During May 2020 two wheat cultivars ('Mv Suba' and 'Mv Kolompos') were grown in a PGR15 reach-in plant growth chamber (Conviron, Winnipeg, Canada) according to the T2 spring program

(Tischner et al. 1997). Plants were inoculated at the beginning of flowering with a conidiospore mixture of *Fusarium graminearum*/*F. culmorum*, but spontaneously showed slight PM symptoms about 15 days later only on plants weakened by *Fusarium* disease (**Annex 9.7 Figure S3**). To test wider applicability and robustness of the identified VOCs in further cultivar-pathotype combinations, sampling of eight healthy control and eight *Fusarium*-inoculated and *Bgt*-infected plants for both wheat cultivars was carried out for 8 h (instead of 24 h, see below).

4.4.2 Dynamic headspace volatile collection and sample handling

Headspace of greenhouse plants was sampled in 2018 and 2020 at 7 days after inoculation (DAI) when first barely visible symptoms emerged and at 14 DAI in the full-disease development stage, but only at 14 DAI in 2019. To create a headspace, plants were covered with specially crafted 2.5-liter glass cups (55 cm x 8 cm O.D.), which were carefully inserted a few cm deep into the soil inside the circumference of the pots without damaging the plants or their roots. At the bottom of the cup, there was an inlet for air with laboratory glass wool and an active charcoal filter (mesh 4-8, Alfa Aesar, Wardhill, MA, USA), and PTFE tubing was connected to its top to serve as an air outlet (**Figure 10.**). Two volumes of air were sucked through the cup, which was then closed and left for one hour prior to sampling. An adsorbent tube containing a load of 50 mg Porapak Q sorbent (mesh 80–100, Waters, Milford, MA, USA) between two layers of gas chromatographic-grade deactivated glass wool and PTFE rings for fixation was connected to the PTFE tubing of the outlet. The adsorbent tube was covered with aluminum foil to prevent any photodegradation or alteration of adsorption capacity potentially caused by exposure of the sorbent to light for a prolonged period. Behind the adsorbent tube, a BA-4AR type flow meter (Kytola Instruments, Muurame, Finland) and a NMP 830 KNDC type pump (KNF-Micro AG, Reiden, Switzerland) were connected by silicone tubing. Sample collection of the headspace was done in each case for 24 hours with a sampling speed of 0.8 L/min, with each collection starting at 10 a.m. on each sampling day. Flow meters were checked regularly during sample collection. After collection, adsorbent tubes were not thermally desorbed but instead eluted with 300 µL of PESTINORM® grade *n*-hexane, then transferred into 1.5 mL GC injection vials with glass inserts closed with caps containing PTFE septum, sealed with Parafilm, and stored at -20 °C until analysis. Reproducibility and direct sorbent recovery, carryover, and stability were tested and verified. After elution with *n*-hexane, adsorbent tubes were cleaned by forced washing in 4x500 µL of each of the following solvents: methanol, methanol:chloroform 3:1, dichloromethane and finally *n-hexane*, followed by drying under a gentle nitrogen stream. Glassware and PTFE tubing and connections were rinsed with ultrapure water, then with acetone, and baked at 130 °C for 3–4 hours, followed by wrapping with thick aluminum foil for storage prior to use for sampling.

All solvents used were at least HPLC-grade (VWR, Radnor, PA, USA). In the growth chamber experiment, the *Fusarium*-infected and control plants' headspaces were created by the use of PTFE bags with gastight sealing (instead of the glass apparatus on **Figure 10.**), and adsorbents were handled after sampling as described above and analyzed by the GC-MS method as described previously.

4.4.3 Data evaluation, mining, quality control and statistical analysis

Mass Hunter Workstation Qualitative Navigator B.08.00 and Quantitative Analysis B.09.00 software tools (Agilent) were used for evaluation and quantitation. Identification of compounds were based on background subtracted mass spectra that were identified by the NIST MS Search program (National Institute of Standards and Technology)/EPA/NIH Mass Spectral and RI Library v17 (2017) and the Wiley Registry® of Mass Spectral Data, 10th edition (2014), and by utilizing *n*-alkane retention indices with a C7-30 *n*-alkanes mix (Sigma-Aldrich, St. Louis, MI, United States). The highest-ranked, consistent library hits (min. 75% similarity with reverse search for mass spectra) and retention index score matches were condsidered for the identification of volatile compounds. Integration was carried out to the most abundant unique ion for each peak **(Annex 9.10 Table S4)**.

Figure 10. Sampling setup for DHS sampling consisting of eight pots of wheat plants and two blank pots under glass cups with air in- and outlets located in the bottom and the top

For unambiguous identification and quantitation commercially available reference materials were used for 1-heptanol, 1-octen-3-ol, 3-octanone (Sigma Aldrich) and (5Z)-octa-1,5-diene-3-ol (Toronto Research Chemicals Inc., North York, Canada). Reproducibility and linearity of the GC-MS method was verified by injecting the reference materials purchased from Sigma Aldrich and diluted their stock solutions as a mixture in n-hexane **(Annex 9.11 Table S5)**. A system suitability test were also conducted with a mixture of styrene, 1,3-dimethoxy-benzene, and longifolene **(Annex 9.12 Table S6)**. To asses chromatographic stability retention times of *n*-alkanes (C7-26) used for calculation of retention index (RI) injections from dilution of submix 10. were evaluated **(Annex 9.13 Table S7)**. For peak areas lower than the limit of quantification (LoQ) the background was always recorded with non-zero values for reliable statistical tests. The distribution of the identified BVOCs was tested in the Metabolite Ecology database of the KNApSAcK Family databases (Afendi et al. 2012), and the mVOC 2.0 database (Lemfack et al. 2018). Genes encoding BVOC biosynthetic enzymes (dioxygenases, monooxygenases and lipoxygenases) were identified by basic local alignment search tool (BLAST) searches (Altschul et al. 1990) in *B. graminis* whole genome sequences maintained in the Ensembl Fungi database (release 48, August 2020) and the Joint Genome Institute Mycocosm Blugr2 database (Frantzeskakis et al. 2018; https://mycocosm.jgi.doe.gov/Blugr2/Blugr2.home.html) as well as by queries in the Universal Protein Resource (UniProt, https://www.uniprot.org/) database. Significance for differences between controls and treatments (symptomatic stages, pathotypes and years) was analyzed by two-sample *t*-tests (IBM SPSS Statistics software version 16) as well as by multivariate PERMANOVA using the 'adonis' function in the 'vegan' package (v. 2.5-7, Oksanen et al. 2020) of the R environment (v3.6.3, R Core Team, 2020). In order to identify potential VOC biomarkers principal component analysis (PCA) was applied for unsupervised reduction of data dimensions after standardization by *z*-score normalization of the original data matrix. Principal components, loadings and scatter (score) plots of the observations were made using the base R function 'prcomp'. The biplot illustration was performed using the 'pca' function of the packages FactoMineR (Lê et al. 2008) and 'factoextra' (Kassambara and Mundt, 2020). To reveal systematic patterns in BVOCs across various treatments colored heat maps were generated by the R packages 'ggplot2' and 'reshape2' (Wickham, 2007). The quantitated BVOC biomarkers were also statistically explored by boxplots (BoxPlotR, http://shiny.chemgrid.org/boxplotr/ Spitzer et al. 2014) and corresponding basic parameters (Real Statistics Resource Pack software, Release 6.2) using Power Query in MS Excel.

5. RESULTS AND DISCUSSION

5.1 Results regarding pilot experiments for surveying different plant-pathogen/pest setups and methods for VOC collection

All results presented under this section were published as Radványi et al. (2019).

5.1.1 Changes in the aroma compounds of three different barley varieties due to *Pyrenophora teres f. teres* infection

Due to the nature of these pilot experiments number of parallel samples were limited or differed , therefore no analysis of significance would yield real statistical results, however peak area comparisons have been conducted to reveal trends in VOC changes. Results of all measurements and compounds are presented in **Appendix 9.5. Table S2.** Changes are summarized in **Table 10.**

5.1.1.1 Harrington aroma profile

Mechanical damage to the Harrington barley variety resulted in the appearance of (Z)-3-hexenyl acetate (C8H14O2, hit value: 93%) in the aroma profile. After 20 days of *Pyrenophora teres f. teres* (*P. teres*) infection, 7 new compounds appeared in the total ion chromatogram (**Table 9.**), which may indicate the presence of infection.

Table 9. New components appearing in the VOC profile of Harrington 20 days after infection

Retention Time (min)	Compound name	Formula	CAS No.
3.61	2-hexanol	C6H14O	626-93-7
4.87	styrene	C8H8	100-42-5
4.97	heptanal	C7H14O	111-71-7
6.52	octanal	C8H16O	124-13-0
9.4	naphthalene	C10H8	91-20-3
9.56	decanal	C10H20O	112-31-2
17.39	6,10,14-trimethyl-2-pentadecanone	C18H36O	502-69-2

The newly appearing compounds could be markers of the infection. During the measurements, the intensity of several compounds showed an increasing (toluene, D-limonene, nonanal, triacetin, α-pinene, 5-hepten-2-one, 6-methyl (sulcatone)) or decreasing (6-methyl tridecane, azulene, 2,2,4,6,6-pentymethyl-heptane) trend (**Table 10.**). Based on the compounds with increasing or decreasing intensity over time, the early and late stages of infection could be recognized.

5.1.1.2 Mv Initium aroma profile

The total ion chromatogram (TIC) of *P. teres* infected Mv Initium differed from that of healthy plants in two areas: the early (RT < 7 min) and middle (15 min < RT < 20 min) sections of the chromatogram (**Figure 11.**).

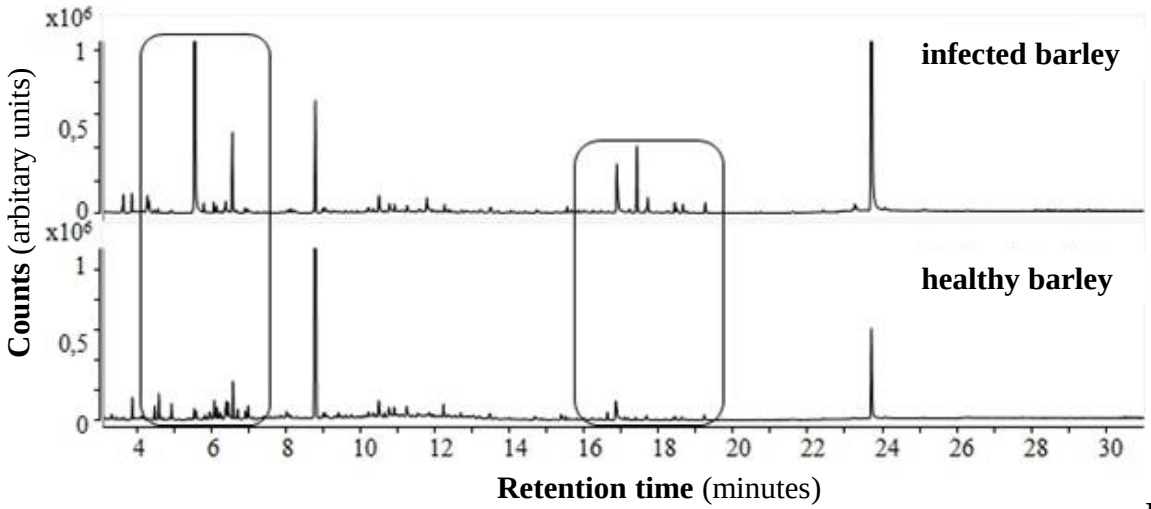


Figure 11. TIC chromatogram and differences observed (circled) of healthy and *P. teres* infected Mv. Initium barley

As a result of an infection caused by a necrotrophic pathogen, four new compounds appeared in the infected plant's volatile profile, which could serve as markers of the infection: 2-hexanol, guanidine, 3-hexen-1-ol, eugenol. 2-hexanol also appeared in the Harrington variety upon infection. The infected plants began to produce 6 compounds with greater intensity (octane, 1-butoxy-2-propanol, (Z)-3-hexenyl acetate, N-butyl-benzenesulfonamide, 6,10,14-trimethyl-2-pentadecanone, dodecyl isobutyl carbonate). (Z)-3-hexenyl acetate appeared in the Harrington variety upon mechanical damage **(Figure 12.**), indicating that it is likely a marker of leaf injury in the Mv Initium variety. We defined 6,10,14-trimethyl-2-pentadecanone as a new compound appearing upon infection in the Harrington variety as well.

Probably as a result of the infection, the intensity of numerous compounds decreased in comparison to the volatile compounds of the control plant (ethylbenzene, p-xylene, (+)-α-pinene, 1-ethyl-2-methyl-benzene, and 1-ethyl-3-methyl-benzene, mesitylene, (+)-3-carene, D-limonene, indane, linalool, naphthalene).

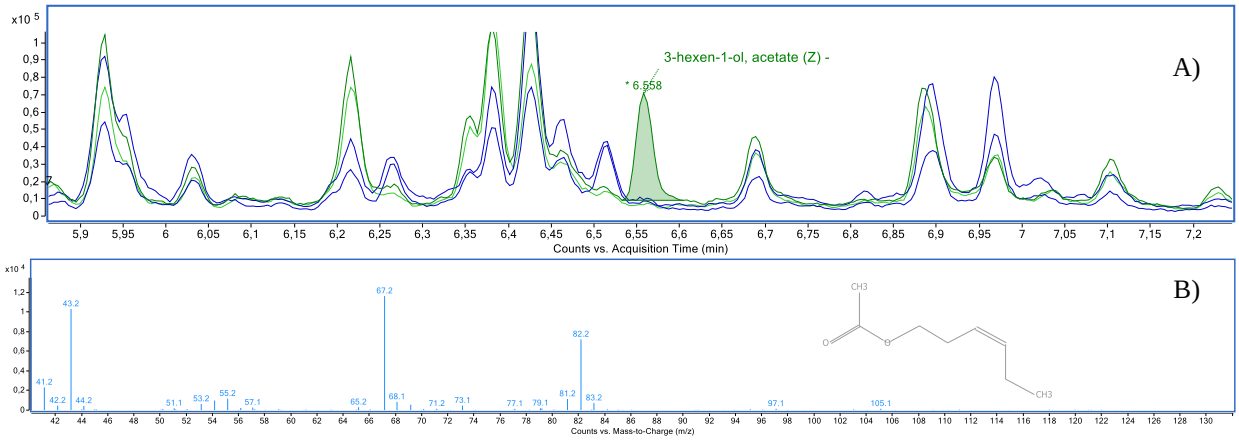


Figure 12 A) 3-hexen-1-ol, acetate, (Z)- appearance on the total ion chromatogram of wounded Harrington barley variety; **B)** 3-hexen-1-ol, acetate, (Z)- mass spectra from the sample

5.1.1.3 KH Hunor's volatile profile

Regarding KH Hunor's volatile profile, we found three compounds that increased in intensity over time ((+)-α-pinene, sulcatone, 6,10,14-trimethyl-2-pentadecanone). By the end of the infection experiment, we also detected newly appearing compounds in the volatile profile (**Table 10.**), which are presumed to be late markers of the infection by *P. teres*.

Table 10. Changes in common compounds in the VOC profiles of three barley varieties (BC 52), (BC 5), (BC 168) due to *Pyrenophora teres* infection

Retention time (minutes)	Compound name	BC 52 (Harrington)	BC 5 (Mv. Initium)	BC 168 (KH Hunor)	Retention time (minutes)	Compound name	BC 52 (Harrington)	BC 5 (Mv. Initium)	BC 168 (KH Hunor)
3.31	toluene	↑			7.635	1,2-oxolinalool			↓*
3.61	2-hexanol	New	New		7.69	6-ethyl-3-octyl ester trichloroacetic acid			New (v.)
3.63	octane		↓		7.75	N-[4-bromo-n-butyl]-2-piperidinone			New (v.)
4.28	guanidine		New	↓*	7.82	1-phenyl-1-butene			New (v.)
4.32	3-hexen-1-ol		New	↓	7.86	5-tridecane			New (v.)
4.46	ethylbenzene		↑		7.94	1-ethenyl-4-ethylbenzene			New (v.)
4.57	p-xylene		↑		8.01	*linalool	New	↑	↓*
4.87	styrene	New			8.08	nonanal	↑		↓*
4.91	1,3-dimethyl-benzene	-	↑		8.21	2,6-dimethylcyclohexanol	New		New (v.)
4.98	heptanal	New			8.97	azulene	↓		↓*
5.52	(+)-α-pinene	↑	↑	↑	9.02	4-ethylbenzaldehyde			New (v.)
5.57	*1-butoxy-2-propanol		↓		9.03	3-ethylbenzaldehyde	↓		-
5.77	4,4-dimethyl-2-pentanol			New	9.34	4-tert-butylanisole			New (v.)
5.93	1-ethyl-3-methylbenzene		↑		9.40	naphthalene	New	↑	
5.95	1-ethyl-2-methylbenzene		↑		9.59	decanal	New		
6.06	3,5,5-trimethyl 2-hexene			-	10.8	1-(4-ethylphenyl)-ethanone	↓		
6.13	1-octen-3-ol			↓*	11.5	triacetin	↑		
6.22	*2 or 3 or 4-ethyltoluene	↓	↑		11.8	eugenol		New	
6.26	sulcatone-	↑		↑	12.2	6-methyl-tridecane	↓		
6.36	2,2,4,6,6-pentamethylheptane	↓			12.4	2-dodecen-1-yl(-) succinic anhydride			New (v.)
					12.7	caryophyllene			↓*
6.43	mesitylene		↑		14.0	1-iodododecane	↓		
6.52	octanal	New			15.5	butyl dodecyl ether	↓↓		
6.56	(Z)-3-hexenyl acetate	New (sn)	↓	↓*	16.9	N-butylbenzenesulfonamide		↓	
6.69	(+)-3-carene		↑		17.2	isopropyl myristate	New		
6.97	D-limonene	↑	↑		17.4	6,10,14-trimethyl-2-pentadecanone	New	↓	↑
7.06	nona-3,5-dien-2-ol			-	17.6	phytyl acetate			New (v.)
7.1	indane		↑		17.7	(Z,E)-2,13-octadecadien-1-ol			New (v.)
7.12	levomenthol			New (v.)	18.0	homosalate	↑		
7.229	(Z)-β-ocimene			↓*	18.4	dodecyl isobutyl carbonate		↓	↓*
Legend:		**↓ Decreasing intensity over time**			**↓* High in initial samples and control, decreases with time**				
		↑ Increasing intensity over time			**↓↓ Below the limit of detection over time**				
		New: Newly appearing compounds upon infection			**sn: Compound appearing in wounded plants**				
		***Different behavior can be observed among the three barley varieties**							

2-hexanol appeared as a new compound in two varieties of barley (Harrington, Mv. Initium) as a result of infection, thus it can be classified as a potential biomarker. 6,10,14-trimethyl-2-pentadecanone behaves as a marker compound in Harrington and KH Hunor varieties, with its quantity increasing, while it was found in smaller amounts in the Initium variety compared to the control plant. (Z)-3-hexenyl acetate appeared in Harrington variety as a result of mechanical damage, indicating leaf injury, while it appeared in Mv Initium variety probably as a result of infection. (+)-α-pinene intensity increased in all barley varieties as a result of infection, thus it is considered a clear marker compound. Linalool and naphthalene compounds appeared in Harrington variety as a result of infection, however, they were already present in control plants of Mv Initium and KH Hunor varieties; their intensity decreased as a result of infection, which is contradictory in the case of the two barley varieties. Sulcatone, D-limonene, and naphthalene

compounds generally increased in intensity due to infection, while the intensity of azulene and dodecyl isobutyl carbonate decreased (**Table 10.**, and **Annex 9.5 Table S2**).

5.1.2 Changes in the odor profiles of different plants (wheat, tomato) as a result of infections

5.1.2.1 Changes in wheat odor profile due to powdery mildew infection

The complete VOC profile of wheat contains nearly 50 volatile compounds. Among these, the most intense were p-ethylacetophenone, p- and o-xylene, limonene, ethyl-benzaldehyde, diethyl-benzene, α-pinene, nonane, 3-carene, pseudocumene, methyl-benzene, ethyl-benzene, decanal, nonanal, dodecane, p-, m-cymene, and indane compounds. During our measurements, we successfully identified compounds that appeared only in healthy or infected plants. 1-octen-3-ol and 3-octanone may be suitable for early detection of infection since they are always more abundant in infected DHS samples from the 2018 pilot experiment (**Figure 13.**). The intensity of these compounds typically increased as the infection progressed, serving as biomarkers for detecting wheat infestations with wheat aphids. Although the literature does not yet describe biomarkers indicative of wheat aphid infection, studies by Tabata et al. (2011) revealed 1-octen-3-ol and 3-octanone as new compounds in the odor profile of aphid-infested pumpkin. In Eva-Maria Becker's doctoral thesis, both compounds are presented as variable compounds in response to *Fusarium* infection in corn (Becker, 2013). 1-octen-3-ol and 3-octanone are also considered indicators of mold infection in stored grains (Börjesson et al. 1989; Kaminski et al. 1974), and based on literary data, both compounds are emitted by the pathogenic fungus itself.

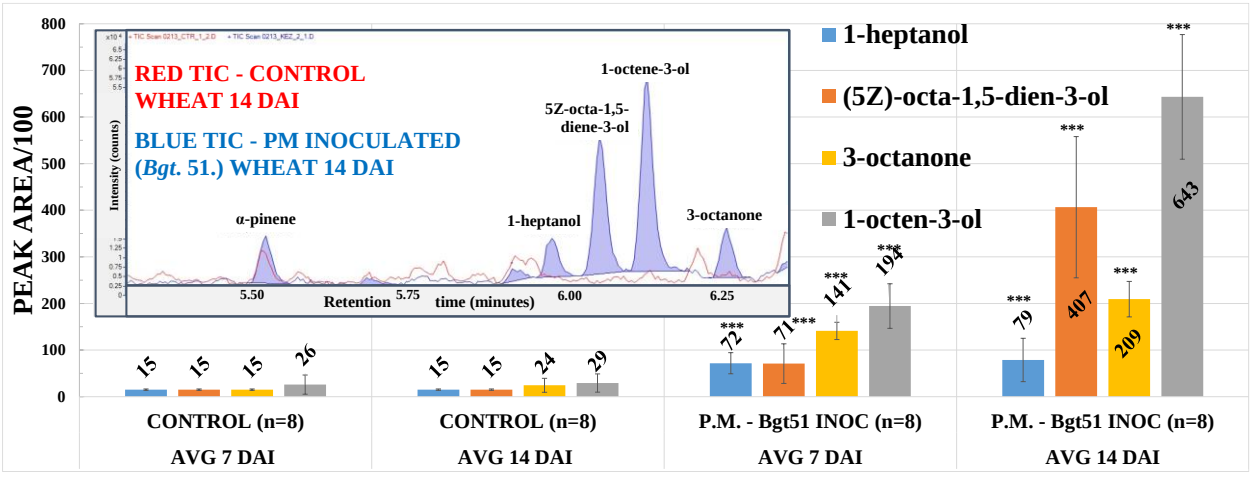


Figure 13. Average peak areas divided by 100, and total ion chromatogram (TIC) comparisons from pilot experiment 2018 for control wheat (Carsten V) and powdery mildew (*Blumeria Graminis f. sp. tritici - Bgt* pathotype 51) infected biomarker VOC candidates, at 7 and 14 days after inoculation (DAI)

5.1.2.2 Changes in the aroma compounds of tomatoes due to gray mold infection

At the beginning of the study, we compared the total ion chromatograms (TIC) of healthy and gray mold-infected tomatoes. To obtain reliable results, we conducted these tests using 10 parallel measurements for both control and infected plants. In total, we detected 78 volatile compounds that are typical for tomatoes, including hexanal, p-xylene, 3-carene, 1R-α-pinene, 2(10)-pinene, β-mycrene, α- and β-phellandrene, α- and γ-terpinene, linalool, decanal, β- and γ-elemene, caryophyllene, and cubebol. In the aroma profile of infected plants, we found 34 compounds that did not appear in the aroma profile of healthy plants. These are typically low-intensity components that could be biomarkers for *B. cinerea*, such as 3-pentanone, 3-hexen-1-ol, p-menth-2-en-1,4-diol, and dimethyl sulfone. Using principal component analysis (PCA) on the previous 78 compounds, the infected and healthy plants were separated, mainly along the second principal component (**Figure 14.**).

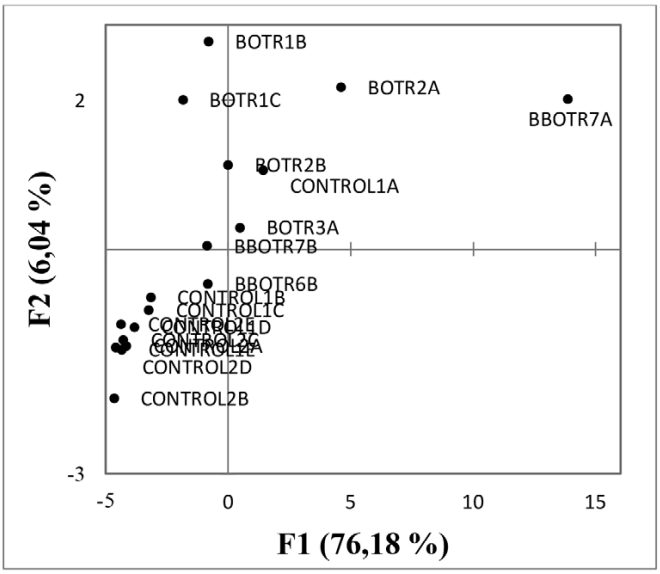


Figure 14. PCA plot of healthy and gray mold-infected tomatoes. All explained variance is 82.22%. F1: first principal component, F2: second principal component.

5.2 pull-type-DHS-SPE-GC-MS method performance tests, results and their interpretation

Some of the results presented under this section are available in Hungarian (Mátyus, 2023) in the MSc thesis that were supervised by the author.

5.2.1 Performance parameters of the GC-MS analysis method for qualitative and quantitative purposes

In this section, I examined the linearity, repeatability, and robustness of the GC-MS measurement method (see section 4.3), with tests presented in section 4.4.2 using various reference mix dilutions. The detailed results are presented in **Annex 9.11. Table S5, 9.12. Table S6 and 9.13. Table S7**. A summary of the performance characteristics can be found in **Table 11., Table 12., and Table 13.**

Table 11. Monitoring of chromatographic stability and MS sensitivity, linearity, and repeatability during 2019-2020 from the injection of the powdery mildew (*Bgt)* BBVOC reference mix (1-heptan-ol, 1-octen-3-ol, 3-octanone) in the range of 0.05-5 µg/ml (n=23).

1-heptanol (SIM - *m/z* 70)				**1-octen-3-ol (SIM - *m/z* 72)**				**3-octanone (SIM - *m/z* 72)**			
AVG RT (min)	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 3 years	**AVG RT**	**SD of RT**	**CV% of RT**	RT drift in 3 years	**AVG RT**	**SD of RT**	**CV% of RT**	RT drift in 3 years
10.15	**0.019**	**0.19**		**10.38**	**0.018**	**0.17**		**10.57**	**0.019**	**0.18**	
AVG accuracy%	**SD of accuracy%**	**CV% of accuracy**	-0.057	**AVG accuracy**	**SD of accuracy**	**CV% of accuracy**	-0.061	**AVG accuracy**	**SD of accuracy**	**CV% of accuracy**	-0.063
103.73	**6.33**	**6.1**		**103.15**	**7.56**	**7.3**		**98.83**	**9.67**	**9.8**	

Table 12. Injections of system suitability mix in 2019-2020 for accuracy, sensitivity, and reproducibility verification for an early, a medium, and a late eluting component. Comparison of extracted ion chromatogram (EIC) and selected ion monitoring (SIM) channel data quality for longifolene (0.05-2.5 µg/ml range, n=27).

styrene - EIC *m/z* 104				**1,3-dimethoxybenzene - EIC *m/z* 138**			
AVG RT (min)	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years	**AVG RT (min)**	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years
8.15	**0.011**	**0.14**		**14.75**	**0.013**	**0.09**	
AVG accuracy%	**SD of accuracy%**	**CV% of accuracy**	-0.017	**AVG accuracy**	**SD of accuracy**	**CV% of accuracy**	-0.056
110.37	**9.05**	**8.2**		**109.25**	**8.35**	**7.6**	
longifolene - EIC *m/z* 161				**longifolene - SIM *m/z* 93**			
AVG RT (min)	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years	**AVG RT (min)**	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years
19.32	**0.008**	**0.04**		**19.32**	**0.009**	**0.05**	
AVG accuracy	**SD of accuracy**	**CV% of accuracy**	-0.026	**AVG accuracy**	**SD of accuracy**	**CV% of accuracy**	-0.031
106.51	**7.38**	**6.9**		**110.03**	**9.74**	**8.8**	

Table 13. Evaluation of retention times for the n-alkane mix (C7-30, C8-26 evaluated) used for Kováts retention index (RI) calculation, in years 2019-2021 (n=15).

Kováts' RI value	**800**	**900**	**1000**	**1100**	**1200**	**1300**	**1400**	**1500**	**1600**	**1700**
RT (min) AVERAGES	**C8**	**C9**	**C10**	**C11**	**C12**	**C13**	**C14**	**C15**	**C16**	**C17**
	5.9	8.4	10.9	13.2	15.4	17.5	19.1	20.2	21.1	21.8
SD of RT-s	0.009	0.016	0.021	0.025	0.027	0.029	0.022	0.018	0.016	0.015
CV% of RT-s	0.15	0.20	0.20	0.19	0.18	0.16	0.11	0.09	0.08	0.07
TOTAL RT DRIFT in 2 years: 19.03-21.02 on HP-5MS UI 30m*0.25mm*0.25um used	**RT drift** (min) **C8**	**RT drift** (min) **C9**	**RT drift** (min) **C10**	**RT drift** (min) **C11**	**RT drift** (min) **C12**	**RT drift** (min) **C13**	**RT drift** (min) **C14**	**RT drift** (min) **C15**	**RT drift** (min) **C16**	**RT drift** (min) **C17**
	0.025	0.054	0.066	0.072	0.077	0.081	0.062	0.048	0.047	0.042
Kováts' RI value	**1800**	**1900**	**2000**	**2100**	**2200**	**2300**	**2400**	**2500**	**2600**	
RT (min) AVERAGES	**C18**	**C19**	**C20**	**C21**	**C22**	**C23**	**C24**	**C25**	**C26**	
	22.5	23.0	23.5	24.0	24.5	24.5	24.9	25.9	26.5	
SD of RT-s	0.015	0.014	0.015	0.015	0.015	0.015	0.016	0.022	0.027	
CV% of RT-s	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.09	0.10	
TOTAL RT DRIFT in 2 years: 19.03-21.02 on HP-5MS UI 30m*0.25mm*0.25um used	**RT drift** (min) **C18**	**RT drift** (min) **C19**	**RT drift** (min) **C20**	**RT drift** (min) **C21**	**RT drift** (min) **C22**	**RT drift** (min) **C23**	**RT drift** (min) **C24**	**RT drift** (min) **C25**	**RT drift** (min) **C26**	
	0.042	0.039	0.039	0.041	0.039	0.039	0.042	0.062	0.075	

As there is currently no consensus on performance parameters and their values for odor analysis, we based our methodology on the calibration and quality assurance parameters outlined in SANTE/11312/2021 (Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis). According to this guidance, individual calibration points can deviate by a maximum of 20% from the linear equation (interpreted as percent recovery or accuracy%); the concentration difference between calibration points should not exceed tenfold; and in the case of bracketing calibration, the higher concentration should be considered 100%, allowing a 20% maximum concentration difference for the lower point. Additionally, achieving an R^2 of at least 0.99 during fitting is mandatory, and retention time should not deviate by more than 0.1 minutes within a sequence. The results demonstrate that our analytical method complies extensively with the SANTE/11312/2021 calibration criteria. For quantification and calibration using extracted ion chromatogram (EIC) and selected ion monitoring (SIM) ion channels, the calibration of longifolene is shown as an example in **Figure 15**. The SIM channel exhibits a better signal-to-noise ratio (S/N) compared to the EIC, which allows for a slightly lower detection limit, especially for terpenoids. However, it is important to note that in the realm of modern single quadrupole MS instruments, the data quality difference (number of data points for better SIM channels and improved signal-to-noise ratio) between EIC and SIM quantification is minimal, and this effect is more pronounced when approaching the detection limit. Regarding identification criteria, it is essential to note that it is no longer accepted to rely solely on the spectral match of background-subtracted or deconvoluted mass spectra for qualitative analysis in the absence of a reference. This is because many components often have very similar fragmentation patterns, so using multiple mass spectral databases and comparing retention indices of compounds with literature or database values is crucial. For example, in the case of identifying an unknown component detected during a wheat powdery mildew infection, as illustrated in **Figure 16,** For (5Z)-octa-1,5-dien-3-ol, the compound was not present in the most popular and recent NIST 17 (NIST/EPA/NIH Mass Spectral and RI Library 17th edition) library. Therefore, the spectrum is suggested as "2-hexene-3,5,5-trimethyl-" in the NIST library (see **Figure 17.**). However, this compound is indeed (5Z)-octa-1,5-dien-3-ol, which is confirmed by a close match in both mass spectral data and retention index from the Wiley MS Database 10th edition.

It is vital to perform a thorough analysis and, if possible, confirm the qualitative identification of the assumed component using a reference substance. However, quantification may be sufficient by performing EIC from scanning data without the need for SIM channel acquisition, especially if the target component is not present in concentrations near the detection limit (**Figure 15.**).

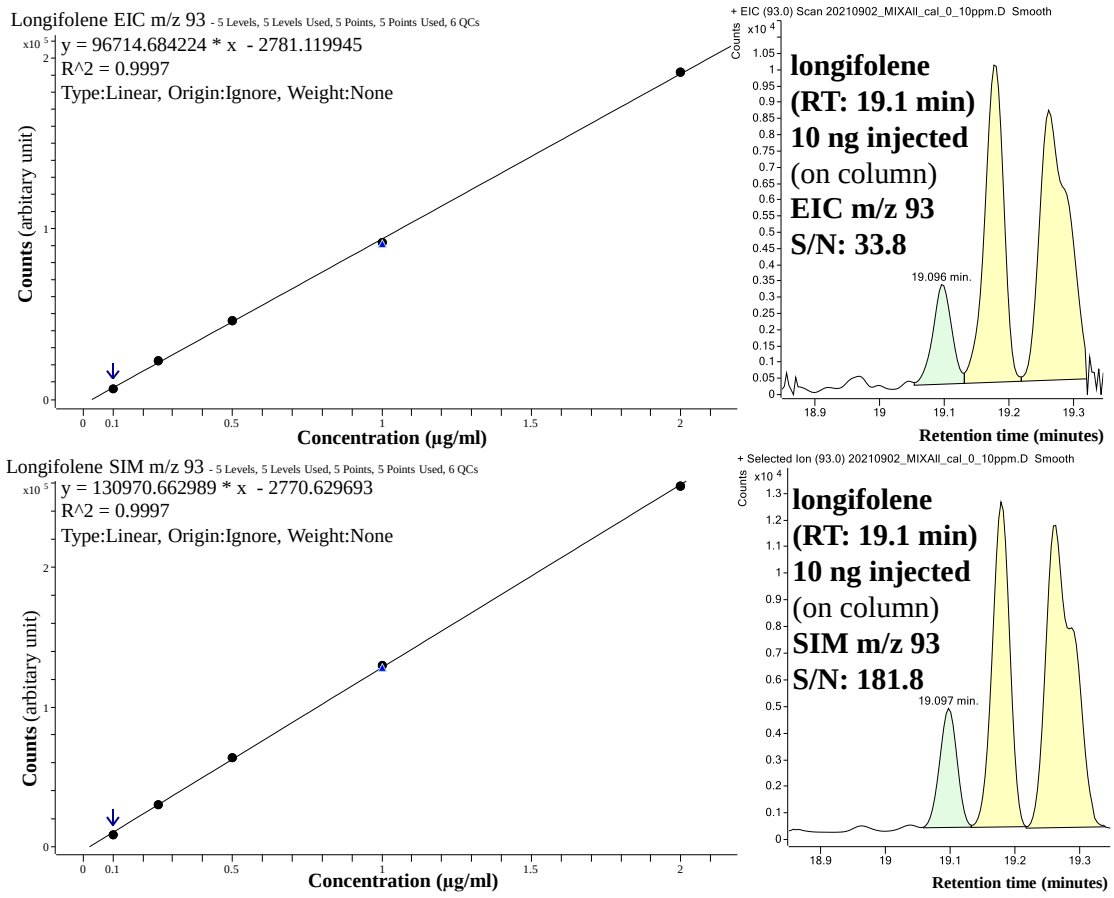


Figure 15. Calibration and signal to noise (S/N) of longifolene represented by extracted ion chromatogram (EIC) m/z 93 and selective ion monitoring (SIM) chromatogram m/z 93 ions in the range of 0.1-2 µg/ml injected with GC-MS method described in section 4.3

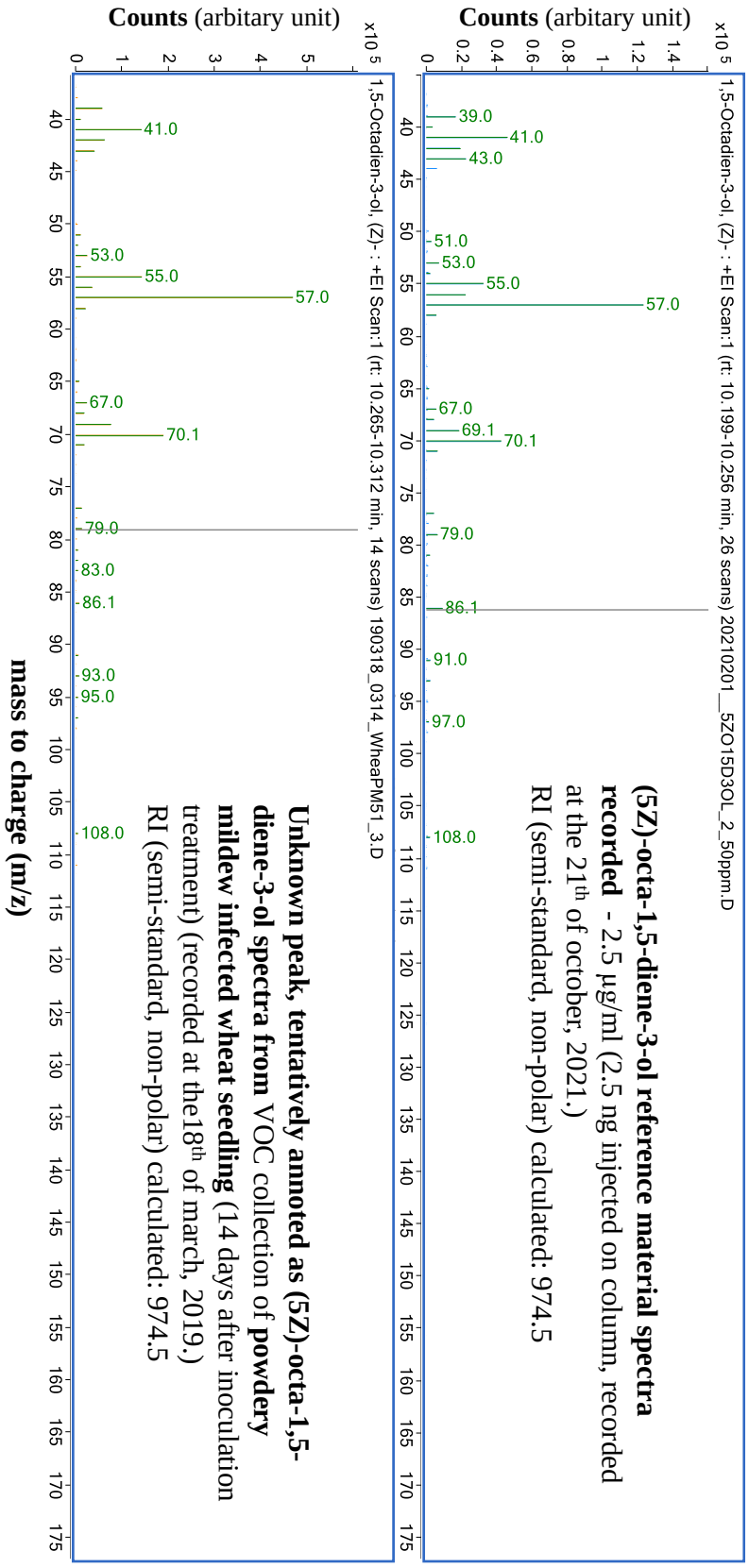


Figure 16. Spectrum of (5Z)-octa-1,5-dien-3-ol reference substance and the spectrum of the assumed (5Z)-octa-1,5-dien-3-ol component in wheat headspace sample 14 days after infection with powdery mildew (*B. Graminis*).

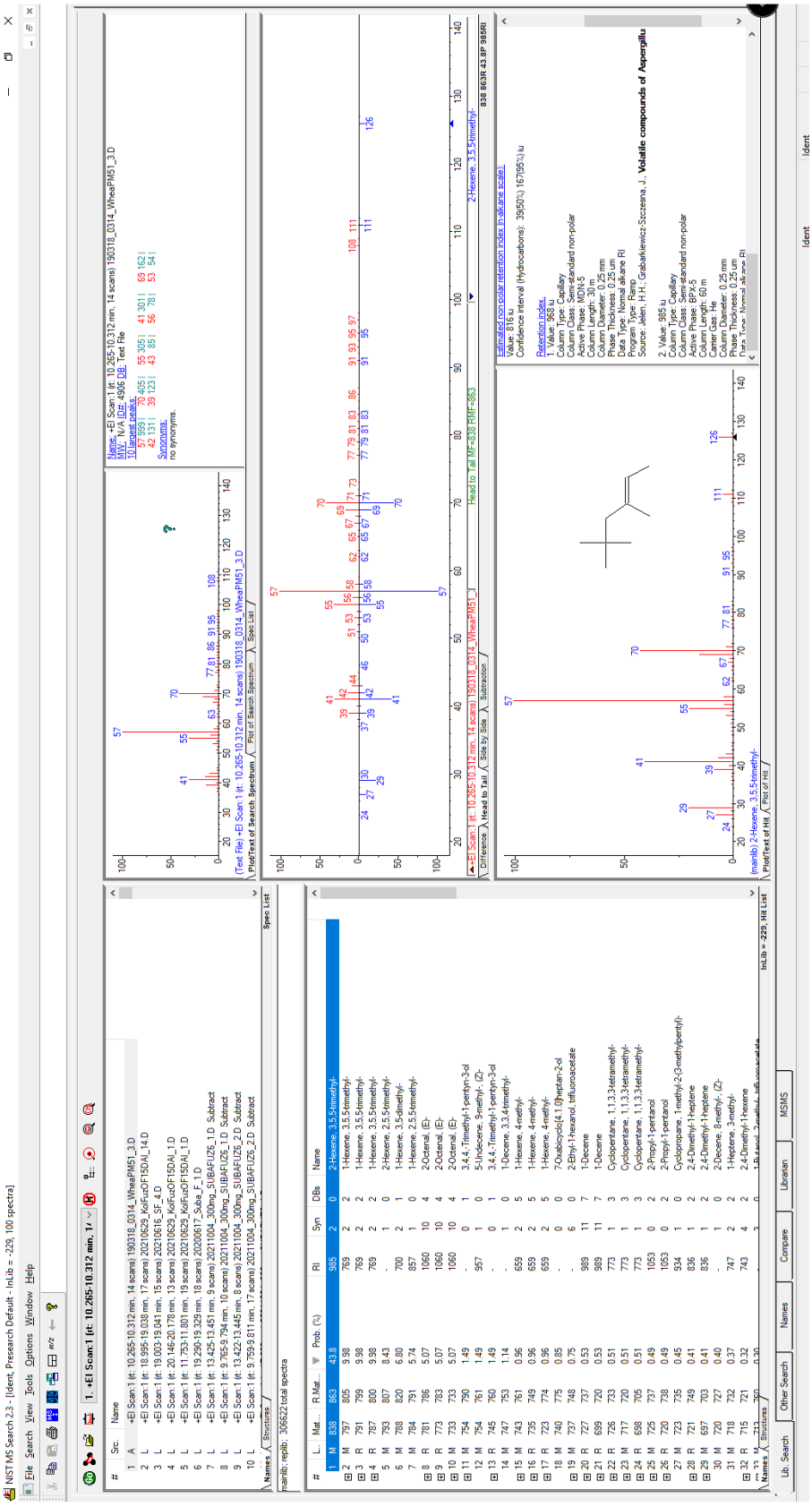


Figure 17. Spectrum search in the NIST 17 MS database for the spectrum of (5Z)-octa-1,5-dien-3-ol, which is not present in this database, leading to the erroneous suggestion of "2-hexene-3,5,5-trimethyl-." with a database RI of 985 (measured and calculated RI 974.5 indicating a possibly false positive match)

5.2.2 Recovery (%) results obtained from spiking of reference mix solutions (submixes) with and without internal standard correction for 1-bromodecane

Recoveries for the ten submixtures individually without and with the correction of the internal standard 1-bromodecane (as described in Section 4.2.2.1) are presented in **Table 14**. In general, components can be overestimated quantitatively by as much as 40–60% when external calibration is applied and when the deviation of elution volume (during odor trap elution, which can vary due to the swelling of sorbent particles) is not controlled with an appropriate internal standard, as we did in our case using 1-bromodecane. In the case of internal standard-corrected recovery results described in Materials and Methods 4.2.2.1 and as shown in **Table 14.**, the recovery of 98 components was examined at a concentration of 1 μg/ml relative to the elution volume. Based on the principles of SANTE/11312/2021 (70–120% recovery, RSD% less than 20%, five parallels for each concentration level), we classified the average recovery into four groups: 0–20, 20–40, 40–60, and >60%. Since odor analysis is a specialized field, I consider recoveries greater than 60% to be acceptable; hence, our tolerance is slightly higher compared to the SANTE document. Based on all of this, it can be seen that using submixes of up to 10 components, we observed 60% or higher recovery in 87 cases out of 96 components when the eluted volume of *n*-hexane was corrected with internal standard 1-bromdecane. For 2-methyltetrahydrofuran-3-one, methyl benzoate, 1,3-dimethoxybenzene, α-terpineol, (S)-(+)-carvone, eugenol, and methyl eugenol, we obtained recoveries between 40 and 60%, which were lower than optimal. Only two compounds, ethyl 3-hydroxybutyrate and methyl jasmonate, performed poorly, with recoveries between 20 and 40%. Methyl jasmonate is especially significant as it is an important plant hormone, so it's crucial to be aware that significant losses can occur during SPE elution when using *n*-hexane elution, especially in the presence of strong variability.

Table 14. partial mixture (submix) – Spiking to the adsorbent surface – at a concentration of 1 µg/ml calculated for elution, characterization of the average recovery (%) and standard deviation, relative standard deviation (RSD%) and confidence interval (CI), using at least three external bracketing calibrations (linear regression, R2>0.99), with and without internal standard (1-bromdecane) correction (Legend: 0-20% - red, 20-40% - orange, 40-60% - yellow, 60%< - green)

Submix number	Retention time (min)	Component english common name	Average recovery (%)	SD	RSD %	CI	Average recovery % with internal standard correction	SD	RSD %	CI
MIX5	5.37	2-hexanone	151.3	20.3	13.4	25.2	99.0	7.3	7.4	9.1
MIX5	5.50	3-hexanol	165.7	12.3	7.4	15.3	99.6	6.8	6.8	8.4
MIX3	5.60	hexanal	151.3	7.8	5.1	9.7	93.2	11.1	11.9	13.7
MIX10	5.62	octane	154.4	13.4	8.7	16.6	92.2	15.5	16.8	19.2
MIX4	5.62	2-hexanol	103.9	10.3	9.9	12.8	66.1	5.6	8.5	6.9
MIX7	5.67	butanoic acid, ethyl ester	153.0	20.3	13.2	25.1	95.7	9.9	10.3	12.3
MIX8	5.76	3(2H)-furanone, dihydro-2-methyl-	95.2	23.4	24.6	29.0	43.2	7.4	17.2	9.2
MIX1	6.89	2-hexenal, (E)-	151.6	8.2	5.4	10.1	81.4	7.6	9.3	9.4
MIX2	6.90	3-hexen-1-ol, (E)-	140.5	10.4	7.4	12.9	73.2	6.3	8.6	7.8
MIX5	7.31	1-hexanol	167.9	15.0	8.9	18.6	77.8	3.5	4.5	4.4
MIX3	7.31	m-xylene	160.8	13.8	8.6	17.1	87.3	8.3	9.5	10.3
MIX1	7.32	p-xylene	164.7	10.0	6.1	12.5	84.0	6.6	7.8	8.1
MIX6	7.54	isopentyl acetate	150.9	15.6	10.4	19.4	97.6	14.3	14.6	17.7
MIX8	7.85	styrene	144.2	12.9	8.9	16.0	72.1	15.1	20.9	18.8
MIX2	7.90	o-xylene	147.9	5.3	3.6	6.6	93.9	5.0	5.3	6.2
MIX5	8.11	2-heptanol	167.1	12.9	7.7	16.0	92.3	6.1	6.6	7.6
MIX10	8.11	nonane	167.5	14.4	8.6	17.9	96.5	15.7	16.2	19.5
MIX4	8.12	2-heptanone	135.9	14.0	10.3	17.4	86.6	6.1	7.1	7.6
MIX9	8.34	propanoic acid, butyl ester	147.8	13.0	8.8	16.2	92.6	6.3	6.9	7.9
MIX6	8.49	acetic acid, pentyl ester	150.2	16.7	11.1	20.8	98.0	15.3	15.6	19.0
MIX9	8.52	anisole	118.6	10.9	9.2	13.5	74.2	6.6	8.9	8.2
MIX2	8.95	α-pinene	159.9	9.9	6.2	12.2	103.9	2.5	2.4	3.1
MIX8	8.96	butanoic acid, 3-hydroxy-, ethyl ester	36.3	26.1	71.8	32.4	27.9	16.9	60.5	20.9
MIX1	9.51	2-heptenal, (E)-	159.3	8.9	5.6	11.1	84.6	7.3	8.7	9.1
MIX3	9.59	benzaldehyde	124.1	2.8	2.3	3.5	66.1	7.6	11.5	9.4
MIX2	9.87	1-heptanol	140.7	3.7	2.6	4.6	75.6	2.3	3.0	2.9
MIX4	9.95	(5Z)-octa-1,5-dien-3-ol	128.6	8.3	6.4	10.3	79.7	7.3	9.2	9.1
MIX7	10.02	(-)-β-pinene	170.1	17.6	10.3	21.8	99.6	12.3	12.4	15.3
MIX1	10.10	1-octen-3-ol	148.5	7.9	5.3	9.8	71.9	8.1	11.3	10.1
MIX2	10.14	phenol	135.4	10.3	7.6	12.7	81.4	2.9	3.6	3.6
MIX3	10.28	5-hepten-2-one, 6-methyl-	160.6	8.6	5.4	10.7	88.5	9.8	11.1	12.2
MIX6	10.40	β-myrcene	168.2	14.0	8.3	17.4	107.5	15.6	14.5	19.4
MIX5	10.49	3-octanol	171.6	12.8	7.5	15.9	104.5	6.5	6.2	8.1
MIX4	10.53	3-octanone	133.5	8.4	6.3	10.4	86.4	5.8	6.7	7.2
MIX8	10.60	hexanoic acid, ethyl ester	161.1	14.7	9.1	18.2	79.2	17.9	22.6	22.2
MIX10	10.61	decane	170.9	15.0	8.8	18.7	96.3	16.0	16.6	19.9
MIX3	10.71	α-phellandrene	177.4	13.0	7.3	16.1	98.1	9.0	9.2	11.2
MIX2	10.78	3-hexen-1-ol, acetate, (Z)-	154.9	5.2	3.4	6.5	98.8	4.9	4.9	6.0
MIX1	10.85	3-carene	174.2	11.0	6.3	13.6	90.4	6.6	7.3	8.2
MIX9	10.93	acetic acid, hexyl ester	148.0	14.1	9.5	17.5	90.1	7.3	8.1	9.1
MIX3	11.20	p-cymene	168.7	11.8	7.0	14.7	94.0	8.3	8.8	10.3
MIX2	11.30	R-(+)-limonene	163.5	4.3	2.6	5.3	106.6	3.6	3.4	4.5
MIX5	11.40	benzyl alcohol	143.6	24.6	17.2	30.6	88.9	4.7	5.3	5.8
MIX7	11.52	cis-β-ocimene	171.3	15.7	9.2	19.5	101.2	12.4	12.3	15.4
MIX7	11.77	trans-β-ocimene	186.4	13.5	7.2	16.7	101.8	12.2	11.9	15.1
MIX4	11.89	2-methylphenol (o-cresol)	115.3	8.0	6.9	9.9	75.2	4.1	5.5	5.1
MIX6	12.17	acetophenone	86.3	20.8	24.2	25.9	62.1	11.8	19.0	14.6
MIX4	12.37	3-methylphenol (m-cresol)	114.3	7.0	6.1	8.7	73.2	5.1	7.0	6.4
MIX1	12.71	α-terpinolene	173.0	11.4	6.6	14.1	89.5	7.0	7.8	8.6

Table 14. continued partial mixture (submix) – Spiking to the adsorbent surface – at a concentration of 1 µg/ml calculated for elution, characterization of the average recovery (%) and standard deviation, relative standard deviation (RSD%) and confidence interval (CI), using at least three external bracketing calibrations (linear regression, R2>0.99), with and without internal standard (1-bromdecane) correction (Legend: 0-20% - red, 20-40% - orange, 40-60% - yellow, 60%< - green)

Submix number	Retention time (min)	Component english common name	Average recovery (%)	SD	RSD %	CI	Average recovery % with internal standard correction	SD	RSD %	CI
MIX8	12.84	benzoic acid, methyl ester	115.8	20.6	17.8	25.6	51.5	8.5	16.5	10.5
MIX4	12.95	linalool	137.0	6.2	4.5	7.7	87.2	6.1	7.0	7.6
MIX10	12.96	undecane	172.1	14.8	8.6	18.3	96.3	16.1	16.7	20.0
MIX2	13.05	nonanal	165.7	6.7	4.1	8.3	94.4	4.9	5.2	6.1
MIX4	13.25	phenylethyl Alcohol	115.6	6.7	5.8	8.3	75.6	5.9	7.8	7.4
MIX7	13.72	cis-limonene oxide	145.3	8.2	5.7	10.2	91.7	12.3	13.4	15.3
MIX7	13.83	trans-limonene oxide	147.2	10.8	7.4	13.5	93.9	12.9	13.8	16.1
MIX1	13.99	isopulegol	162.5	7.2	4.4	9.0	86.2	9.2	10.7	11.4
MIX8	14.45	benzene, 1,3-dimethoxy-	101.3	19.6	19.4	24.4	45.0	7.7	17.1	9.5
MIX9	14.53	benzoic acid, ethyl ester	114.8	10.6	9.2	13.2	69.4	5.9	8.6	7.4
MIX5	14.83	1-nonanol	159.0	25.3	15.9	31.5	86.2	10.1	11.7	12.6
MIX7	14.97	1-dodecene	177.6	15.4	8.7	19.1	102.4	12.3	12.0	15.3
MIX8	14.99	α-terpineol	110.3	25.0	22.7	31.1	53.7	15.1	28.1	18.7
MIX9	15.06	methyl salicylate	108.2	9.5	8.8	11.8	69.0	6.7	9.8	8.3
MIX10	15.15	dodecane	174.3	15.1	8.7	18.8	96.8	16.1	16.7	20.0
MIX2	15.26	decanal	162.9	7.1	4.3	8.8	101.4	3.6	3.5	4.4
MIX4	15.72	β-citronellol	131.0	7.5	5.7	9.3	83.6	6.2	7.4	7.7
MIX1	16.01	pulegone	160.9	9.5	5.9	11.8	82.8	8.4	10.2	10.4
MIX8	16.09	(S)-(+)-carvone	123.2	24.8	20.1	30.8	56.7	11.6	20.4	14.4
MIX9	16.60	citral	107.7	10.9	10.1	13.5	66.7	6.9	10.4	8.6
MIX3	16.79	phenol, 4-ethyl-2-methoxy-	141.0	6.7	4.7	8.3	82.0	9.5	11.6	11.8
MIX6	16.97	(-)-bornyl acetate	140.4	14.7	10.5	18.3	91.9	16.3	17.8	20.3
MIX5	17.05	2-undecanone	179.9	14.1	7.8	17.5	111.6	5.7	5.1	7.1
MIX10	17.18	tridecane	173.9	14.6	8.4	18.1	97.1	14.8	15.3	18.4
MIX6	18.14	decane, 1-bromo-	165.5	14.1	8.5	17.5	**internal standard (MIX6 redone without it)**			
MIX9	18.29	eugenol	86.8	7.9	9.1	9.8	58.8	7.7	13.2	9.6
MIX9	18.65	geranyl acetate	137.4	10.9	8.0	13.6	83.0	6.9	8.3	8.6
MIX10	18.89	tetradecane	175.2	14.6	8.3	18.1	99.5	13.5	13.6	16.8
MIX8	18.96	methyl eugenol	94.5	22.6	23.9	28.0	46.0	14.0	30.5	17.4
MIX2	19.09	longifolene	163.0	5.8	3.5	7.2	105.1	4.1	3.9	5.1
MIX6	19.18	α-cedrene	163.8	13.7	8.4	17.0	100.0	17.1	17.1	21.3
MIX1	19.26	caryophyllene	169.6	10.9	6.4	13.5	90.1	7.8	8.7	9.7
MIX9	19.29	β-cedrene	154.0	11.9	7.8	14.8	96.5	8.7	9.0	10.8
MIX6	19.66	α-humulene	162.1	13.8	8.5	17.1	98.3	16.5	16.8	20.5
MIX3	19.96	trans-β-ionone	163.5	5.7	3.5	7.1	93.4	9.9	10.6	12.3
MIX10	20.04	pentadecane	175.0	15.1	8.6	18.7	101.4	11.9	11.8	14.8
MIX7	20.08	valencene	168.0	11.7	7.0	14.6	94.5	11.1	11.7	13.8
MIX7	20.66	trans-nerolidol	134.3	5.6	4.2	7.0	92.0	11.7	12.7	14.6
MIX8	20.76	dodecane, 1-bromo-	179.2	18.3	10.2	22.7	**(MIX8 redone without it)**			
MIX10	20.93	hexadecane	175.7	14.9	8.5	18.5	101.7	11.3	11.1	14.1
MIX9	20.93	caryophyllene oxide	132.5	9.9	7.4	12.3	78.6	6.4	8.1	7.9
MIX7	21.35	methyl jasmonate	46.2	20.0	43.2	24.8	20.6	11.0	53.5	13.7
MIX10	21.66	heptadecane	174.7	15.3	8.7	18.9	103.2	10.9	10.6	13.5
MIX1	21.84	trans-farnesol	163.3	12.7	7.8	15.8	87.3	10.7	12.2	13.3
MIX10	22.30	octadecane	173.6	13.3	7.7	16.5	103.6	11.7	11.3	14.5
MIX10	22.87	nonadecane	173.9	13.0	7.5	16.2	103.7	11.8	11.4	14.7
MIX10	23.40	eicosane	171.5	13.2	7.7	16.3	104.2	11.3	10.8	14.0
MIX10	23.89	heneicosane	172.0	13.4	7.8	16.6	104.1	11.6	11.1	14.4
MIX10	24.35	docosane	170.9	13.5	7.9	16.8	104.9	12.2	11.6	15.2

5.2.3 Recovery (%) results obtained from spiking of reference mixture solutions (submixes) and complete mixture with internal standard correction for 1-bromodecane

We also conducted experiments with the complete mixture as described in Section 4.2.2.2 and compared them to the results presented in Section 5.2.1, as shown in **Annex 9.14, Table S8**. We did not characterize the *n*-alkanes in this case, so we were able to make comparisons for 81 components. Among these, benzyl alcohol had weak recoveries (<40%), 25 components highlighted in yellow had moderate recoveries (40–60%), but 55 components performed well (>60%). In general, the complete mixture yielded slightly lower recoveries compared to submixes, especially for compounds with lower recoveries observed there. However, for example, methyl jasmonate had much better and less variable recoveries in the total mix compared to submixes. Based on all these results, it may be important to investigate the effects on quantitative accuracy by calibration mixtures in more detail in the future.

5.2.4 Recovery tests by spiking, followed by continuous and periodic DHS sampling

The determination of recovery was performed separately for the mix containing normal alkanes (submix 10) and for all other components using the complete mixture as described in Section 4.2.3. To assess the effect of boiling point (as shown in **Figure 18.** and **Annex 9.15 Table S9),** the *n*-alkane series (submix 10) and to investigate the effect of material quality, the complete mixture (**Figure 19. and Annex 9.16 Table S10**) were used. Additionally, classification is based on the color scale applied to the spiking above and presented in the attachments. As shown in **Figure 18.** and **Annex 9.15, Table S9**, we observed a critical loss in recoveries for compounds with lower boiling points (BP), especially at octane (C8). This phenomenon was improved by the novel periodic DHS method we introduced, limiting the breakthrough by reducing the flow volume during sampling. For nonane (C9) and higher boiling point alkanes, the loss was within an acceptable range in all cases, but the variability of periodic sampling was consistently lower than that of continuous sampling; however, the number of parallels should be higher since CI values are high, probably due to the low number of repetitions. Since the breakthrough points and desorption of analytes depend on the applied adsorbent and its capacity, as well as primarily on temperature and the boiling point of a given component, as well as on total flow volume (total flow volume depends on sampling time and flow rate), according to the literature, it was expected that the recovery of the smallest boiling point substances would be problematic. For example, in GC x GC cryomodulation, components with boiling points close to C8 are also poorly modulated; the results are in line with the literature, as cryomodulation is also a kind of trapping associated with a breakthrough point or other desorption effects. Regarding the recovery tests presented in **Figure 19**. and in depth for all components in **Annex 9.16 Table S10**, which were characterized by adding

the complete mix by spiking, it is also observed that there was a strong loss mainly for components with boiling points close to octane, i.e., with retention times similar to it. Periodic sampling was able to limit this loss to some extent, but only to a small extent. This loss was mainly observed for problematic components, as was in the case of direct additions; the most significant losses were observed for compounds with a hidroxyl functional group belonging to the chemical class of alcohols.

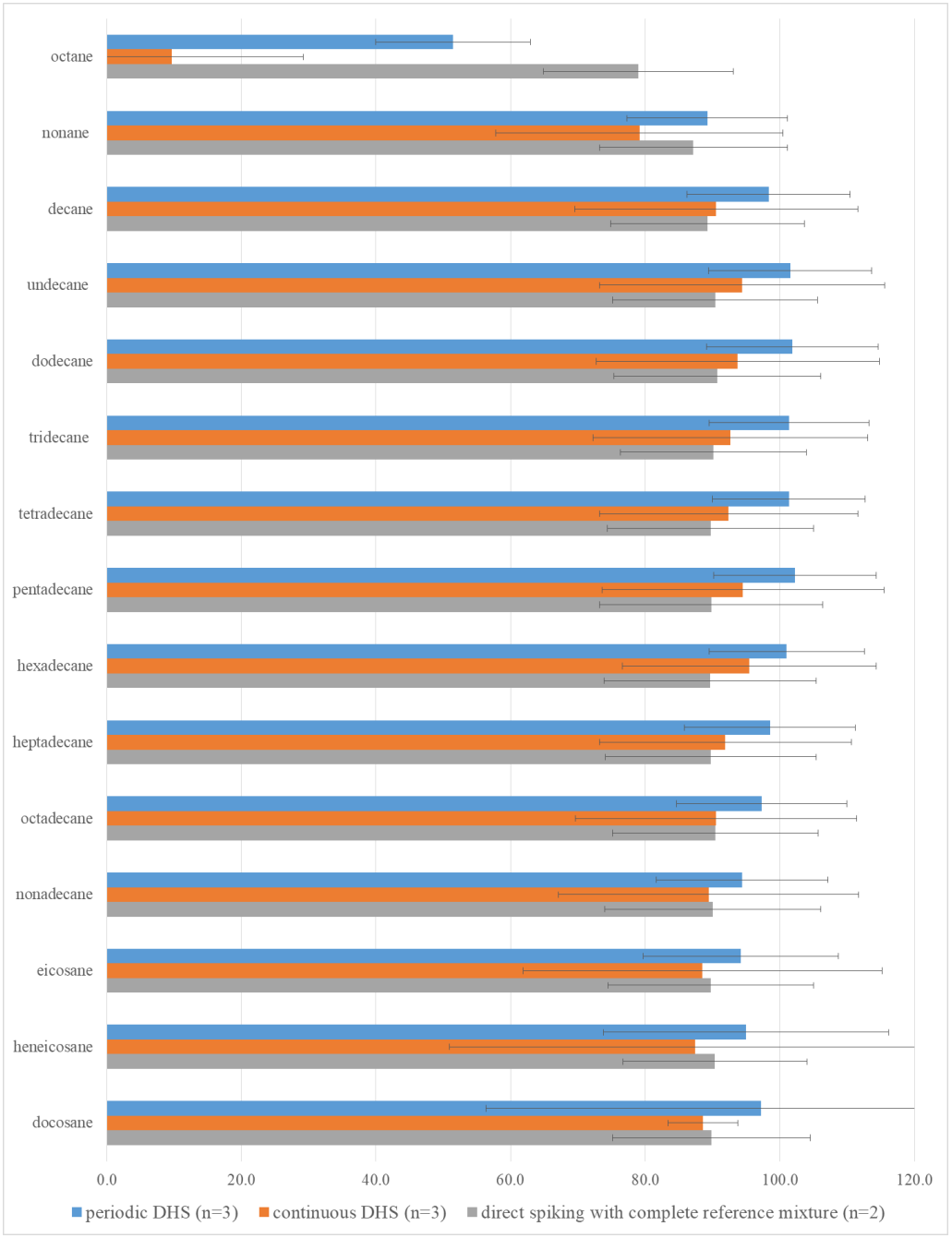


Figure 18. Comparison of average IS (1-bromodecane) corrected recovery (%) for n-alkanes C8-22 in case of periodic and continuous DHS method and spiking at 1 µg/ml (with respect to elution volume)

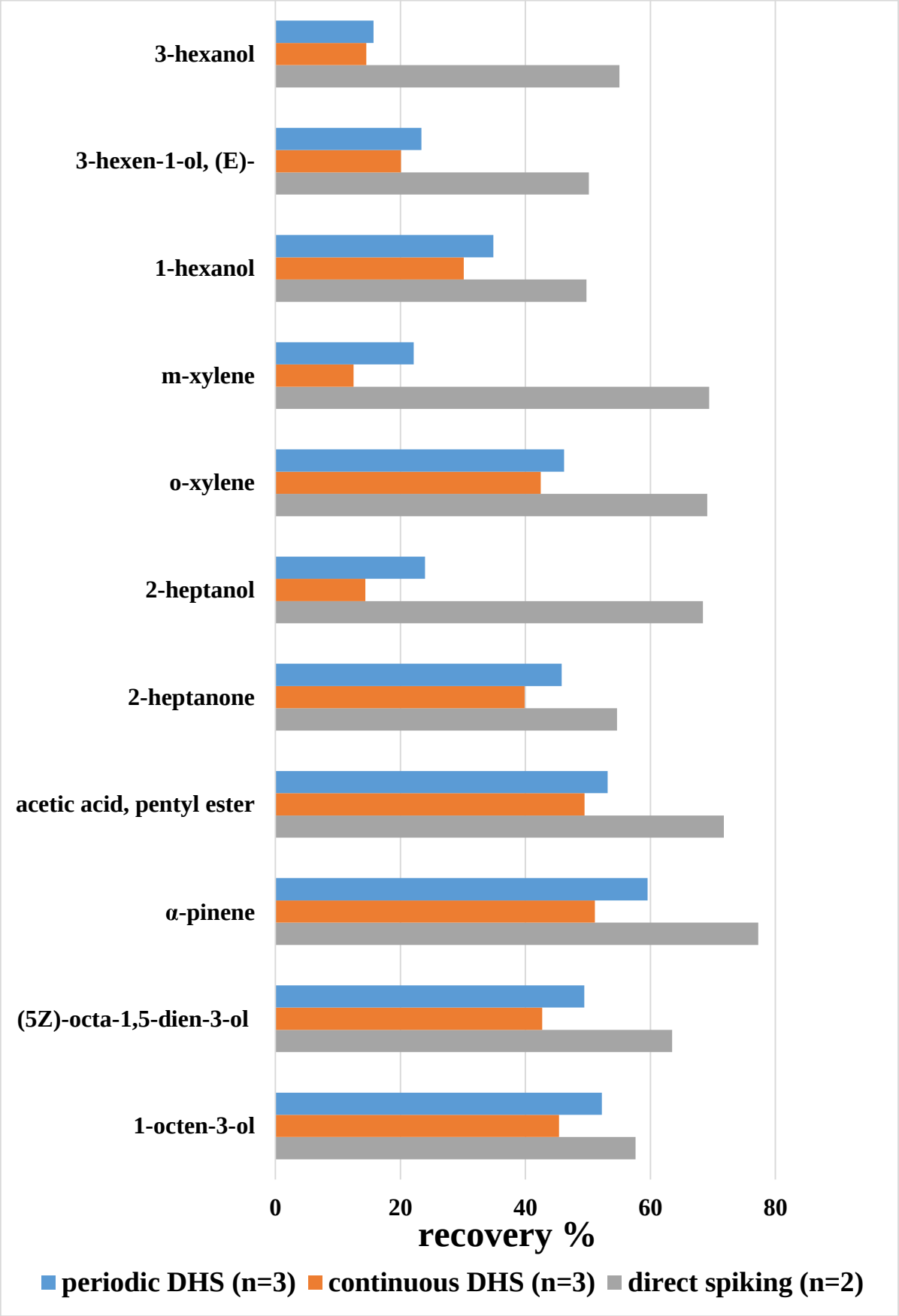


Figure 19. Examples for comparison of average IS (1-bromodecane) corrected recovery (%) for some of the complete mixture compounds in case of periodic and continuous DHS method and direct spiking at 1 µg/ml (with respect to elution volume)

According to the results, different components showed differences in terms of material quality regarding the loss due to desorption. Therefore, in the future, by involving the analysis of additional components, quantitative accuracy can be improved by determining the limitations of DHS sampling for even more compounds. Additionally, periodic DHS sampling can reduce desorption losses and potentially decrease variability in sampling between parallel samples, possibly causing less disturbance to plant emissions in plant studies compared to continuous sampling. In the future, it would be worthwhile to optimize the conditions for periodic sampling, including flow rate, sampling time, and active collection stage, at different temperatures, cooling the VOC traps in combination with periodic sampling.

5.3 Results and evaluation of binding site competition tests

In the binding site competition tests described under Section 4.2.4, we obtained a high overall background due to sampling taking place in a closed room with a high environmental temperature. In general, our research at CAR has shown that sampling in buildings yields higher backgrounds compared to outdoor sampling (except for certain flowering periods in nature) because odorants associated with objects in artificial environments (furniture, wall paint, etc.) accumulate in the confined spaces of rooms. In the case of greenhouse measurements, where the surface of the confined area is mainly made of glass, the odor background is less pronounced. In nature, external air comes from an unrestricted space, and instead of accumulating, volatile organic compounds (VOCs) emitted mix continuously and leave the external, unconfined natural air. Despite the high background levels, we conducted sample collection from two strongly scented fruit matrices. In preliminary experiments, we found both common and differing components in the case of tomato and pear matrices, with similar concentration ranges for each matrix. Therefore, we chose these two matrices for our study. The components found in the blank and emitted from the matrices, as well as their quantitative evaluation, are illustrated in **Figure 20.** The results of components found in the blank, matrices, and their combinations are shown in **Figures 21. and 22.**, and also in detail at **Annex 9.17 Table S11 (A)** for qualitative and **(B)** quantitative results. It is also important to note that blank samples are of paramount importance for the proper interpretation of results. They play a significant role in environmental research in determining the origin of components from the background (external air, soil microbiome, if not excluded from the air space) and emissions from plants (and/or plant-pathogen/pest interactions), which unfortunately is often not detailed or omitted in many studies related to chemical ecology. According to **Figures 21. and 22.,** it can be stated that even in the case of a high background, the quantity of odorants emitted and trapped by extremely scented but high-moisture matrices was not affected by the simultaneous presence of matrices in the vapor chamber under uniform conditions and relative surface areas. Therefore,

significant competition among the evaluated VOC components was not observed during the study. If the investigated component did not occur in the blank or only to a slight extent compared to the matrix samples, and it had a lower abundance in one matrix and a higher abundance in the other matrix, then the quantity measured in the air containing both matrices was detected quantitatively, as can be observed, for example, in the case of hexan-1-ol and methyl-E,Z-2,4-decadienate. It is also crucial to note that often the background can partially or entirely mask the components from the vapor space to be investigated on total ion chromatograms. Thus, VOCs with the least abundance that are not of background origin or components masked by the most abundant blank background components become visible only through deconvolution-based data processing, contrary to those that can be determined with simple background subtraction.

In conclusion, based on the results presented in Section 5.2.1, it is apparent that the SIM channel has a better signal-to-noise ratio compared to the EIC; however, its significance is mainly noticeable when approaching the detection or quantification limit. Therefore, quantification can be sufficient to use EIC from the scanning measurement without necessarily needing to acquire SIM channels if the component of interest is not present in concentrations near the detection limit. Obtaining sufficient data points from the peaks during scanning measurements for quantitative determination is still important for appropriate accuracy.

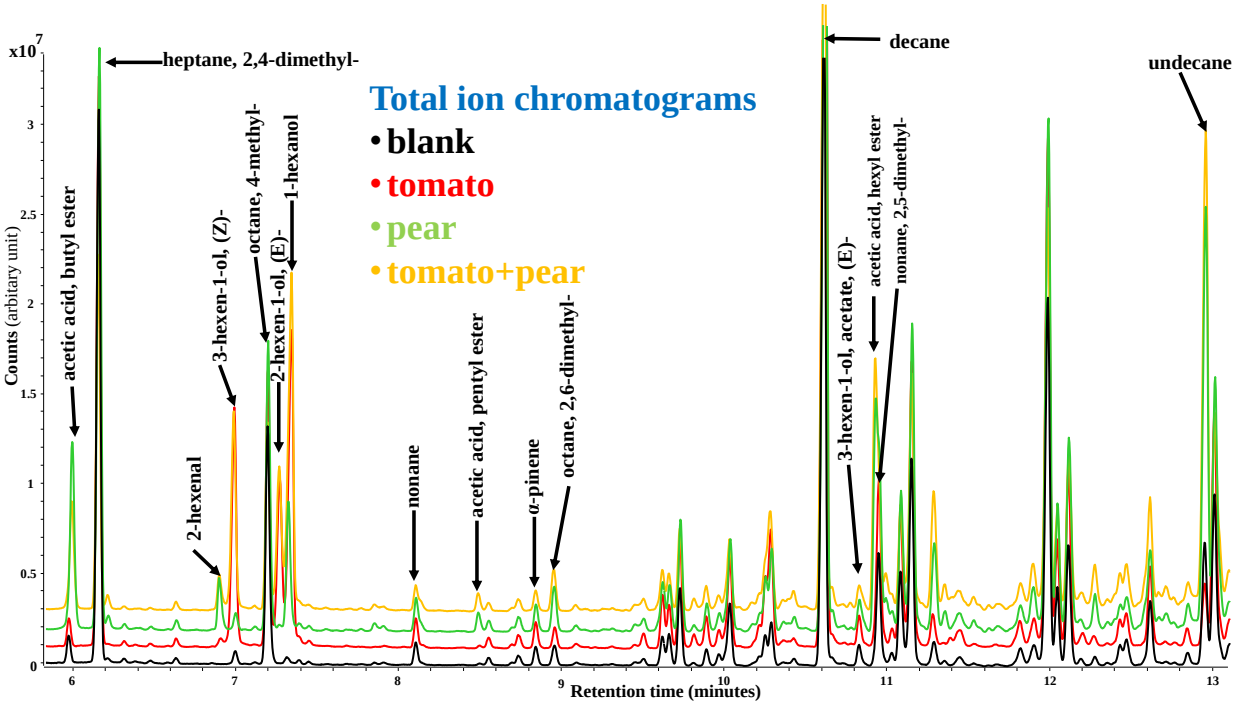


Figure 20. Relevant section of total ion chromatograms from DHS sampling in binding site competition tests for tomato and pear odor patterns.

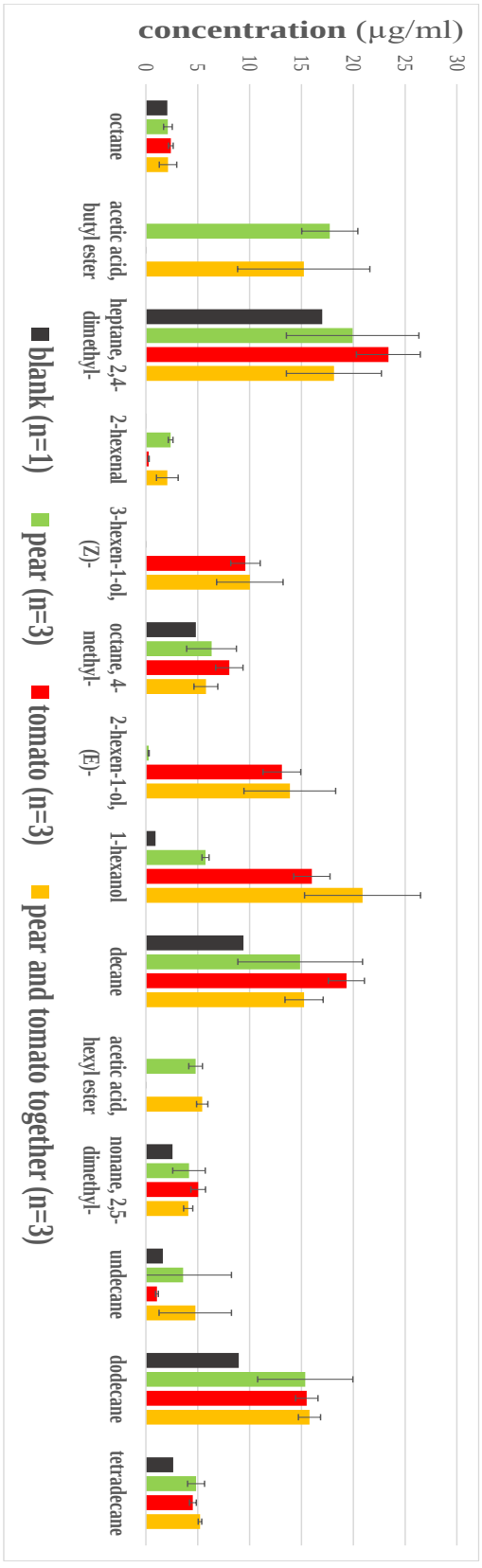


Figure 21. Results of quantitative analysis (relative quantitation against nonane with correction by internal standard 1-bromdecane) of binding site competition tests for components measured up to a maximum concentration range 1.5-30 µg/ml for blank, tomato, pear, and tomato and pear matrix open-loop-pull-type-DHS sampling and SPE elution by n-hexane.

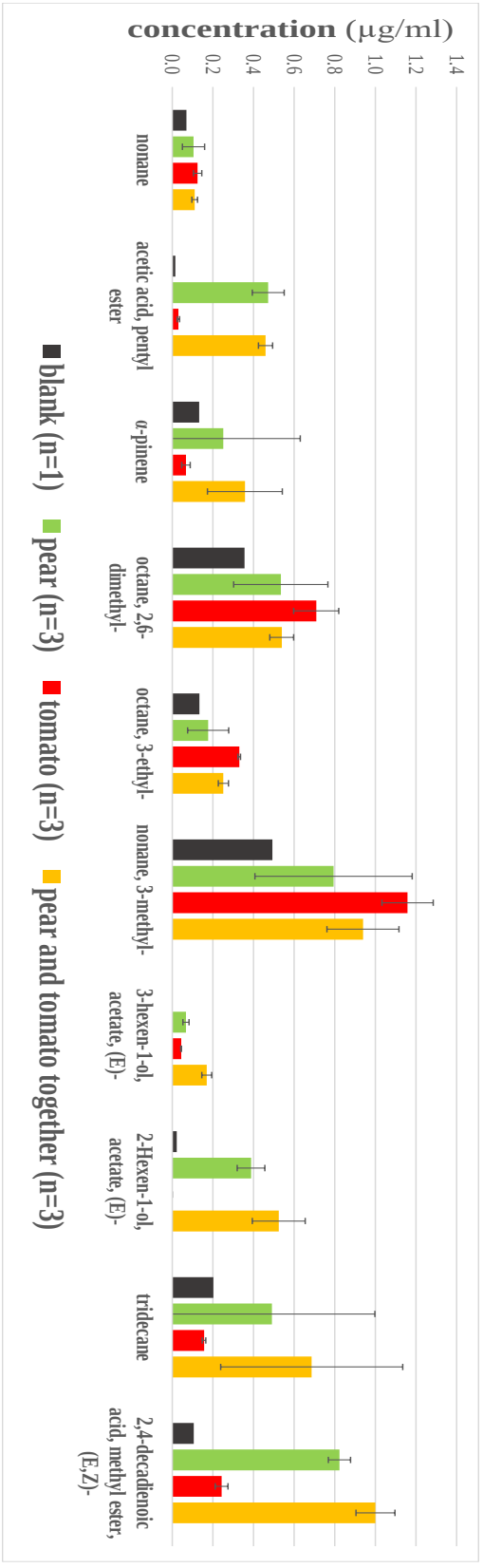


Figure 22. Results of quantitative analysis (relative quantitation against nonane with correction by internal standard 1-bromdecane) of binding site competition tests for components measured up to a maximum concentration of 1.5 µg/ml for blank, tomato, pear, and tomato and pear matrix open-loop-pull-type-DHS sampling and SPE elution by n-hexane

From the recovery results obtained by directly adding reference solution mixtures (section 5.2.2), it can be concluded that generally we can overestimate the quantities of components by up to 40–60% when external calibration is applied, and the signal difference due to deviation in elution volume during odor trap elution is not corrected using some internal standard (in our case, 1-bromodecane). When examining the submixes, out of the 96 compounds, 87 achieved a recovery of 60% or higher with internal standard correction. For compounds like 2-methyltetrahydrofuran-3-one, methyl benzoate, 1,3-dimethoxybenzene, α-terpineol, (S)-(+)-carvone, eugenol, and methyl eugenol, recovery values between 40 and 60% were obtained, while only two compounds, ethyl 3-hydroxybutyrate and methyl jasmonate, performed poorly with recoveries between 20 and 40%. The latter is a crucial plant hormone, so it's essential to be aware that significant losses may occur during *n*-hexane elution of this component, especially with high variability. Overall, it's worth examining in more detail the effects of calibration mixtures on quantitative accuracy in the future. When characterizing the recoveries of the sampling procedure (section 5.2.4), critical losses were observed for compounds with lower boiling points than octane (C8). However, the introduced segmented DHS method improved this issue by reducing the flow volume during sampling, thus aiding in reducing desorption losses. For nonane (C9) and higher-boiling alkanes, the losses and therefore recoveries were within an acceptable range for all cases. However, periodic sampling exhibited smaller variations compared to continuous sampling. Regarding the recovery characterized using the complete mixture (sections 5.2.3 and 5.2.4), it is noticeable that primarily for early (close to octane) retention time components, significant losses were observed, presumably due to their low boiling points. The periodic DHS was somewhat capable of reducing this, but only to a limited extent. In general, it can be concluded that periodic DHS showed slightly better recoveries and lower variations for the overall set of components, but some compounds still exhibited significantly poorer recoveries despite their higher boiling points. These components mainly belonged to the group of alcohols and were typically problematic even with direct addition recovery experiments. In the case of methyl jasmonate, for example, the total mixture exhibited much better and less scattering recovery than the submixes. Based on the binding site competition tests in Section 5.2.4, it can be stated that even with a high background, the presence of extremely scented but high-moisture matrices in the vapor chamber did not influence the quantity of compounds emitted and trapped by the matrices. Thus, significant competition among the evaluated VOC components was not observed during the study.

5.4. Emission of novel volatile biomarkers of wheat powdery mildew

Results were published in Hamow et al. (2021) presented in this section.

5.4.1. Volatile profile analysis from the headspace of wheat plants

In total, 48 BVOCs were identified by GC-MS scans in 2018 and 2019 from headspace samples collected at 7 DAI and 14 DAI representing early (barely visible to the naked eye) and full symptomatic stages, respectively from experiments described in section 4.4. These BVOCs belonged to the following chemical classes: aliphatic hydrocarbons, aromatic hydrocarbons, polycyclic aromatic hydrocarbons, aldehydes, ketones, fatty alcohols, and different terpenoids (**Table 14.**). A more in-depth description of the compounds by their identifiers in various standard databases and their reported occurrences in wheat and in *B. graminis* (KNApSAcK and mVOC 2.0 databases) is presented in **Annex 9.10 Table S4**. Out of the 48 BVOCs only 13 (27%) were described previously in wheat seedlings and plants and none of them in *B. graminis*.

Significant differences between samples from uninoculated control (healthy) and *Bgt*-inoculated (diseased) plants were found for 36 compounds at some time points, however only six of them exhibited highly reproducible and statistically significant quantitative differences at all time points and samples in all years **(Annex 9.18 Table S12; Annex 9.19 Table S13; Annex 9.20 TableS14).** Multivariate data analysis (PCA loading plot part on **Figure 23**; PERMANOVA **Annex 9.21 Figure S5**) and heat maps **(Annex 9.22 Table S6 A –** for year 2018**,** and **B** – for year 2019) revealed a cluster of up to eight compounds, including the six significant ones, with strong and consistent effects as well as a highly positive correlation among each other. This observation confirmed that the six BVOCs can be considered as BBVOCs, diagnostic of PM infection.

5.4.2. Identification of diagnostic BVOCs for powdery mildew

Out of the detected BVOCs, the most evident difference between control and *Bgt*-inoculated plants could be narrowed to six compounds, which were only present in the headspace of inoculated plants. These seven- or eight-carbon (C7-C8) BVOCs were: 1,3-octadiene, 1,3(Z),5(Z)-octatriene, 1-heptanol, (5Z)-octa-1,5-dien-3-ol, 1-octen-3-ol and 3-octanone as demonstrated by the pooled extracted ion chromatogram (EIC) of a headspace sample from healthy and *Bgt*-inoculated plants (**Figure 24.**). The six BBVOCs were abundant in headspaces of *Bgt*-inoculated plants while in the blanks and uninoculated controls their presence was below or around the LoQ.

The six BVOCs represent C7-C8 fatty alcohols (3), acyclic hydrocarbons (2) and a ketone (**Annex 9.10 Table S4**). The first key step in the biosynthesis of fatty alcohols in fungi and plants is the oxidation of α-linoleic acid by several types of oxygenase enzymes (Fischer and Keller, 2016) followed by further catalysis into volatile oxylipins including various short-chain (C6-C8) fatty alcohols. As a bioinformatic proof of this pathway in our experimental setup a BLAST search in

B. graminis genome sequences confirmed that several genes encoding two groups of linoleate diol synthases (a dioxygenase) as well as numerous monooxygenases homologous to classical fungal enzymes are present in this pathogen. Further analysis revealed that all these genes are functional in two f.spp. of *B. graminis* based on evidence for their transcription as well as translation into proteins **(Annex 9.23 Table S15**).

Table 14. Characterization of volatile organic compounds identified from the headspace of control and *Bgt*-inoculated wheat 'Carsten V' in 2018 and 2019.

No.	*Common name* [a]	CAS No.[b]	RT min[c]	RI calc.[d]	RI lit.[e]	*m/z* quant.[f]
1	Octane	111-65-9	5.91	800.0	800	71
2	Heptane, 2,4-dimethyl-	2213-23-2	6.45	821.2	821±1 (41)	85
3	**1,3-Octadiene**	1002-33-1	6.54	824.9	827±1 (9)	54
4	Ethylbenzene	100-41-4	7.43	860.3	855	91
5	Octane, 4-methyl-	2216-34-4	7.53	864.2	863	85
6	*m*-Xylene	108-38-3	7.63	868.2	866±7 (170)	91
7	**1,3-*cis*,5-*cis*-Octatriene**	40087-62-5	7.90	878.7	879	79
8	3-Heptanone	106-35-4	8.09	886.5	887±3 (33)	85
9	Styrene	100-42-5	8.18	890.1	893±5 (91)	104
10	*o*-Xylene	95-47-6	8.22	891.7	887±8 (178)	91
11	Nonane	111-84-2	8.43	900.0	900	71
12	α-Pinene	80-56-8	9.30	934.6	935±7	93
13	Benzaldehyde	100-52-7	9.95	960.5	962±3 (416)	106
14	Benzene, 1-ethyl-3-methyl-	620-14-4	9.98	961.9	957±8 (67)	105
15	Benzene, 1,3,5-trimethyl-	108-67-8	10.16	969.1	972±9	105
16	**1-Heptanol**	111-70-6	10.19	970.2	970±2 (68)	70
17	**(5Z)-Octa-1,5-dien-3-ol**	50306-18-8	10.30	974.5	975±2	57
18	β-Pinene	127-91-3	10.37	977.3	979, 974	93
19	**1-Octen-3-ol**	3391-86-4	10.43	979.8	980±2 (355)	72
20	**3-Octanone**	106-68-3	10.62	987.4	986±3 (101)	72
21	β-Myrcene	123-35-3	10.73	991.8	991	93
22	Benzene, 1,2,4-trimethyl- (Pseudocumene)	95-63-6	10.78	993.7	990±6 (83)	105

Table 14. continued

No.	*Common name* [a]	CAS No.[b]	RT min[c]	RI calc.[d]	RI lit.[e]	m/z quant.[f]
23	Decane	124-18-5	10.94	1000.0	1000	71
24	*3-Carene*	13466-78-9	11.21	1011.5	1011±2 (336)	93
25	*p-Cymene*	99-87-6	11.54	1025.6	1025±2 (820)	119
26	(+)- Limonene	138-86-3	11.63	1029.6	1030±2 (1004)	93
27	Indane	496-11-7	11.80	1036.7	1029±11 (36)	117
28	Benzene, 1,2-diethyl-	135-01-3	12.14	1050.9	1045±8 (22)	105
29	Acetophenone	98-86-2	12.51	1067.0	1065±4 (134)	105
30	Benzene, 2-ethyl-1,3-dimethyl-	2870-04-4	12.83	1080.3	1080±20 (12)	119
31	3-Octanol, 3,7-dimethyl-	78-69-3	13.25	1098.0	1100±13 (8)	73
32	Undecane	1120-21-4	13.29	1100.0	1100	71
33	Nonanal	124-19-6	13.39	1104.3	1104±2 (556)	70
34	Benzene, 1,2,3,4-tetramethyl-	488-23-3	13.68	1117.8	1116±9 (32)	119
35	Benzene, 1,2,3,5-tetramethyl-	527-53-7	13.76	1121.5	1117±9 (24)	119
36	Benzaldehyde, 3-ethyl-	34246-54-3	14.73	1165.7	1168±N/A (1)	134
37	Benzaldehyde, 4-ethyl-	4748-78-1	15.04	1180.0	1180±16 (5)	134
38	Naphthalene	91-20-3	15.18	1186.4	1182±8 (183)	128
39	Dodecane	112-40-3	15.48	1200.0	1200	71
40	Decanal	112-31-2	15.60	1206.0	1206±2 (406)	70
41	Undecane, 2,6-dimethyl-	17301-23-4	15.76	1214.1	1210±3 (18)	71
42	Ethanone, 1-(4-ethylphenyl)-	937-30-4	17.21	1284.8	1277±4 (8)	133
43	Tridecane	629-50-5	17.52	1300.0	1300	71
44	Tridecane, 3-methyl-	6418-41-3	18.72	1374.4	1371±1 (15)	71
45	Tetradecane	629-59-4	19.14	1400.0	1400	71
46	Longifolene	475-20-7	19.35	1418.7	1413±5	93
47	β-Caryophyllene	87-44-5	19.52	1434.2	1423-1442	93
48	Pentadecane	629-62-9	20.25	1500.0	1500	71

Bold, identified biomarker BVOCs; [a] according to the NIST/EPA/NIH Mass Spectral Library v17 and the Wiley Registry of Mass Spectral Data, 10th edn; [b] Chemical Abstracts Service registry number; [c] retention time in min; [d] Kováts' Retention Index calculated (Kováts, 1958), experimentally determined using *n*-alkane retention indices; [e] Retention Index literature, from corresponding data in NIST v17 and the PubChem repository (in brackets: no. of experimental records); [f] selected fragment ion (*m*/*z*) for quantitation.

All six BBVOCs showed statistically significant differences in their emitted quantities between the healthy control and inoculated wheat plants, and this irrespective of *Bgt* pathotype (51 and 71), symptomatic stage (7 DAI and 14 DAI) and experimental year (2018-2019-2020) represented on **Figure 25.** In other words, control plants exhibited for all six BBVOCs a concentration around or below LoQ, whereas *Bgt*-inoculated plants produced a massive, often magnitudes higher quantities of these BBVOCs. On the whole, there was no significant difference in the BBVOCs' emission rates between plants inoculated with the two tested *Bgt* pathotypes when compared at any identical symptomatic stage and year.

A systematic comparison of the temperature profiles during the incubation periods and the sampling days revealed striking differences over the three experimental years (**Annex 9.8 Figure S4**): the average temperature as well as its range was higher in each consecutive year for both time parameters. This seasonal or annual effect was readily confirmed by the PCA performed for inoculations with *Bgt* pathotype 51 only with the six diagnostic BVOCs according to the three years and two symptomatic stages (**Figure 23.**). Control and inoculated treatments clearly clustered separately on the scatter plot according to experimental years both at 7 DAI (**Figure 26. A**) as well as 14 DAI (**Figure 26. B**). All the above observations point to the same conclusion that the selected six BVOCs shuld be considered as BBVOCs, and they are reliable indicators of the onset and progression of PM disease in wheat (Hamow et al. 2021).

5.4.3. Confirmation of VOC biomarkers in mixed pathogen background

In an independent experiment designed to evaluate the reaction of two further cultivars to *Fusarium* spp. in a growth chamber, mild PM symptoms appeared spontaneously about 2 weeks after *Fusarium* inoculation at the beginning of flowering. This additional infection with unknown *Bgt* strain(s) provided an unexpected opportunity to test the more general utility of the diagnostic BVOCs identified above.

Of these six BBVOCs, the three most abundant ones, namely (5Z)-1,5-octadiene-3-ol, 1-octen-3-ol, and 3-octanone were detected above the limit of quantitation and quantitated (**Figure 27.**) in the headspace of plants with early PM symptoms (**Annex 9.7 Figure. S3**). Similarly to 'Carsten V' plants in the greenhouse (**Figure 25.**), all three major BBVOCs exhibited significantly higher emission in PM-symptomatic plants than in their parallel controls, and this in both, hitherto untested wheat cultivars (**Figure 27.**). This consistent pattern further supports that these BVOC combinations can be utilized as biomarkers of PM disease (Hamow et al. 2021).

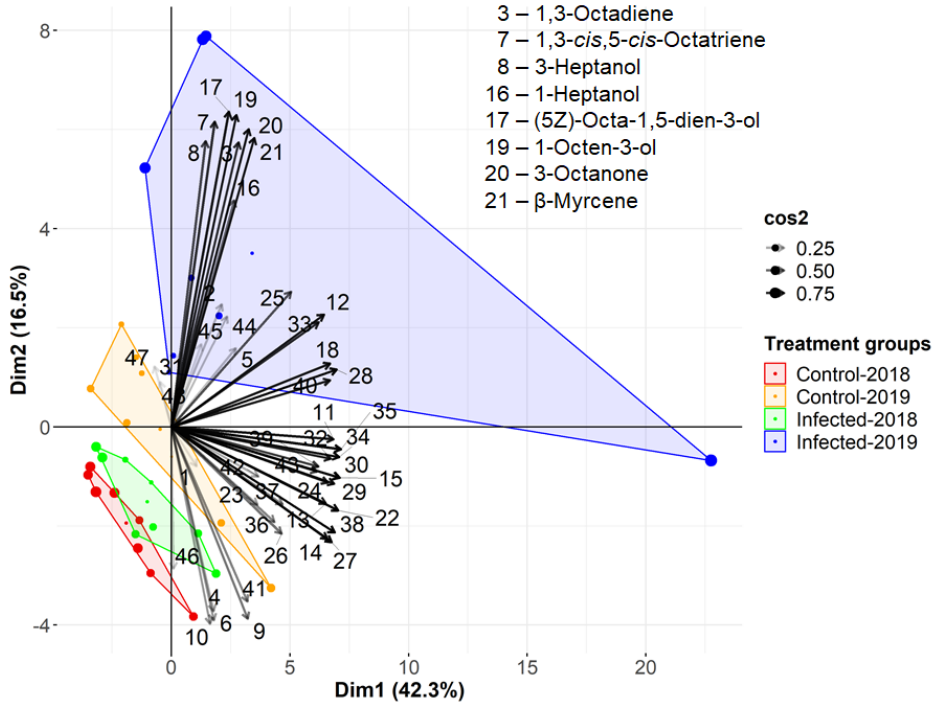


Figure 23. PCA biplot analysis for all 48 BVOCs at 14 DAI in wheat headspace samples from 2018 and 2019 (n=16 and 20, resp.). C, healthy control; I, *Bgt*-inoculated; Table 15. for numbers of BVOCs

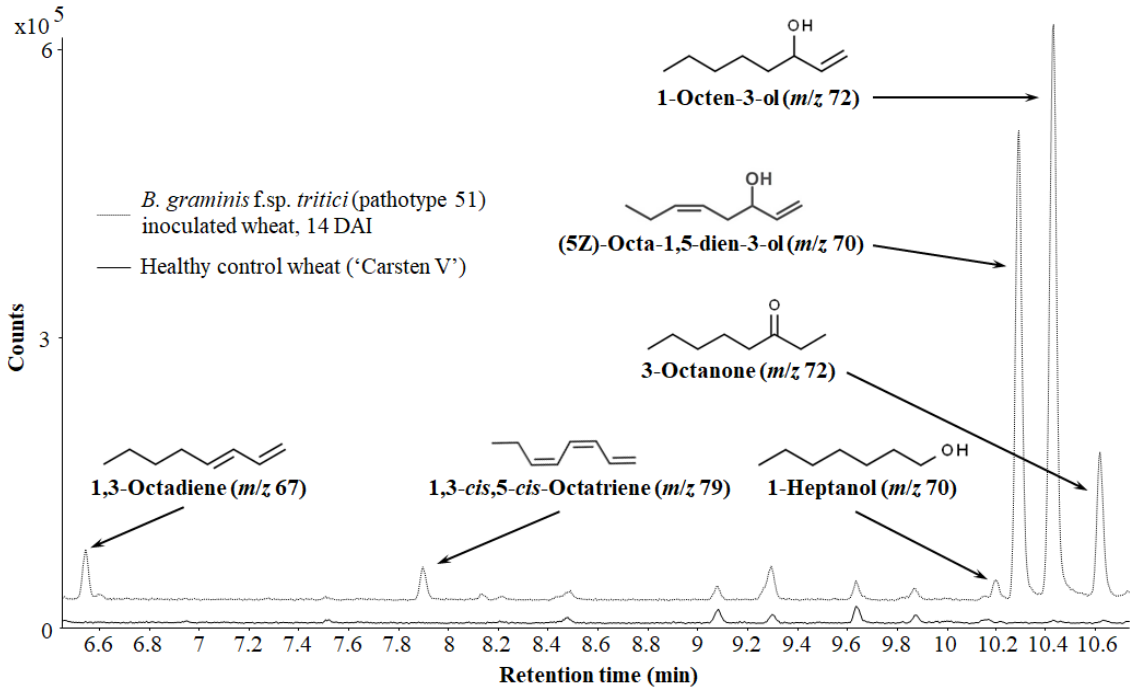


Figure 24. Pooled extracted ion chromatograms of the optimal unique mass peaks to compare the six biomarker BVOCs between samples collected from healthy (base line) and *Bgt*-inoculated (upper line) wheat plants.

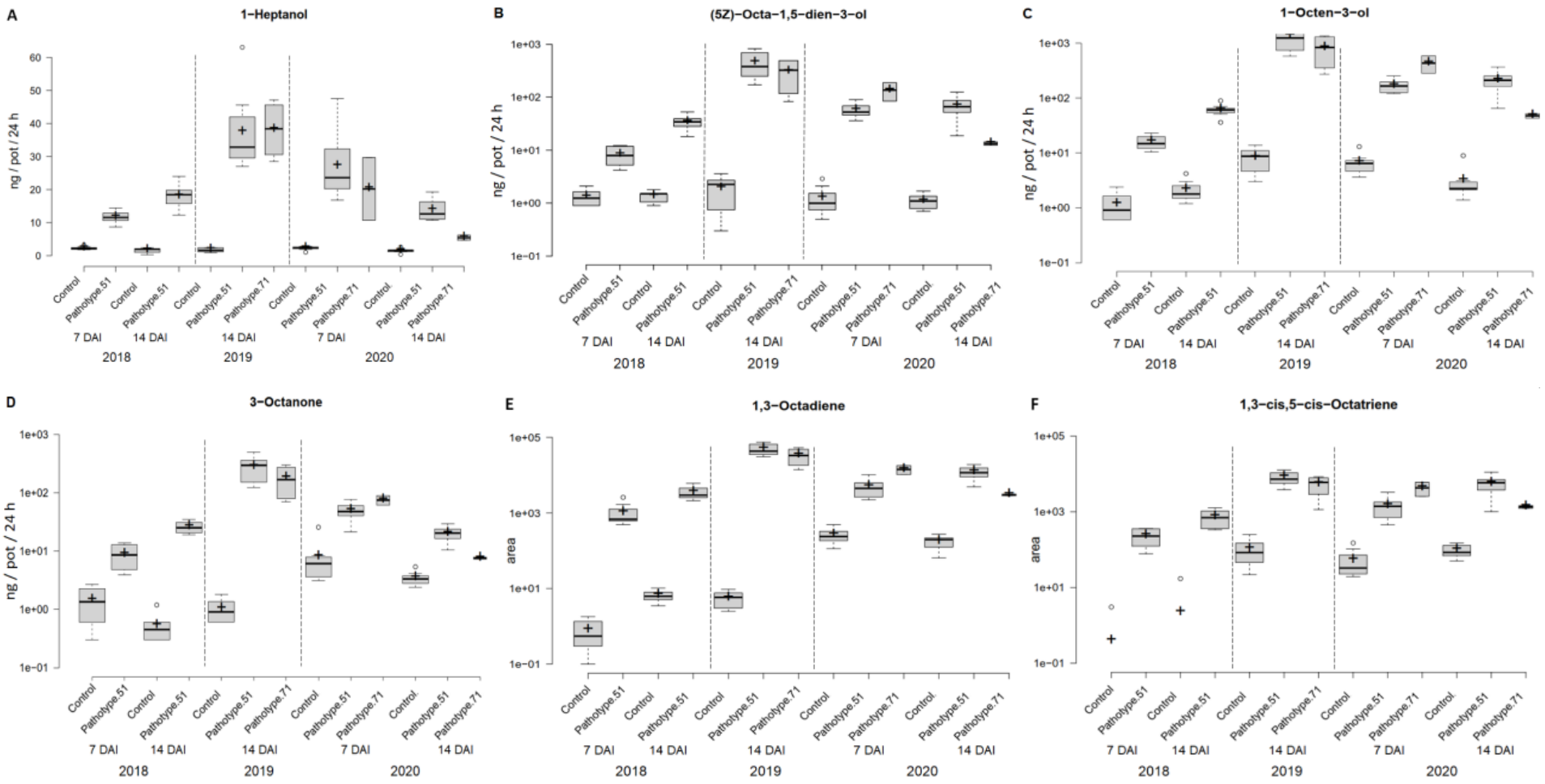


Figure 25. Quantitative analysis of six diagnostic BVOCs at two time points (7 DAI and 14 DAI) in the headspace of 'Carsten V' wheat seedlings after inoculation in 2018-2020 with two pathotypes (51 and 71) of *Bgt* (powdery mildew fungus).

(A) 1-heptanol, (B) (5Z)-octa-1,3-dien-3-ol, (C) 1-octen-3-ol, (D) 3-octanone, (E) 1,3-octadiene, (F) 1,3(Z),5(Z)-octatriene. Quantitation by standards (A-D) and by area (E-F). Box=interquartile range (IQR), cross and bar within box=mean and median, whiskers=±1.5×IQR; widths of boxes are proportional to square-roots of the number of observations; n=8 (for pathotype 71 n=4); DAI, days after inoculation. All scales are logarithmic except for (A).

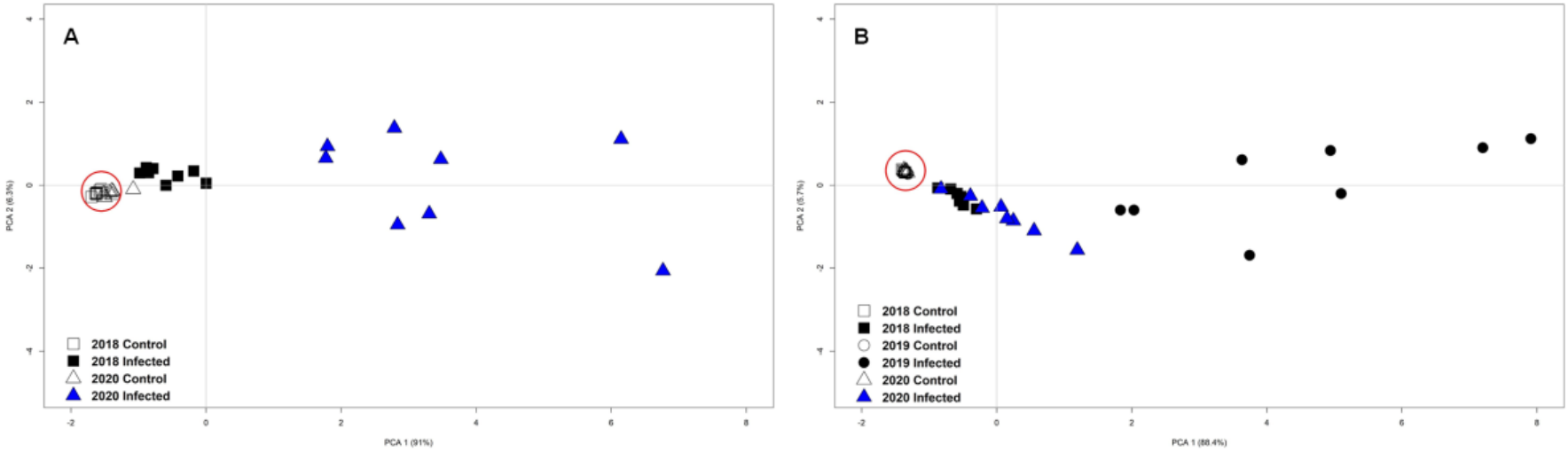


Figure 26. PCA scatter plot of six diagnostic BVOCs at two time points, 7 DAI (A) and 14 DAI (B) in the headspace of 'Carsten V' wheat seedlings (n=8) after inoculation in 2018-2020 with pathotype 51 of *Bgt*. Circle, all controls group in a distinct cluster.

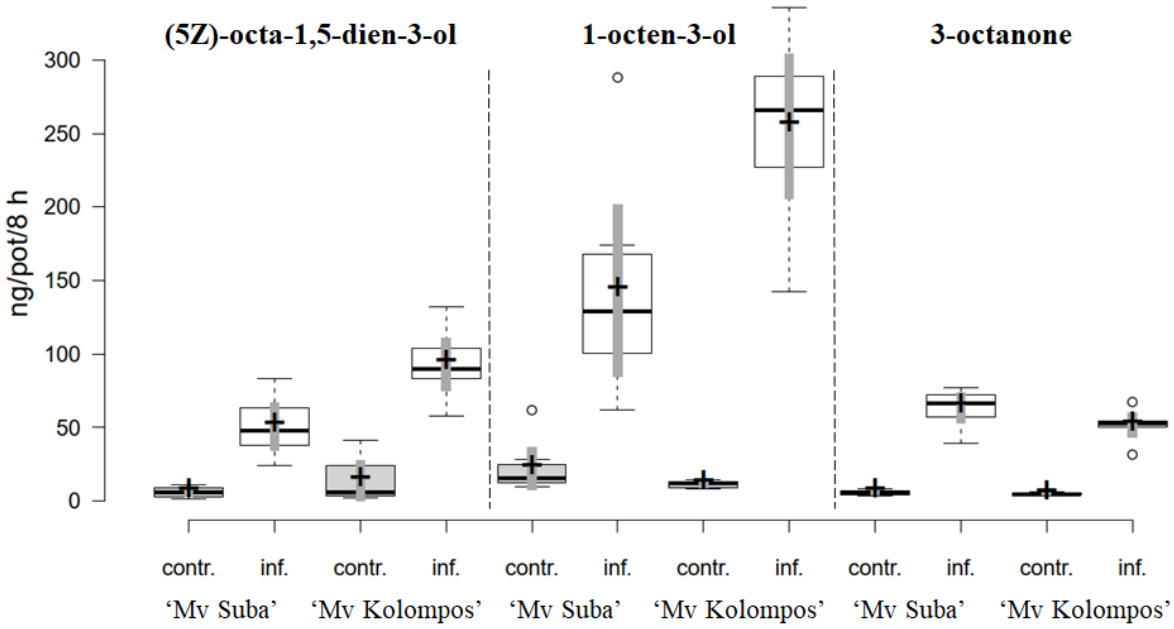


Figure 27. Emission of three biomarker BVOCs from healthy control and spontaneously *Bgt*-infected early phase plants (n=8) of two wheat cultivars. Gray stripes in boxes indicate 95% confidence intervals for the corresponding mean values.

5.4.4. Calculation of aerial emission quantities

Based on the quantitative determination of the four most abundant biomarker BVOCs at two symptomatic stages in three consecutive years (2018-2020) Our group attempted an educated estimation about the aerial emission of biomarker BVOCs from infected wheats in the field. According to the experimental data the average release (in ng/pot/day) of *Bgt*-inoculated young wheat plants were: 22.2 (1-heptanol), 135.3 ((5Z)-octa-1,5-dien-3-ol), 389.0 (1-octen-3-ol) and 82.1 (3-octanone) (**Annex 9.24 Table S16**). Extrapolating these data to a density of ca. 700 developed tillers/m^2 results in a total daily release of 31.5 µg/m^2 (or 0.5-0.6 µg/g dry weight per day) for these four BBVOCs, which corresponds to a monthly emission of 9.4 g/ha. Assuming an annual 10 percent infection rate (Saunders and Doodson, 1970; Morgounov et al. 2012) over the global wheat production area of roughly 200 million ha, this figure amounts to 188 tons (Mg) BVOCs/month worldwide, which can be attributed to PM disease alone. It should be noted, however, that adult plants may emit significantly higher quantities (**Figure 25.** and **Figure 27.**).

5.4.5. Aerial release of discovered BVOCs of the wheat-powdery mildew interaction, discussing associated literature about their role, other occurrences and emission origins

To the best of ourknowledge, none of the 48 BVOCs has so far been identified in *B. graminis* (**Annex 9.10 Table S4**, columns 9 and 10). Based on a comprehensive statistical analysis six BVOCs turned out to be of diagnostic value at both sampling times in two consecutive years and could thus be considered as volatile biomarkers for PM disease in wheat.

These six BVOCs are distributed in three chemical groups: three short-chain fatty alcohols (1-heptanol, (5Z)-octa-1,5-dien-3-ol and 1-octen-3-ol), two hydrocarbons (1,3-octadiene and 1,3(Z),5(Z)-octatriene) and a ketone (3-octanone). Only 1-octen-3-ol (OTL) was previously found in wheat plants (**Annex 9.10 Table S4**, column 9), though proper controls for the exclusion of possible contamination sources were not shown in the references (**Annex 9.10 Table S4**). Possibly, even this BVOC is not produced by wheat plants. On the other hand, BVOCs were already described in a broad range of non-pathogenic and phytopathogenic fungi (Darriet et al. 2002), but none of them in *B. graminis*. It is safe to conclude that these diagnostic BVOCs have not yet been characterized in the wheat-PM interaction. As additional preliminary proof, when three standard algorithms (an artificial neural network, Naive Bayes and Random Forest) were applied to our results as training and tester dataset, machine learning algorithms also separated three of the six identified BVOC biomarkers (1,3-octadiene, (5Z)-octa-1,5-dien-3-ol and 1-heptanol) between healthy and *Bgt*-inoculated wheat samples, where random forest based model yielded the best, 99.7% accuracy to decide whether a plant is infected or not by *Bgt.* (unpublished results, based on partner Printnet Ltd. during E-nose project). The three minor components (1,3-octadiene, 1,3(Z),5(Z)-octatriene and 1-heptanol) exhibited very limited presence in plants (Suinyuy et al. 2013) or their pathogens (Börjesson et al. 1992; Kalalian et al. 2020). It is therefore quite unique and distinctive that they occur together during PM disease development. The three major BBVOCs ((5Z)-octa-1,5-dien-3-ol, OTL and 3-octanone; **Figure 25. and 27.**), however, appear to be abundant in the anthropogenic biosphere. For example, OTL, also called 'mushroom alcohol' because it was first detected in an edible mushroom (Murahashi, 1936), is a characteristic component in animal breath and human sweat as the major attractant for tsetse fly (Hall et al. 1984) and mosquitoes (Kline et al. 2007), respectively, including the vector for malaria (Cork and Park, 1992). Another major urban source for the aerial emission of these major BBVOCs are abandoned or neglected housing facilities and warehouses – all due to contaminating filamentous fungi or molds (Pasanen et al. 1997; Korpi et al. 1998; Van Lancker et al. 2008; Zhao et al. 2017). The agricultural ecosystem as a whole represents essential contribution to BVOC emission into the atmosphere. The three major BBVOCs, especially OTL, have long been known to occur in the soil (Jüttner, 1990), some plants (Naves, 1943; Andersson et al. 1963; Honkanen and Moisio, 1963) and molds (Kaminski et al. 1974). I demonstrate here, for the first time, the aerial release of substantial amounts of characteristic BVOCs during the interaction of a major phytopathogenic fungus (*Bgt*) and wheat plants cultivated on 200 million ha or 2 million km^2 globally. As indicated, the advantage of *Bgt* as an obligate biotrophic pathogen is that only active, 'live' infections exist and can be monitored for BVOCs. On the other hand, since the process of *Bgt* infection requires a living host and the fungus cannot be maintained separately it is difficult to ascertain, without

proper controls, whether the detected BVOCs are produced by the plant and/or the pathogen itself? Two types of controls were incorporated in the present experiments: (i) pots filled with identical soil but without wheat plants (blanks) to monitor baseline BVOC release (*e.g.* by aerobic and anaerobic metabolism of microbes) and (ii) pots with uninoculated, healthy wheat plants to check for background BVOC production. Both types of controls resulted in quantities at or below the detection limit of the diagnostic BVOCs and below the limit of quantification, respectively (**Figure 25.**), a significant difference compared to the inoculated plants, which points to the direction of *Bgt* as the source of these BVOCs. Theoretically, it is possible that these BVOCs are derived from the wheat plant upon induction by *Bgt*. However, the facts that wheat (and other) plants usually do not contain or only a very low quantity of these BVOCs (**Annex 9.10 Table S4**) whereas a broad range of fungi have massive quantities (Kaminski et al. 1974; Pyysalo, 1976; Börjesson et al. 1992; Mau et al. 1997; Fischer et al. 1999; Zawirska-Wojtasiak, 2004), contradict this possibility. For example, comparable levels of OTL and 3-octanone are found in wheat grain or meal only when contaminated with molds (Sinha et al. 1988; Tuma et al. 1989). In addition, the right precursor for these C8 oxylipins, 10-hydroperoxyoctadecadienoic acid (10-HPODE) is known to be present in several fungi (Wurzenberger and Grosch, 1984; Kermasha et al. 2002; Matsui et al. 2003; Akakabe et al. 2005), but not in plants. 10-HPODE might also be generated in *B. graminis* via a dioxygenase enzyme encoded by one of the genes identified by BLAST search (**Annex 9.23 Table S15**). Taken together, these arguments strongly support that the six diagnostic BVOCs are all emitted by *Bgt* rather than wheat (Hamow et al. 2021). Three explanations are offered here for the role some of the BVOCs may play in this or similar host-pathogen interactions. First, they can simply be the by-products of lipase- and lipoxygenase-catalyzed reactions required to degrade cellular lipid membranes during the adhesion and germination of conidiospores (Feng et al. 2009). Additionally, they may even actively be involved in the regulation of these processes. Two sources of BVOCs from the wheat-PM interaction can be considered in relation to aerial emission, *i.e.*, spores and mycelia within the plant canopy and spores moving above the plant canopy, primarily confined to the lowest, surface boundary layer (ca. 1-50 m) of the atmosphere. The quantity of spores in and above a field can be estimated from data collected in a number of independent observations: a moderate figure of 25 colonies (pustules) per leaf (Daamen, 1986) with four functional leaves per tiller at any stage of development (Large and Doling, 1962) will result in ca. 100 colonies in a tiller. Taking a conservative three productive tillers this yields about 300 colonies per plant, which corresponds to some 10^9 colonies per ha.

There is a consensus that a single colony can release at least 10^5 conidiospores during its lifetime of about 20 days (Hall et al. 2000; Moriura et al. 2006), which corresponds to a total release of 10^{14} spores in this period from a single ha. Above the canopy (2-3 m height) the spore concentration can be in the range of 50-200/m^3 of air (Cao et al. 2012; Cao et al. 2016; Gu et al. 2020). It is known that OTL (and to a lesser extent 3-octanone) is a self-inhibitor of spore germination (Chitarra et al. 2004) and mycelial growth (Okull et al. 2003) in *Penicillium* spp., *Trichoderma* (Nemčovič et al. 2008) and *Aspergillus* (Herrero-Garcia et al. 2011). OTL also inhibits mycelial growth in other fungi belonging to different genera (Chitarra et al. 2004), which indicates that it may act as a general developmental signal for many species (Eastwood et al. 2013). Finally, some of these BVOCs may function alone or in mixtures (Ndomo-Moualeu et al. 2016) as attractants for dwelling or visiting insects that can transmit the pathogen's spores (Agrios, 1980). Indeed, OTL proved to be attractive for some plant-associated mites (Ozawa et al. 2000; Brückner et al. 2018), thrips (Zhang et al. 2015), beetles (Pierce et al. 1991; Malik et al. 2016) and flies (Birkett et al. 2004; Wu and Duncan, 2020) not only in closed laboratories, but even outdoors (Stevens et al. 2019). More evidence for the potential insect-mediated transfer of powdery mildews specifically comes from the strong association of mildew-infected plants with thrips (Yarwood 1943), mites (Reding et al. 2001) and beetles (Tabata et al. 2011), in the latter case with direct involvement of OTL. It is thus plausible that OTL and other BVOCs provide a chemical cue for insects that are then used as vectors for the mildew pathogen. The source tissue of these important BVOCs can in general be both the spores (Chitarra et al. 2004; Nemčovič et al. 2008) and the mycelium (Schindler and Seipenbusch, 1990), which in our case can explain their growing concentration during the infection process (7 DAI vs. 14 DAI, **Figure 25.** and **Annex 9.18-19-20 Table S12-S13-S14**) as well as their massive quantities emitted (see 5.4).

6. CONCLUSIONS AND SUGGESTIONS

6.1 Conclusion and future perspectives for below ground sampling

Volatile organic compounds emitted by plant roots and pathogenic and beneficial fungi, particularly mycorrhizal fungi, can shape trophic interactions in belowground systems. Fungal VOCs mediate plant growth, metabolites, and consequences of interactions between insects, pathogens, and plants. An approach using combined methods is proposed to collect VOCs and analyze the effect of each originated VOC in real-time. With the approach, the effect of each originated VOC on belowground trophic interactions can be precisely evaluated. Because of the essential roles of VOCs in inter- and intraspecific communication, using VOCs of certain fungal species may be a promising and sustainable way to reduce the incidence of diseases derived from soil borne phytopathogens. In addition, using fungal VOCs to increase plant tolerance against abiotic stresses is an area for future research with great potential. Despite various reports on interactions between belowground VOCs derived from fungi and plants and root VOCs and fungi that result in benefits for one or both partners, the actual mechanisms involved remain unknown. Therefore, the molecular mechanisms responsible for volatile production by VOC producers (plants and fungi, including fungal symbionts), perception by VOC receivers, and genetic reprogramming of VOC receivers need to be investigated further. Moreover, there are few reports on VOCs during mycorrhization, which should be a research area with great potential interest because of the importance of AMF in agriculture and ecosystems. In addition, most knowledge on VOC emissions by fungi is based on single strains under laboratory conditions, which can differ from rhizospheric conditions with complex microbial communities. Therefore, to facilitate practical VOC application, inoculated strains should be integrated into complex rhizosphere communities in order to mimic the natural conditions in soil (Duc et al. 2022).

6.2 Proposed future *in-situ* system design for dynamic and static combined automated sampling and experimental setup for VOC origin characterization

The challenge with passive and dynamic methods is in collecting the many different original belowground VOCs and establishing emission origins. To meet the challenge, a new experimental setup and methods can be optimized to minimize the disadvantages of the two approaches (**Figure 28.)**. An experimental system can be set up in which both sampling approaches are used simultaneously, and different treatments or events (blank pot with soil only, healthy plant, plant exposed to fungi, plant exposed to belowground herbivore, plant exposed to fungi and belowground herbivore) are used to compare differences in VOCs. After comparison and subtraction of VOC patterns of different events, emission origins and abundance of VOCs can be established. Sharifi et al. (2022) presented an *in-situ* design suitable for sampling belowground

VOCs that used a perforated polytetrafluoroethylene (PTFE) tube exposed to communities of plant roots and soil microorganisms.

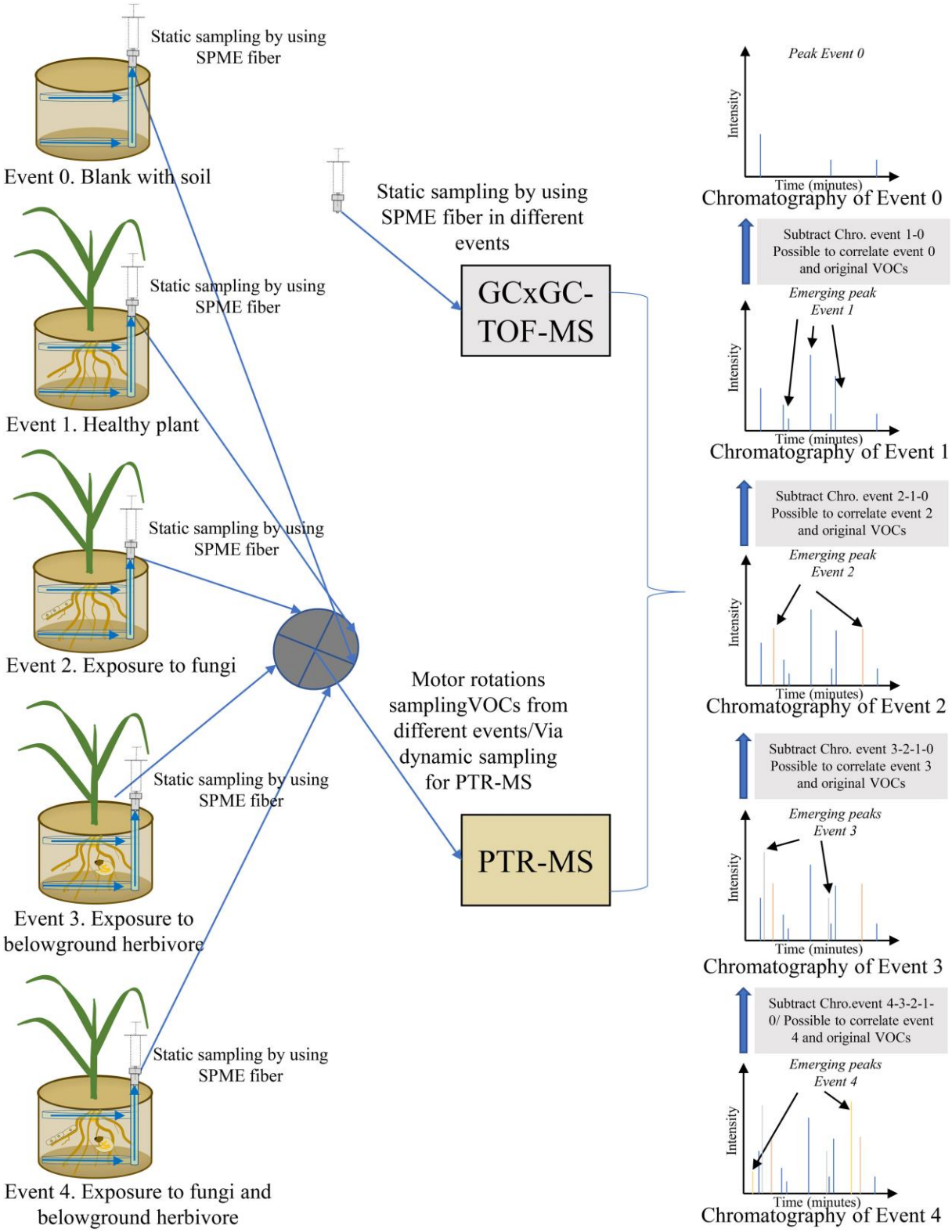


Figure 28. Schematic illustration of an *in-situ* design to collect and analyze belowground volatile organic compounds (VOCs) by a combined technique. Original VOCs are distinguished by subtracting chromatographic peaks of certain events (Duc et al. 2022).

The tube is placed in a pot before sowing seeds to avoid disturbing the soil and rhizosphere when belowground VOCs are collected. Belowground VOCs are collected by an SPME syringe extracted *via* a network of tubing. To separate the original VOCs, an experimental setup is suggested according to Sharifi et al. (2022) that can continuously sample different treatments or events by SPME fibers inserted into PTFE tube systems. After collection of VOCs, SPME fibers are analyzed in a cyclic manner by GC-MS or GCxGC-TOF-MS. The tube systems can also be sampled by a dynamic approach in which different treatments are connected by motor rotation switch valves to a PTR-MS. With this approach, SPME collections obtained by frequent static sampling cycles can provide a good approximation of real-time resolution in emissions of individual VOCs, in addition to VOC composition and abundance. The PTR-MS can characterize actual real-time continual emissions of different events. After subtraction and comparison of different events, VOC origins and emissions can be characterized on the basis of the combined sampling and analysis methods to yield a highly accurate approximation of VOC patterns and emission origins (**Figure 27.**).

6.3 open-loop-pull-type-DHS-SPE-GC-MS method performance characteristics

The aim was to investigate the performance characteristics of the pull-type DHS-SPE-GC-MS methodology used for collecting and analyzing plant volatiles and further refine the methodology. Performance characteristics are scarce in the literature despite their popular use and application in many scientific fields, such as chemical ecology. Results clearly indicated quantitative inaccuracies resulting from SPE elution, calibration, and desorption effects. To control elution volume, the use of internal standards is important to improve accuracy. SPE recoveries should be checked for individual components and mixtures as well; a more thorough investigation would be desirable for the effects of calibration mixtures on quantitation, especially for those containing a large number of compounds. Desorption effects can be mitigated by the proposed novel approach of periodic DHS sampling. It would be advisable to further optimize the sampling conditions in the future, including flow rate, sampling time, active collection phase duration, and evaluation at different temperatures, as well as the cooling of VOC traps as a form of cryotrapping. By reducing the temperature at the stationary phase, desorption losses and breakthrough of components could probably be further reduced. Another good idea is to test adsorbents by thermal desorption measurements (no dilution and elution by solvents), also with SPE elution by different organic solvents could be conducted and compared in the future, not to mention testing and comparison of different stationary phases for DHS sampling, also open-loop and closed loop systems, and desorption losses, and comparisons of different SPME samplings as static method with different conditions to test volatile profiling and limits to its utmost, since a high possibility exist that total volatile fingerprints always contain more components and differing emissions in reality than based

on just one sampling and analysis method applied by many researchers. Considering these results, the non-invasive pull-type DHS-SPE-GC-MS methodology applied may be suitable for describing the volatile profile of further plant-pathogen relationships and for identifying and quantifying biomarkers associated with other infections.

6.4 Emission of novel volatile biomarkers of wheat powdery mildew

Despite the economic importance of wheat there is a clear gap in the knowledge on BVOC composition and release, especially during vegetative growth in the field, which is relevant to detect and elucidate important fungal pathogens such as the obligatory biotroph *Blumeria graminis* f.sp. *tritici* (*Bgt*) causing powdery mildew disease worldwide. The 48 different VOCs were identified and quantitatively compared, out of which six compounds, namely 1,3-octadiene, 1,3(Z),5(Z)-octatriene, 1-heptanol, (5Z)-octa-1,5-dien-3-ol, 1-octen-3-ol and 3-octanone were found to be present only in the headspace of *Bgt*-inoculated plants. These six biomarker BVOCs showed a unique and highly reproducible pattern in their presence and quantities during a three year follow-up period. The latter three and as the most abundant BBVOCs were robustly applicable for differentiation between healthy and *Bgt*-inoculated wheat plants, as early as 7 days after inoculation, in a number of wheat genotypes at various developmental phases, two symptomatic stages and even for unidentified *Bgt* strains. These BVOCs are therefore proposed as novel biomarkers, BBVOCs for chemical monitoring powdery mildew disease in wheat. To the best of my knowledge, this was the first study to systematically assess specific BVOC emission patterns during the interaction of a cereal plant with a foliar fungal pathogen.

6.4.1 The diagnostic VOCs are biomarkers of PM disease

Out of the many criteria for a good biomarker (and any marker in general) sensitivity and specificity (Yerushalmy, 1947), reproducibility and robustness are deemed here to be the most relevant in relation to the six diagnostic BVOCs identified in the wheat-PM interaction. Sensitivity (correct identification of all diseased plants) and specificity (no healthy plants are found to be false positive) has been fulfilled for the six BVOCs in all the analyzed specimens, in total 120, which were collected from 56 healthy control and 64 diseased pots. Reproducibility has been demonstrated by the consistently significant differences for all these BVOCs between 40 healthy control and 48 inoculated pots in three consecutive years representing different temperature conditions during the incubation period and sampling days. Finally, robustness, *i.e.*, the stability of detection in this BBVOC set under non-optimal conditions, could be verified in the growth chamber experiment. The spontaneous infection with *Bgt* of additional wheat genotypes originally inoculated with *Fusarium* spp. provided a serendipitous opportunity to test these BBVOCs in a complex background. Indeed, in a real-time scenario in the field detection of a pathogen should

happen in the presence of other microorganisms, pathogens and pests. The three most abundant *Bgt*-specific BBVOCs (C8 oxylipins) were easily detected even in the early symptomatic phase compared to the control whereas just *Fusarium*-positive plants did not release these BVOCs, but primarily sesquiterpenes (results yet unpublished, but submission of a related article expected in 2024 spring). Since the main potential sources, molds are associated with wheat during grain storage (section 5.4.3) these data again indicate the *Blumeria*-specificity of these biomarkers in wheat plants. Another proof of the robustness of these BBVOCs was the full-grown (flowering) stage of plants in this experiment, which is far from optimal for PM disease development (Cunfer, 2002). While in 2018 and 2019 untargeted analyses were performed in order to discover diagnostic BVOCs, in 2020 the targeted analysis of the six VOCs validated their utility in monitoring PM disease and *Bgt* pathotypes. According to the temperature records there was a warming trend in the consecutive years, and despite that exactly 2020 was the warmest test period, especially towards the samplings at 14 DAI the biomarkers performed as expected during these variable years. The only systematic exception appeared in 2020 at 14 DAI when inoculations with pathotype 71 resulted in significantly lower quantities released for all six BBVOCs. This reaction coincided with high extremities during the day (max. 44.2 ºC) and night (min. 10.3 ºC) temperatures during the incubation period between 7 DAI and 14 DAI in 2020. I also realized that quantitative results given and calculated for wheat powdery mildew infection, approximately half of the emitted concentration of the components in the article were quantified because the internal standard for 1-bromodecane was not available during the 2018-19 period, and therefore, the calculated quantities were not corrected for elution volume. Thus, based on the results obtained, the components would have been quantified to be roughly 50% higher (section 5.2.2) than their actual emitted concentrations, if we would not take into account the results from testing breakthrough and desorption (section 5.2.4) during continuous sampling, the results regarding these compounds should be correct, since loss due to breakthrough for these compounds were roughly 50 %, therefore actual emitted quantity calculations should be correct with 10-20% uncertainty. It can be concluded that the diagnostic BVOCs meet the basic requirements of reliable biomarkers, however, further confirmation is required under field conditions (confirmed for OTL, unpublished results under e-nose project). Additional follow-up experiments in the field with extension of genotypes, other cereal cultivars and years under open field conditions worldwide would be required for. Powdery mildew related BVOC biomarkers should also be useful for early disease detection in the agroecosystem for the purposes of plant protection, precision agriculture and environmental monitoring in the field (in progress). The above results are currently utilized in machine learning where random forest based model built by our partner (Printnet Ltd.) using presented datasets, where 2/3 of the data available were used for teaching and 1/3 for testing the

models from the measurements conducted and presented in this thesis regarding wheat powdery mildew interaction. The random forest based model yielded a remarkable 99.7% accuracy (to distinguish between healthy and PM infected samples) as an additional proof of their diagnostic value.

6.4.2 Atmospheric release and relevance: reactivity and toxicology

Does a substantial part of the estimated 188 tons of biomarker BVOCs/month released worldwide by PM-diseased wheat plants reach the atmosphere? The detection of C6-C9 BBVOCs (including OTL) called green leaf volatiles by independent aircraft and satellite observations (Joutsensaari et al. 2015; Yli-Pirilä et al. 2016) suggests that the answer is a definite 'yes'. However, the fate and actual atmospheric concentrations of the biomarker BVOCs depend on the interaction and balanced effects of numerous factors. These factors include fluxes (Bachy et al. 2016; Bachy et al. 2020) determined by diffusion rate, stability and reactivity with atmospheric components to form secondary organic aerosols (SOA) – all largely unknown for these BBVOCs. OTL, at least, was found to be highly reactive in chamber experiments with ozone and hydroxy radical (Li et al. 2018; Fischer et al. 2020) as well as with chlorine (Grira et al. 2020), the major troposphere oxidants. Besides the internal alcoholic hydroxyl group, the terminal unsaturated double bond may be primarily responsible for this reactivity, which indicates that OTL is likely to form oxygenated products with various types of atmospheric nitrogen oxides (NO_x), too. The estimated half-life of OTL in the atmosphere appears to depend on the reaction type: due to its higher concentration reactions with the hydroxyl radical are predominant and result in a shorter half-life (about 3 h), whereas during ozonolysis it may amount to more than one day (Li et al. 2018). These data indicate that OTL and perhaps other biomarker BVOCs may definitely contribute to the formation of SOA in agroecosystems (Hamow et al. 2021). On the basis of these observations, major BVOCs released in agroecosystems and especially by phytopathogenic fungi should in the future be considered for monitoring their effects on biodiversity in these ecosystems as well as the major VOC emissions of agriculturally important cultivars ranking in the top twenty for example considering their cultivation area and extent worldwide. Also VOC emissions from these cultivation areas with a special focus related to their most important infectious agents, pests and pathogens and characterization of BVOC-s of these and average infection rates and monitoring of these emissions for consecutive years would be advisable. Important emissions of VOC-s from agri- and horticulture could be established to reveal component emissions and facilitate the monitoring of their emission and environmental fate, and impact on regarding their cultivation on the atmosphere and tropospheric ozone layer, that once again degraded as reported recently above the southern pole.

7. NEW SCIENTIFIC RESULTS

1. Tested and critically evaluated (based on SANTE/11312/2021 guideline) the performance of the Porapak Q adsorbent was for nearly a hundred different reference compounds using an open-loop-pull-type dynamic headspace VOC collection, n-hexane SPE elution, and GC-MS analysis method. This work has never been done to such an extent before.
2. Proved the value of applying 1-bromodecane as an internal standard (IS) when n-hexane is used to elute an adsorbent's SPE. Concentrations between 40 and 60 percent are the consequence of overestimating recoveries in the absence of internal standard correction. However, 90% of the 96 compounds examined showed an average recovery of 60% or above after accounting for the elution volume using 1-bromdecane.
3. Introduced the concept of periodic DHS (self-developed refinement of a technique). Recovery trials for both continuous and periodic DHS-VOC monitoring for 96 compounds exhibited losses for alcohols and low-boiling-point VOCs that might be minimized by periodic DHS. Desorption effects and breakthrough have been attributed to these losses.
4. Demonstrated by testing the adsorbent trap capacity and competition of components for adsorbent binding sites during continuous DHS sampling that even in cases of high background, no competition was observed, and the quantitative abundance of VOCs trapped from different emission sources in the sampled headspace (tomato and pear fruit) could be considered additive.
5. Successful BVOC-based differentiation of healthy and *Bgt.* powdery mildew (PM) infected wheat plants, by characterizing biomarker biogenic volatile organic compounds (BBVOC) as indicators of infection. Minor BBVOCs discovered were 1,3-octadiene, 1,3(Z),5(Z)-octatriene and 1-heptanol. Major novel BBVOCs were (5Z)-octa-1,5-diene-3-ol, 1-octen-3-ol and 3-octanone. The emission of these BBVOCs increased with disease progression and severity.
6. Proved that BBVOCs of *Bgt* are robust in various environmental conditions, years, and even in mixed pathogen background (*Fusarium* inoculated wheat genotypes also infected by PM).
7. Biomarker VOC discovery and results suggested that these and possibly other BVOCs of *Bgt* were estimated to be emitted by agroecosystems in massive quantities (ca. 188 metric tons per month) possibly participating in affecting atmospheric processes significantly by forming secondary organic aerosols.

8. SUMMARY

The E-nose Laboratory (established in 2017-2018) at the Centre for Agricultural Research, Martonvásár, Hungary, aimed to develop an innovative artificial sensory system capable of discerning the odor compositions of agricultural plants. Our group established a comprehensive database of VOC patterns, deploying machine learning and AI for statistical analysis. In my thesis, I presented part of the work our group carried out that served as baseline data for the project through VOC collection and GC-MS analysis to characterize volatile organic compound biogen biomarkers (BBVOC) that serve as indicators for adverse plant states. In the introduction, emphasis is placed on the significance of VOCs in plant metabolic processes, their roles, particularly their release in response to diverse stressors, especially during fungal infections, and their utilization for differentiation between healthy and infected or sick plants based on the volatile fingerprint, especially the discovery of BBVOCs that are reliable indicators of adverse health states. The knowledge gap regarding cereals and their fungal disease-induced BBVOCs, especially in the case of wheat powdery mildew (caused by the obligatory biotroph pathogen *Blumeria Graminis* f. sp. *tritici)*, interaction. An extensive literature review in this thesis covers the chemical groups of plant VOCs and their biosynthesis, abiotic and biotic stress-induced volatiles, the original physiological roles of these compounds, and the significance of VOCs in agroecosystems. The effects of plant belowground VOCs on fungal pathogens and the reciprocal influence of fungal VOCs on plants, as well as the impact of mycorrhizae, were discussed. Various methodologies for collecting and analyzing VOCs, including static and dynamic headspace sampling, possibilities of analysis methods, and focusing on gas chromatographic separation and detection, were thoroughly reviewed to select, adapt, (if possible, even refine), test, and furthermore apply a non-invasive VOC collection method for the discovery and emission characterization of BVOCs, especially BBVOCs related to wheat and PM interaction. Three main aims were set, and related main results and conclusions were drawn as described below.

The first aim sought the pre-survey and selection of a non-invasive static/dynamic sampling and analysis approach founded on pilot experiments. Investigation into various barley varieties revealed distinct aroma profiles. Mechanical damage induced the appearance of green leaf volatiles such as (Z)-3-hexenyl acetate. In the case of *P. teres*-infected barley, new compounds appeared on the chromatograms compared to controls. Varied trends in compound intensity were observed, signifying potential markers for infection stages. Similarly, the analysis of tomato odor profiles in relation to gray rot and especially wheat powdery mildew interaction that our group focused on identified promising biomarker BVOC candidates.

The second aim involved adaptation, implementation, performance testing, and, if possible, development by refinements for the open-loop pull-type DHS-SPE-GC-MS methodology. The approach proved to be a non-invasive, robust dynamic sampling methodology where SPE elution by *n*-hexane enabled storage and reanalysis of samples collected by GC-MS and other techniques. This approach has been used by many experts worldwide, but little is known about its performance characteristics, especially for Porapak Q-based adsorbents. The methodological approach that was adopted and tested for compliance with the qualitative and quantitative analytical requirements was in conformity with the SANTE/11312/2021 guidelines that are used for pesticide residue analysis. Adsorbent SPE elution recovery with (IS 1-bromdecane) and without internal standard correction have been tested. Findings about the direct spiking of VOC traps by reference mixes, SPE elution, and recovery assessment suggested that recovery may have been overestimated. Recovery meant that if IS correction was not applied to the elution volume, the quantitative accuracy of concentration was overstated by 40–60%. 87 VOCs' average recovery in the IS correction scenario involving 96 chemicals was categorized as being over 60%. Recovery ranged from 40 to 60% for 2-methyltetrahydrofuran-3-one, methyl benzoate, 1,3-dimethoxybenzene, α-terpineol, (S)-(+)-carvone, eugenol, and methyl eugenol. Recovery for methyl jasmonate and ethyl 3-hydroxybutyrate was between 20 and 40 percent.

Regarding the second aim set, additional tests included characterizing the effects of sorbent breakthrough and desorption through recovery experiments by comparing continuous and novel periodic DHS-VOC sampling. This could be a potential improvement to the approach that aimed to reduce total flow volume by periodically starting and stopping flow, thereby mitigating potential breakthrough and desorption losses. These were observed primarily in the case of low-boiling-point compounds that are early eluters in the C8-C9 elution region and compounds containing hydroxyl groups, such as alcohols. Periodic DHS displayed a trend of slightly higher recoveries with less deviation, but further optimization (sampling duration, cycle times, flow rates, adsorbent quality and quantity, temperature of VOC traps, and elution solvent type for SPE) would be advisable in the future. As a final test, it was determined that even at high background levels, the VOC traps applied have adequate capacity for trapping and can even additively semi-quantify different strong smells coming from various sources in the closed headspaces sampled. This is in line with the second aim-set evaluation of sorbent trap capacity and the competition of VOCs for the volatile trap binding sites for continuous DHS sampling.

The third aim involved the application of this methodology to explore the interaction and discovery of BVOCs in wheat powdery mildew (*Blumeria Graminis* f. sp. *tritici*). Six BVOCs proposed as novel BBVOCs as indicators of infection in early and advanced states have been identified.

Three minor (1,3-octadiene, 1,3(Z),5(Z)-octatriene, 1-heptanol), and three major BBVOCs (1-octen-3-ol, 5Z-octa-1,5-diene-3-ol, and 3-octanone) were identified. BBVOC emissions (in various abiotic conditions, genotypes, mixed pathogen backgrounds, and different plant growth stages and years) increased with disease severity from early (7 DAI) to advanced stages (14 DAI). To sum up, the pull-type DHS-SPE-GC-MS methodology has proven to be a flexible way for differentiating between wheat plants that are healthy and those that have powdery mildew. The creation of VOC databases for machine learning-based prediction model development made use of collected datasets. With an amazing 99.7% accuracy, a random forest-based model produced the best results for VOC-based distinction between healthy plants and those affected by powdery mildew. This provides additional support for pathotyping and prediction; using VOC fingerprinting, early disease identification can be accomplished.

Hundreds of tons of these BVOCs with variable half-lives may have been released into the atmosphere based just on the projected BBVOC emission from the wheat-powder-mildew interaction. The identified BBVOCs may have aided in the creation of SOA by taking part in atmospheric processes such as the catalytic breakdown of tropospheric ozone. Therefore, the scientific community should give it top priority to reevaluate and carry out research to determine the precise composition, geographic distribution, impact, and fluxes associated with BVOC emissions from the agri-environment for the most significant diseases and BBVOCs related to fungal pathogens of cultivars grown in large areas of the world.

My thesis and research work show the advantages and limitations of the open-loop pull-type DHS-SPE-GC-MS methodology to non-invasively collect and analyze VOCs; it introduces concepts such as periodic DHS sampling; it proposes innovative *in-situ* system designs by combining static and dynamic VOC collection, sampling, and different analysis methods; and it is the first comprehensive and extensive description of this approach and method setup tested in its performance and reliability for hundreds of compounds. Thus, it is a reliable tool for non-invasive VOC characterization and BVOC and BBVOC discovery that establishes a robust foundation for prediction by VOC fingerprints, especially BBVOCs useful for pathotyping, early disease detection, and differentiation, and hopefully contributes to future BVOC utilization in precision agriculture. The fragrant language of VOCs has the potential to revolutionize how we perceive and manage agricultural ecosystems; for me, at least BBVOC discovery and their utilization in agriculture and food safety have been fully developed into the utmost enthusiasm that I aim to pursue as a lifelong immersion.

8. ÖSSZEFOGLALÁS

A HUN-REN Agrártudományi Kutatóközpontban, Martonvásáron az E-orr projekt 2017-2018-as alapítása óta innovatív mesterséges szenzoros rendszer kifejlesztését célozta, amely képes felismerni a mezőgazdasági növények illatmintázatát. Ennek egyik alapja a biogén illékony szerves vegyületek (BVOC) közül a biomarker (BBVOC) jellegűek gyűjtése és nem-célzott GC-MS analízise egészséges és fertőzött növények illat alapú megkülönböztetéséhez. Az illatmintázatokból átfogó adatbázist hoztunk létre, gépi tanulást és mesterséges intelligenciát is alkalmazva a statisztikai elemzéshez és predikciós modellépítéshez a differenciáldiagnosztikára. E munka egy része szolgált doktori munkám témájaként. A tézis bevezetésében ismertettem a VOC-k növényi anyagcsere-folyamatokban betöltött jelentőségét, különféle stresszhatásokra, különösen a gombapatogének általi fertőzésekre. A szakirodalmi áttekintés során kitértem a növényi VOC-k kémiai csoportjaira és bioszintézisére, az abiotikus és biotikus stressz által kiváltott illékony anyagokra, e vegyületek eredeti fiziológiai szerepére. Továbbá VOC-k jelentőségére az agroökoszisztémákban, hangsúlyozva növény-patogén gombák kölcsönhatásában és a mikorrhiza szimbiózisban betöltött szerepüket. A növények által termelt föld alatti VOC-k gombakórokozókra gyakorolt hatásaival, illetve a fordított eset, a gomba eredetű VOC-k hatását a növényekre külön taglaltam, ahogy a mikorrhiza gombák hatását a rizoszféra mikrobiomára, valamint a mikorrhizák által kiváltott növényi illékony anyagok szerepét az abiotikus és biotikus stressz leküzdésében. A VOC-k gyűjtésének és elemzésének különböző módszerei, beleértve a statikus és dinamikus gőztéranalízis mintavételi eljárások és a szóba jövő elemzési módszerek lehetőségeit, különös tekintettel a gázkromatográfiás elválasztási és detektálási lehetőségekre alaposan ismertettem. Az irodalmi áttekintés kulcsfontosságú volt a VOC mintavételezés és mintakezelés, illetve az analitikai módszertan kiválasztásának és tesztelésének, valamint a búza lisztharmat kölcsönhatásának vizsgálatára vonatkozó kísérletek előkészítésében. A következő három fő célt tűztem ki, amelyekhez a kapcsolódó fő eredményeket és következtetéseket a továbbiakban foglalom össze és ismertetem.

Az első cél egy nem-invazív statikus/dinamikus mintavételi és elemzési megközelítés kiválasztása és kipróbálása volt. Ezt pilot kísérleteken alapulva végeztem. Így például különböző árpafajták vizsgálata során eltérő aromaprofilokat tártam fel. Mechanikai sérülés indukálása esetén specifikusan megjelenő zöld levél alkohol (GLV), a (Z) -3-hexenil-acetát megjelenését észleltem a szakirodalommal összhangban. A *P. teres* által okozott levélrozsda (előrehaladott időszakában) új vegyületek megjelenését eredményezte az illatprofilban. Változatos tendenciákat figyeltem meg az illékony vegyületek intenzitásában, a fertőzés hatására különböző árpa genotípusok esetén, ami potenciális BBVOC-kat jelez a fertőzési stádiumokban.

Hasonlóképpen, a búza és kórokozója a *Bgt.* által okozott lisztharmat, illetve a paradicsom esetén a szürkepenészt okozó *B. cineare* illatprofiljának elemzése számos VOC vegyület változását hozta kórokozóikkal való mesterséges fertőzés esetén. A búza lisztharmat betegségének relációjában az illékony komponensek közül több, például az okt-1-én-3-ol ígéretes jelöltnek mutatkozott az előkísérletek során, mint illékony biomarkerek.

A második cél a végül kiválasztott open-loop pull-type-dinamikus légtércsapdázást követő n-hexános SPE elúció és GC-MS analízis megközelítés adaptálása, esetleges fejlesztése és tesztelése volt. Annak terepre vihető, könnyen kivitelezhető és olcsó, dinamikus és non-invazív volta és analízisismételhetősége miatt választottuk e megközelítést. Népszerűsége és frekventált alkalmazása ellenére e megközelítésnek, (különösen Porapak Q adszorbens esetén) teljesítményparamétereiről a szakirodalom legjobb esetben is szórványosnak tekinthető. Az adaptált megközelítés tesztelése során kimutattuk, hogy minőségi és mennyiségi analízis céljára (retenciós időstabilitás, érzékenység, linearitás, ismételhetőség) megfeleltek a SANTE/11312/2021 irányelv szerinti követelményeknek. Az adszorbens VOC illatcsapdákra referencia keverékoldatok (más néven mixek, közel 100 VOC komponens) direkt hozzáadásával és az adszorbens (Porapak Q) *n*-hexánnal történő szilárd fázisú extrakció (SPE) elúciója és GC-MS analízise során tapasztalt visszanyerés százalékok meghatározásával végeztünk teszteket. Az elúciós térfogat kontrolljához 1-brómdekán belső standard (IS) pontosságra gyakorolt hatását vizsgáltuk. Adszorbens SPE elúció *n*-hexánnal belső standard korrekció nélkül, és 98 vegyületet tartalmazó referenciakeverékek közvetlen hozzáadása esetén az adszorbenshez 40-60%-kal túlbecsülte visszanyerést, így a mért koncentrációt is. Azonban az 1-brómdekánnal végzett elúciós térfogatra vonatkozó IS korrekció a 96 vizsgált vegyület 90%-a 60%-os vagy magasabb átlagos visszanyerést mutatott, így az IS korrekció az eredmények pontosságát javítja, használata fontos tényező a pontosabb kvantálás érdekében. Több tucat komponenst tartalmazó keverékek használata és hatásai a kapott mennyiségi eredményre további vizsgálatokat indokolna.

A második cél kapcsán további törekvés volt a módszer finomítása, fejlesztése, a szakaszos dinamikus illatanyaggyűjtés koncepciójának bevezetése és tesztelése. A komponensek áttörési pontjához, vagy más deszorpciós jelenségekkel összefüggő veszteségeinek jellemzésére az alkalmazott, szakirodalomban ismertetett folyamatos DHS, illetve az általam koncepcionált és az E-orr csoport által épített prototípus „nose-e” programozható hordozható illatmintavevő egység segítségével elsőként alkalmaztam szakaszos DHS mintavételt. A folyamatossal szemben a szakaszos mintavételnél a rendszer (tetszőlegesen programozható) ciklikusan ismételve képes az áramlás ki- (kísérletünkben 10 perc) illetve bekapcsolására (5 perc). Kísérleteink során 66,66%-ban csökkentve a teljes áramlási térfogatot a mintavétel ideje alatt, ezáltal trendszerűen tompítva

VOC-k deszorpciós veszteségeit. A deszorpció a hőmérséklet, áramlási sebesség, mintavétel hosszának és alkalmazott álló fázisnak (Porapak Q) a függvénye. Veszteséget a 96 VOC-ból főleg hidroxil csoportot tartalmazó vegyületek (alkoholok), valamint az alacsony forráspontú vegyületek (C8-C9 alkánok régiójában eluálódók) mutattak. A veszteséget a szakaszos mintavétel akár jelentősen mérsékelheti, valamint tendenciózusan jobb átlagos visszanyeréseket és szórást eredményezett. A jövőben érdemes optimálni a mintavétel körülményeit, áramlási sebesség, mintavételi idő, aktív gyűjtési szakasz ideje szerint. Fejlesztési lehetőség a VOC csapdák hűtése is lehet a jövőben, hiszen a megkötődést segítené ez és deszorpciót gátolná.

A második célon belül további kísérlet volt az adszorbensek kapacitásának értékelése és a VOC-k versengése kötőhelyeikért folyamatos DHS-mintavétel során. Az eredmények szerint még magas háttérszintnél is megfelelő kapacitással rendelkeznek a csapdák, kompetíció nem volt megfigyelhető, sőt a háttér és a kétféle mátrixból eredő (paradicsom és körte) illatkomponensek csapdázása additív mennyiségi eredményt szolgáltatott.

A harmadik cél a búza lisztharmat betegsége, amelyet a *Bgt*. okoz, és e kölcsönhatás feltárása volt, ahogy a hozzá köthető BVOC-k közül a BBVOC-k meghatározása is a DHS-SPE-GC-MS módszer akalmazásával. A *Bgt* obligált biotróf kórokozó, azaz csak élő növények levelein nő. Korábban e fontos kölcsönhatás VOC mintázatait senki sem vizsgálta. A búza (valamint a kalászos gabonák és egyszikűeké általában) VOC-kibocsátása kevésbé összetettnek tűnik a többi növényhez képest (Gomez et al. 2019; Bachy et al. 2020). Ez a viszonylag „zajszegény" illatháttér egy eddig észrevétlen előnyt biztosít, és kiváló kísérleti rendszert jelent a specifikus gombafertőzésekhez köthető BVOC-k kiszűrésére. A gombapatogének ugyanis igen erős illatemisszióval jellemezhetőek, specifikus és sajátos illékony másodlagos anyagcsereterméket állítva elő a növény-patogén kölcsönhatás során. A búza és *Bgt*. kölcsönhatás során robusztus biogén illékony biomarker molekulákat (BBVOC) fedezhettünk fel. Ezek a fertőzés indikátoraira korai (7 DAI) és előrehaladott (14 DAI) állapotban. Elsőként azonosítottunk így három mellék markert, (okta-1,3-dién, (3Z,5Z)-okta-1,3,5-trién, heptán-1-ol) valamint három fő markert (okt-1-én-3-ol, (5Z)-okta-1,5-dién-3-ol, oktán-3-on). Kibocsátásuk (különböző abiotikus körülmények, genotípusok, vegyes patogén háttér, különböző növényi növekedési stádiumokban és évek esetén) a betegség súlyosságával a korai stádiumtól az előrehaladott stádiumig növekedést mutatott ezen BBVOC-knak. Az általam alkalmazott, nem-invazív open-loop pull-type-DHS-SPE-GC-MS módszertan alkalmas volt a fenti esetben BVOC-k detektálására és monitorozására, így ígéretes további növény-patogén kapcsolatok illékony profiljának leírására, BBVOC-k felfedezésére. Csak a búza lisztharmat kölcsönhatás fő BBVOC-iből származó becsült kibocsátás kapcsán több száz tonna kerül a légkörbe változó felezési idővel e vegyületekből olyan hónapok

alatt, amikor ez az obligált biotróf patogén világszerte megjelenik a búzanövények 200 millió hektárra tehető vetésterületén. További szakirodalmi kutatással kiderült, hogy a *Bgt*. BVOC marker vegyületei, különösen az okt-1-én-3-ol más kutatók által végzett vizsgálatokban másodlagos szerves aeroszolok képződésében vesz részt és egyéb légkörkémiai reakciókban, például a troposzférikus ózon katalitikus lebontásában is. Ilyen módon az agrárkörnyezetből származó BVOC-kibocsátások pontos összetételének, időbeli, földrajzi eloszlásának és fluxusainak feltárására fontos feladat (különösen a legfontosabb betegségek és gombapatogének esetében, amelyek fertőzik a hatalmas vetésterületű haszonnövényeink). Ezen patogének BBVOC karakterizálása és emmissziómonitorozása, légköri sorsuk és hatásaik kutatása kiemelten fontos atmoszférikus folyamatokban jó eséllyel szignifikáns impaktjuk miatt. Az E-orr Laboratórium partnereivel és munkatársaival való együttműködés eredményeként létrejöttek a VOC adatbázisok melyeket gépi tanuláson alapuló modellek, köztük a legjobban teljesítő random forest megközelítésű modell (Printnet Kft.) algoritmus tanítására és tesztelésére használtunk elérve a kimagasló 99,7%-os pontosságot az egészséges és a lisztharmattal fertőzött növények VOC alapú megkülönböztetésében. Ez további megerősítésként szolgál a VOC ujjlenyomat és mintázat, különösen a biomarker és más BVOC-k hasznosításán alapuló korai betegségdetektálás, előrejelzés lehetőségeinek és azok potenciáljának bemutatása kapcsán.

Doktori dolgozatom és kutatási munkám reményeim szerint hozzájárulhat idővel a precíziós mezőgazdaság innovatív megoldásaihoz. Munkám leírja az open-loop pull-type-DHS-SPE-GC-MS módszer előnyeit és korlátait a VOC-k non-invazív gyűjtésére és elemzésére. Olyan eljárásokat is bevezetve, mint például a szakaszos DHS-mintavétel, valamint javaslatokat *in-situ* rendszer dizájnra, amelyben kombinálnám a statikus és dinamikus mintavételezést és különböző analízis technikákat, a jövőbeli minél teljesebb VOC karakterizálás érdekében. Véleményem szerint a VOC-k változatos világa és azok kutatása, hasznosítása képes forradalmasítani, hogyan tekintünk és manageljük mezőgazdasági ökoszisztémáink, számomra legalábbis a BBVOC felfedezése és hasznosítása a mezőgazdaságban és az élelmiszer-biztonságban olyan lelkes kíváncsisággá fejlődött, amelyet élethosszig tartó elmélyülésként kívánok folytatni kutatásaim során.

9. ANNEXES

9.1 List of references

(All records in this list where accessibility should be checked, such as electronic publications, links, and doi linkings, were checked and accessed on February 25–26, 2024.)

1. Abdulsalam, O., Wagner, K., Wirth, S., Kunert, M., David, A., Kallenbach, M., Boland, W., Kothe, E., Krause, K. (2021): Phytohormones and volatile organic compounds, like geosmin, in the ectomycorrhiza of tricholoma vaccinum and Norway spruce (Picea abies). *Mycorrhiza* 31(2), *pp.* 173–188. doi: 10.1007/s00572-020-01005-2
2. Abis, L., Loubet, B., Ciuraru, R., Lafouge, F., Houot, S., Nowak, V., Tripied, J., Dequiedt, S., Maron, P. A., Sadet-Bourgeteau, S. (2020): Reduced microbial diversity induces larger volatile organic compound emissions from soils. *Sci. Rep.* 10, *pp.* 6104. doi: 10.1038/s41598-020-63091-8
3. Acton, W. J. F., Jud, W., Ghirardo, A., Wohlfahrt, G., Hewitt, C. N., Taylor, Hansel, A. (2018): The effect of ozone fumigation on the biogenic volatile organic compounds (BVOCs) emitted from *brassica napus* above- and below-ground. *PloS One* 13, e0208825. doi: 10.1371/journal.pone.0208825
4. Afendi, F.M., Okada, T., Yamazaki, M., Hirai-Morita, A., Nakamura, Y., Nakamura, K., Ikeda, S., Takahashi, H., Altaf-UI-Amin, M.D.,Ikeda, Hiroki Takahashi, Md. Altaf-Ul-Amin, Darusman, L. K., Saito, K., Kanaya, S. (2012): KNApSAcK family databases: integrated metabolite-plant species databases for multifaceted plant research. *Plant and Cell Physiology*, Volume 53(2), doi: 10.1093/pcp/pcr165
5. Agrios, G.N., 1980. Insect involvement in the transmission of fungal pathogens. In: Harris, K.F., Maramorosch, K. (Eds.), *Vectors of Plant Pathogens*. Academic Press, USA: New York, *pp.* 293–324.
6. Akakabe, Y., Matsui, K., Kajiwara, T. (2005): Stereochemical correlation between 10-hydroperoxyoctadecadienoic acid and 1-octen-3-ol in *Lentinula edodes* and *Tricholoma matsutake* mushrooms. *Biosci. Biotechnol. Biochem.* 69(8), *pp.* 1539–1544. doi: 10.1271/bbb.69.1539
7. Aksenov, A.A., Novillo, A., Sankaran, S., Fung, A.G., Pasamontes, A., Martinelli, F., Cheung, W. H. K., Ehsani, R., Dandekar, A. M., Davis, C. E. (2013): Volatile Organic Compounds (VOCs) for Noninvasive Plant Diagnostics. [In ACS Symposium Series.], (*Pest Management with Natural Products*) Vol. 1141, *pp. 73–95.* doi: 10.1021/bk-2013-1141.ch006
8. Altschul, S.F., Gish, W., Miller, W., Myers, E.W., Lipman, D.J. (1990): Basic local alignment search tool. *J. Mol. Biol*. 215(3), *pp.* 403–410. doi: 10.1016/S0022-2836(05)80360-2.
9. Andersen, R. A., Hamilton-kemp, J. T. R., Hildebrand, D. F., Mccracken, C. T., Collins, R. W., and Fleming, P. D. (1994): Structure-Antifungal Activity Relationships among Volatile C6 and C9 Aliphatic Aldehydes, Ketones, and Alcohols. *J. Agric. Food Chem.*, 42(7), *pp.* 1563–1568. doi: 10.1021/jf00043a033
10. Andersson, J., Bosvik, R., Sydow, E.V. (1963): The composition of the essential oil of black currant leaves (*Ribes nigrum L.*). *J. Sci. Food Agr.* 14, *pp.* 834–840. doi: 10.1002/jsfa.2740141110.
11. Arimura, G., Ozawa, R., Shimoda, T., Nishioka, T., Boland, W., Takabayashi, J. (2000): Herbivory-induced volatiles elicit defence genes in lima bean leaves. *Nature*, 406(6795), *pp.* 512-515. doi: 10.1038/35020072
12. Arimura, G., Kost, C., Boland, W. (2005): Herbivore-induced, indirect plant defences. *Biochimica et Biophysica Acta (BBA)* - Molecular and Cell Biology of Lipids, 1734(2), 91-111. doi: 10.1016/j.bbalip.2005.03.001
13. Arimura, G., Matsui, K., Takabayashi, J. (2009): Chemical and Molecular Ecology of Herbivore-Induced Plant Volatiles: Proximate Factors and Their Ultimate Functions, *Plant and Cell Physiology*, 50(5), *pp.* 911–923. doi: 10.1093/pcp/pcp030

14. Arthur, C. L. and Pawliszyn, J. (1990): Solid phase microextraction with thermal desorption using fused silica optical fibers. *Analytical Chemistry*, 62(19), *pp.* 2145–2148. doi: 10.1021/ac00218a019
15. Arzani, A.; Ashraf, M. (2017): Cultivated ancient wheats (*Triticum* spp.): A potential source of health-beneficial food products. *Comp. Rev. Food Sci. Food Saf.*, 16(3), *pp.* 477–488. doi: 10.1111/1541-4337.12262
16. Atkinson, R. (2000): Atmospheric chemistry of VOCs and NO. *Atmospheric Environment*, 34(12-14), *pp.* 2063–2101. doi: 10.1016/S1352-2310(99)00460-4
17. Aziz, M., Nadipalli, R. K., Xie, X., Sun, Y., Surowiec, K., Zhang, J. L., et al. (2016): Augmenting sulfur metabolism and herbivore defense in arabidopsis by bacterial volatile signaling. *Front. Plant Sci*. 7. doi: 10.3389/fpls.2016.00458
18. Bachy, A., Aubinet, M., Amelynck, C., Schoon, N., Bodson, B., Delaplace P., et al. (2020): Dynamics and mechanisms of volatile organic compound exchanges in a winter wheat field. *Atmos. Environ.* 221, 117105. doi: 10.1016/j.atmosenv.2019.117105
19. Bachy, A., Aubinet, M., Schoon, N., Amelynck, C., Bodson, B., Moureaux, C., Heinesch, B. (2016): Are BVOC exchanges in agricultural ecosystems overestimated? Insights from fluxes measured in a maize field over a whole growing season. *Atmos. Chem. Phys.* 16, *pp.* 5343–5356. doi: 10.5194/acp-16-5343-2016
20. Bailly, A., Weisskopf, L. (2012): The modulating effect of bacterial volatiles on plant growth: current knowledge and future challenges. *Plant Signal. Behav*. 7, *pp.* 79–85. doi: 10.4161/psb.7.1.18418
21. Baldwin, I. T., Halitschke, R., Paschold, A., Von Dahl, C. C., Preston, C. A. (2006): Volatile signaling in plant-plant interactions: 'Talking trees' in the genomics era. *Science*, vol. 311, no. 5762, *pp.* 812–815, 2006. doi: 10.1126/science.1118446
22. Baldwin, I. T., Kessler, A., Halitschke, R. (2002): Volatile signaling in plant–plant–herbivore interactions: what is real? *Curr. Opin. Plant Biol*. 5, *pp.* 351–354. doi: 10.1016/S1369-5266(02)00263-7
23. Baldwin, I. T., Schultz, J. C. (1983): Rapid changes in tree leaf chemistry induced by damage: evidence for communication between plants. *Science*, vol. 221, *pp.* 277–279. doi: 10.1126/science.221.4607.277
24. Bapela, T.; Shimelis,H.; Terefe, T.; Bourras, S.; Sánchez-Martín, J.; Douchkov, D.; Desiderio, F.; Tsilo, T.J. (2023): Breeding Wheat for Powdery Mildew Resistance: Genetic Resources and Methodologies—A Review. *Agronomy*, 13, *pp.* 1173. https://doi.org/10.3390/agronomy13041173
25. Basandrai, A.K., Basandrai, D. (2018): Powdery mildew of wheat and its management. In: Singh, D.P. (Ed.), *Management of Wheat and Barley Diseases*. Apple Academic Press, USA: Waretown, *pp.* 133–182.
26. Becker, E.M. (2013): New strategies for the detection of Fusarium infection and mycotoxin contamination of cereals and maize, Doctoral (PhD) dissertation, Georg-August-Universität Göttingen
27. Bertin, C., Yang, X., Weston, L.A. (2003): The role of root exudates and allelochemicals in the rhizosphere, *Plant and Soil* 256: *pp.* 67–83.
28. Bianchi, G., Falcinelli, B., Tosti, G., Bocci, L., Benincasa, P. (2019): Taste quality traits and volatile profiles of sprouts and wheatgrass from hulled and non-hulled *Triticum* species. *J. Food Biochem*. 43(7), e12869. doi: 10.1111/jfbc.12869
29. Bicchi, C., Cordero, C., Liberto, E., Rubiolo, P., and Sgorbini, B. (2004): Automated headspace solid-phase dynamic extraction to analyze the volatile fraction of food matrices. *J. Chromatogr. A*, vol. 1024, no. 1–2, *pp.* 217–226, 2004. doi: 10.1016/j.chroma.2003.10.009
30. Bier, M. C., Medeiros, A. B., Soccol, C. R. (2017): Biotransformation of limonene by an endophytic fungus using synthetic and orange residue-based media. *Fungal Biol.* 121, *pp.* 137–144. doi: 10.1016/j.funbio.2016.11.003

31. Bindschedler, L.V., McGuffin, L.J., Burgis, T.A., Spanu, P.D., Cramer, R. (2011): Proteogenomics and *in silico* structural and functional annotation of the barley powdery mildew *Blumeria graminis* f. sp. *hordei*. *Method*s 54 (4), *pp.* 432–441. doi: 10.1016/j.ymeth.2011.03.006
32. Birkett, M.A., Bruce, T.J.A., Martin, J.L., Smart, L.E., Oakley, J., Wadhams, L.J. (2004): Responses of female orange wheat blossom midge, Sitodiplosis mosellana, to wheat panicle volatiles. *J. Chem. Ecol.* 30, *pp.* 1319–1328. doi:10.1023/B:JOEC.0000037742.05022.9f
33. Bitas, V., Kim, H. S., Bennett, J. W., Kang, S. (2013): Sniffing on microbes: diverse roles of microbial volatile organic compounds in plant health. *Mol. Plant Microbe Interact*. 26, *pp.* 835–843. doi: 10.1094/MPMI-10-12-0249-CR
34. Blande, J. D., Holopainen, J. K., Niinemets, Ü. (2014): Plant volatiles in polluted atmospheres: stress responses and signal degradation. *Plant, Cell & Environment*, 37(8), *pp.*1892-1904. doi: 10.1111/pce.12352
35. Blasioli, S., Biondi, E., Samudrala, D., Spinelli, F., Cellini, A., Bertaccini, A., Cristescu, S.M., Braschi, I. (2014): Identification of Volatile Markers in Potato Brown Rot and Ring Rot by Combined GC-MS and PTR-MS Techniques: Study on *in Vitro* and *in Vivo* Samples. *Journal of Agricultural and Food Chemistry*, 62(2), *pp.* 337–347. doi: 10.1021/jf403436t
36. Boland, W., Ney, P., Jaenicke, L., and Gassmann, G. (1984): A 'closed-loop-stripping' technique as a versatile tool for metabolic studies of volatiles. In *Analysis of Volatiles*, P. Schreier (Ed.), *pp.* 371–373. Berlin: Walter de Guyter.
37. Börjesson, T., Stöllman, U., Adamek, P., Kaspersson, A. (1989): Analysis of volatile compounds for detection of molds in stored cereals. *Cereal Chem.*. 66(4). *pp.* 300-304.
38. Börjesson, T., Stöllman, U., Schnürer, J., (1992): Volatile metabolites produced by six fungal species compared with other indicators of fungal growth on cereal grains. *Appl. Environ. Microbiol.* 58, *pp.* 2599–2605. doi: 10.1128/aem.58.8.2599-2605.1992
39. War, A.R., Sharma, H.C., Paulraj, M.G., War, M.Y., Ignacimuthu, S. (2011): Herbivore. induced plant volatiles: their role in plant defense for pest management. *Plant Signal Behav.* 6(12) *pp.* 1973-8. doi: 10.4161/psb.6.12.18053
40. Braun U., Cook R.T.A. (2012): Taxonomic manual of the *Erysiphales* (powdery mildews). CBS-KNAW Fungal Biodiversity Centre, Utrecht, The Netherlands. 707 p.
41. Braun, U., Cook, R. T. A., Inman, A. J., H.-D. Shin (2002): The taxonomy of the powdery mildew fungi (*pp.* 13-54). In Bélanger, R., Dik, A. J. & Bushnell, W. R. (Eds.): *The powdery mildews: a comprehensive treatise*. APS Press, USA, St. Paul.
42. Bruce, T. J., Wadhams, L. J., Woodcock, C.M. (2005): Insect host location: A volatile situation. Trends Plant Sci. 10, *pp.* 269–274. doi: 10.1016/j.tplants.2005.04.003
43. Brückner, A., Schuster, R., Smit, T., Pollierer, M.M., Schäffler, I., Heethoff, M. (2018): Track the snack – olfactory cues shape foraging behaviour of decomposing soil mites (Oribatida). *Pedobiol*. 66, *pp.*74–80. doi: 10.1016/j.pedobi.2017.10.004
44. Brundrett, M. C (2002): Coevolution of roots and mycorrhizas of land plants. *New Phytologist*, 154(2), *pp.* 275-304. doi: 10.1046/j.1469-8137.2002.00397.x
45. Burger, B. V., Munro, Z. M., Visser, J. H. (1988): Determination of plant volatiles 1: analysis of the insect-attracting allomone of the parasitic plant *Hydnora africana* using Grob-Habich activated charcoal traps. *J. High Resol. Chromatogr.*, 11 *pp.* 496-499. doi:10.1002/jhrc.1240110613
46. Buttery, R.G., Ling, L.C., Wellso, S.G. (1982): Oat leaf volatiles: Possible insect attractants. *J. Agric. Food Chem.* 30, *pp.*791–792. doi: 10.1021/jf00112a045
47. Buttery, R.G., Xu, C., Ling, L.C. (1985): Volatile components of wheat leaves (and stems): Possible insect attractants. *J. Agric. Food Chem.* 33, *pp.*115–117. doi: 10.1021/jf00061a033
48. Camarena-Pozos, D. A., Flores-Núñez, V. M., López, M. G., López-Bucio, J., Partida-Martínez, L. P. (2019): Smells from the desert: Microbial volatiles that affect plant growth and development of native and non-native plant species. *Plant Cell Environ.* 42 (4), *pp.* 1368–1380. doi: 10.1111/pce.13476

49. Cao, X.R., Duan, X.Y., Zhou, Y.L., Luo, Y. (2012): Dynamics in concentrations of *Blumeria graminis* f. sp. *tritici* conidia and its relationship to local weather conditions and disease index in wheat. *Eur. J. Plant Pathol.* 132, *pp.* 525–535. doi: 10.1007/s10658-011-9898-8
50. Cao, X.R., Yao, D.R., Zhou, Y.L., West, J.S., Xu, X.M., Luo, Y., et al. (2016): Detection and quantification of airborne inoculum of *Blumeria graminis* f. sp. *tritici* using quantitative PCR. *Eur. J. Plant Pathol*. 146, *pp.*225–229. doi: 10.1007/s10658-016-0908-8
51. Casarrubia, S., Sapienza, S., Fritz, H., Daghino, S., Rosenkranz, M., Schnitzler, J. P., et al. (2016): Ecologically different fungi affect arabidopsis development: Contribution of soluble and volatile compounds. *PloS One* 11 (12), e0168236. doi: 10.1371/journal.pone.0168236
52. Chen, Y., Bonkowski, M., Shen, Y., Griffiths, B. S., Jiang, Y., Wang, X., et al. (2020): Root ethylene mediates rhizosphere microbial community reconstruction when chemically detecting cyanide produced by neighbouring plants. *Microbiome* 8, 4. doi: 10.1186/s40168-019-0775-6
53. Chitarra, G.S., Abee, T., Rombouts, F.M., Posthumus, M.A., Dijksterhuis, J. (2004): Germination of *Penicillium paneum conidia* is regulated by 1-octen-3-ol, a volatile self-inhibitor. *Appl. Environ. Microbiol*. 70, *pp.* 2823–2829. doi: 10.1128/aem.70.5.2823-2829.2004
54. Choi, J., Summers, W., Paszkowski, U. (2018): Mechanisms underlying establishment of arbuscular mycorrhizal symbioses. *Annual Review of Phytopathology*, 56, *pp.* 135-160. doi: 10.1146/annurev-phyto-080516-035521
55. Ciccioli, P., Brancaleoni, E., Frattoni, M., Maris, C. (2002): Sampling of atmospheric volatile organic compounds (VOCs) with sorbent tubes and their analysis by GC-MS. In Environmental Monitoring Handbook, F. R. Burden (Ed.). New York: McGraw-Hill Publisher, *pp.* 21.1-21.85.
56. Clavijo McCormick, A., Unsicker, S. B., Gershenzon, J. (2012): The specificity of herbivore-induced plant volatiles in attracting herbivore enemies. *Trends Plant Sci.* 17, *pp.*303–310. doi: 10.1016/j.tplants.2012.03.012
57. Colquhoun, T.A., Schwieterman, M.L., Gilbert, J.L., Jaworski, E.A., Langer, K.M., Jones, C.R., Rushing, G.V., Hunter, T.M., Olmstead, J., Clark, D.G. and Folta, K.M. (2013): Light modulation of volatile organic compounds from petunia flowers and select fruits. *Postharvest Biology and Technology*, 86: *pp.* 37–44.
58. Conchou, L., Anderson, P., Birgersson, G. (2017): Host Plant Species Differentiation in a Polyphagous Moth: Olfaction is Enough. *J. Chem. Ecol.*, 43, *pp.* 794–805. doi: 10.1007/s10886-017-0876-2
59. Cordovez, V., Mommer, L., Moisan, K., Lucas-Barbosa, D., Pierik, R., Mumm, R., et al. (2017): Plant phenotypic and transcriptional changes induced by volatiles from the fungal root pathogen Rhizoctonia solani. *Front. Plant Sci.* 8. doi: 10.3389/fpls.2017.01262
60. Cordovez, V., Schop, S., Hordijk, K., de Boulois, H. D., Coppens, F., Hanssen, I., et al. (2018): Priming of plant growth promotion by volatiles of root-associated microbacterium spp. *Appl. Environ. Microbiol.* 84, e01865-18. doi: 10.1128/AEM.01865-18
61. Cork, A., Park, K.C. (1996): Identification of electrophysiologically-active compounds for the malaria mosquito, *Anopheles gambiae*, in human sweat extracts. *Med. Vet. Entomol*. 10, *pp.* 269–276. doi: 10.1111/j.1365-2915.1996.tb00742.x.
62. Crespo, E., Hordijk, C. A., De Graaf, R. M., Samudrala, D., Cristescu, S. M., Harren, F. J. M. and Van Dam, N. M. (2012): On-line detection of root-induced volatiles in *Brassica nigra* plants infested with *Delia radicum* L. root fly larvae. *Phytochemistry*, 84: *pp.* 68–77. doi: 10.1016/j.phytochem.2012.08.013
63. Cruz, A.F., Hamel, C., Yang, C., Matsuhara, T., Gan, Y., Singh, A.K., et al. (2012): Phytochemicals to suppress *Fusarium* head blight in wheat–chickpea rotation. *Phytochemistry* 78, *pp.* 72–80. doi: 10.1016/j.phytochem.2012.03.003.

64. D'Alessandro, M., Erb, M., Ton, J., Brandenburg, A., Karlen, D., Zopfi, J. (2014): Volatiles produced by soil-borne endophytic bacteria increase plant pathogen resistance and affect tritrophic interactions. *Plant Cell Environ*. 37, *pp.* 813–826. doi: 10.1111/pce.12220
65. Daamen, R.A. (1986): Measures of disease intensity in powdery mildew (*Erysiphe graminis*) of winter wheat. 1. Errors in estimating pustule number. *Neth. J. Plant Pathol.* 92, *pp.*197–206. doi: 10.1007/BF01977686.
66. D'Alessandro, M., Turlings, T. C. (2005): *In situ* modification of herbivore-induced plant odors: a novel approach to study the attractiveness of volatile organic compounds to parasitic wasps. *Chemical Senses*, 30(9), 739-753. doi: 10.1093/chemse/bji066
67. Danner, H., Samudrala, D., Cristescu, S. M., Van Dam, N. M. (2012): Tracing hidden herbivores: time-resolved non-invasive analysis of belowground volatiles by proton-transfer-reaction mass spectrometry (PTR-MS). *J. Chem. Ecol.* 38, *pp.* 785–794. doi: 10.1007/s10886-012-0129-3
68. Darriet P, Pons M, Henry R, Dumont O, Findeling V, Cartolaro P, Calonnec A, Dubourdieu D. (2002): Impact odorants contributing to the fungus type aroma from grape berries contaminated by powdery mildew (*Uncinula necator*); incidence of enzymatic activities of the yeast *Saccharomyces cerevisiae*. *J Agric Food Chem.* 50(11) *pp.* 3277-82. doi: 10.1021/jf011527d.
69. Das, A., Lee, S. H., Hyun, T. K., Kim, S. W., Kim, J. Y. (2012): Plant volatiles as method of communication. *Plant Biotechnol. Rep*. 7, 9–26. doi: 10.1007/s11816-012-0236-1
70. De Moraes, C. M., Mescher, M. C., and Tumlinson, J. H. (2001): Caterpillar-induced nocturnal plant volatiles repel conspecific females. *Nature*, 410 *pp.* 577–580. doi: 10.1038/35069058
71. Delaney, K.J., Wawrzyniak, M., Lemańczyk, G., Wrzesińska, D., Piesik, D. (2013): Synthetic cis-jasmone exposure induces wheat and barley volatiles that repel the pest cereal leaf beetle, *Oulema melanopus* L. J. *Chem. Ecol.* 9, *pp.* 620–629. doi:10.1007/s10886-013-0281-4.
72. Delory, B. M., Delaplace, P., du Jardin, P., Fauconnier, M. L. (2016a): Barley (*Hordeum distichon* l.) roots synthesise volatile aldehydes with a strong age-dependent pattern and release (E)-non-2-enal and (E, z)-nona-2,6-dienal after mechanical injury. *Plant Physiol. Biochem*. 104, *pp.* 134–145. doi: 10.1016/j.plaphy.2016.03.028
73. Delory, B. M., Delaplace, P., Fauconnier, M. L., du Jardin, P. (2016b): Root-emitted volatile organic compounds: can they mediate belowground plant-plant interactions? *Plant Soil* 402, *pp.* 1–26. doi: 10.1007/s11104-016-2823-3
74. Dewulf, J., and Van Langenhove, H. (2002): Analysis of volatile organic compounds using gas chromatography. *Trends in Analytical Chemistry*, 21, *pp.* 637–646.
75. Di, X., Shellie, R. A., Marriott, P. J., Huie, C. W. (2004): Application of headspace solid-phase microextraction (HS-SPME) and comprehensive two-dimensional gas chromatography (GC × GC) for the chemical profiling of volatile oils in complex herbal mixtures. *J. Sep. Sci.*, 27, *pp.* 451–458. doi: 10.1002/jssc.200301642
76. Dicke, M., Baldwin, I. T. (2010): The evolutionary context for herbivore-induced plant volatiles: beyond the 'cry for help'. *Trends in Plant Science*, 15(3), *pp.*167-175. doi: 10.1016/j.tplants.2009.12.002
77. Dicke, M., Hilker, M. (2003): Induced plant defences: from molecular biology to evolutionary ecology. *Basic Appl. Ecol.*, 4, *pp.* 3–14. doi: 10.1078/1439-1791-00129
78. Dicke, M., Loreto, F. (2010): Induced plant volatiles: from genes to climate change. *Trends Plant Sci.*, vol. 15, no. 3, *pp.* 115–117. doi: 10.1016/j.tplants.2010.01.007
79. Dicke, M., Sabelis, M. W., Takabayashi, J., Bruin, J., Posthumus, M. A. (1990): Plant strategies of manipulating predator-prey interactions through allelochemicals: prospects for application in pest control. *Journal of Chemical Ecology*, 16(11), *pp.* 3091-3118. doi: 10.1007/BF00979614

80. Ditengou, F. A., Müller, A., Rosenkranz, M., Felten, J., Lasok, H., van Doorn, M. M., et al. (2015): Volatile signalling by sesquiterpenes from ectomycorrhizal fungi reprogrammes root architecture. *Nat. Commun*. 6 (1), *pp.* 6279. doi: 10.1038/ncomms7279
81. Dixon, R. A., Achnine, L., Kota, P., Liu, C. J., Reddy, M. S. S., Wang, L. (2009): The phenylpropanoid pathway and plant defence—a genomics perspective. *Molecular Plant Pathology*, 3(5), *pp.* 371-390.
82. Donath, J., Boland, W. (1995): Biosynthesis of acyclic homoterpenes enzyme selectivity and absolute configuration of nerolidol precursor. *Phytochemistry*, 39(4), *pp.*785–790.
83. Dowarah, B., Gill, S. S., Agarwala, N. (2021): Arbuscular mycorrhizal fungi in conferring tolerance to biotic stresses in plants. *J. Plant Growth Regul.* 110, *pp.* 999. doi: 10.1007/s00344-021-10392-5
84. Dreher, D., Baldermann, S., Schreiner, M., Hause, B. (2019): An arbuscular mycorrhizal fungus and a root pathogen induce different volatiles emitted by *Medicago truncatula* roots. *J. Advanced Res.* 19, *pp.*85–90. doi: 10.1016/j.jare.2019.03.002
85. Duc, N.H., Vo, H.T. N., Cong, v.D., Hamow, K.Á., Le, K.H., Posta, K. (2022): Volatile organic compounds shape belowground plant–fungi interactions. *Frontiers in Plant Science*, Vol 13. doi: 10.3389/fpls.2022.1046685
86. Dudareva, N., Klempien, A., Muhlemann, J.K., Kaplan, I., (2013): Biosynthesis, function and metabolic engineering of plant volatile organic compounds. *New Phytol.* 198, *pp.*16–32. doi: 10.1111/nph.12145.
87. Dudareva, N., Negre, F., Nagegowda, D. A., Orlova, I. (2006): Plant volatiles: recent advances and future perspectives. *Crit. Rev. Plant Sci* 25, *pp.* 417–440. doi: 10.1080/07352680600899973
88. Dudareva, N., Pichersky, E., & Gershenzon, J. (2004): Biochemistry of Plant Volatiles. Plant Physiology, 135(4), *pp.*1893–1902. doi: 10.1104/pp.104.049981.1.
89. Dudareva, N., Pichersky, E., Gershenzon, J. (2004): Biochemistry of plant volatiles. Plant Physiol. 135, *pp.*1893–1902. doi: 10.1104/pp.104.049981
90. Eastwood, D.C., Herman, B., Noble, R., Dobrovin-Pennington, A., Sreenivasaprasad, S., Burton, K.S. (2013): Environmental regulation of reproductive phase change in *Agaricus bisporus* by 1-octen-3-ol, temperature and CO2. *Fungal Genet. Biol.* 55, *pp.*54–66. doi: 10.1016/j.fgb.2013.01.001.
91. Ebel, R. C., Mattheis, J. P., Buchanan, D. A. (1995): Drought stress of apple trees alters leaf emissions of volatile compounds. *Physiol. Plant.,* 93, *pp.*709–712.
92. Effah, E., Holopainen, J. K., McCormick, A. C. (2019): Potential roles of volatile organic compounds in plant competition. *Perspect. Plant Ecol. Evol. Syst.* 38, *pp.*58–63. doi: 10.1016/j.ppees.2019.04.003
93. Effah, E., Svendsen, L., Barrett, D. P., McCormick, A. C. (2022): Exploring plant volatile-mediated interactions between native and introduced plants and insects. *Sci Rep* 12, 15450. doi: 10.1038/s41598-022-18479-z
94. Effmert, U., Kalderas, J., Warnke, R., Piechulla, B. (2012): Volatile mediated interactions between bacteria and fungi in the soil. *J. Chem. Ecol.* 38, *pp.*665–703. doi: 10.1007/s10886-012-0135-5
95. Elad, Y., Pertot, I., Cotes Prado, A. M. Stewart, A. (2016): Plant Hosts of *Botrytis spp.* In S. Fillinger, Y. Elad (Eds.), *Botrytis* -- the *Fungus, the Pathogen and its Management in Agricultural Systems* (*pp.*413–486).
96. Engelberth, J., Alborn, H. T., Schmelz, E. A., Tumlinson, J. H. (2004): Airborne signals prime plants against insect herbivore attack. *Proc. Natl. Acad. Sci.*, vol. 101, no. 6, *pp.* 1781–1785.
97. Fang, Y., Ramasamy, R. P. (2015): Current and Prospective Methods for Plant Disease Detection. *Biosensors*, 5(3), *pp.* 537–561. doi: 10.3390/bios5030537
98. FAO, 2020. FAOSTAT statistical database. FAO, Italy: Rome. http://www.fao.org/faostat/en/.

99. Feng, J., Wang, F., Liu, G., Greenshields, D., Shen, W., Kaminskyj, S. et al. (2009): Analysis of a *Blumeria graminis*-secreted lipase reveals the importance of host epicuticular wax components for fungal adhesion and development. *Mol. Plant–Microbe Interact.* 22, *pp.*1601–1610. doi: 10.1094/MPMI-22-12-1601
100. Fiers, M., Lognay, G., Fauconnier, M. L., Jijakli, M. H. (2013): Volatile compound-mediated interactions between barley and pathogenic fungi in the soil. *PloS One* 8 (6), e66805. doi: 10.1371/journal.pone.0066805
101. Fincheira, P., Quiroz, A. (2018): Microbial volatiles as plant growth inducers. *Microbiol. Res.* 208, *pp.* 63–75. doi: 10.1016/j.micres.2018.01.002
102. Fischer, G., Schwalbe, R., Möller, M., Ostrowski, R., Dott, W. (1999): Species-specific production of microbial volatile organic compounds (MVOC) by airborne fungi from a compost facility. *Chemosphere* 39, *pp.* 779–810. doi: 10.1016/s0045-6535(99)00015-6.
103. Fischer, G.J., Keller, N.P. (2016): Production of cross-kingdom oxylipins by pathogenic fungi: An update on their role in development and pathogenicity. *J. Microbiol.* 54, *pp.* 254–264. doi: 10.1007/s12275-016-5620-z
104. Fischer, K.B., Gold, C.M., Harvey, R., Petrucci, A.N., Petrucci, G.A. (2020): The ozonolysis chemistry and phase behavior of 1-octen-3-ol derived secondary organic aerosol. *ACS Earth Space Chem.* 4, *pp.* 1298–1308. doi: 10.1021/acsearthspacechem.0c00092.
105. Flamini, G., Cioni, P. L., Morielli, I., Macchia, M., Ceccarini, L. (2002): Main Agronomic − Productive Characteristics of Two Ecotypes of *Rosmarinus officinalis L*. and Chemical Composition of Their Essential Oils. *J. Agric. Food Chem.*, 50, 3512–3517. doi: 10.1021/jf011138j
106. Frantzeskakis, L., Kracher, B., Kusch, S., Yoshikawa-Maekawa, M., Bauer, S., Pedersen, C., et al. (2018): Signatures of host specialization and a recent transposable element burst in the dynamic one-speed genome of the fungal barley powdery mildew pathogen. *BMC Genomics* 22, *pp.* 381. doi: 10.1186/s12864-018-4750-6.
107. Frauenstein, K., Meyer, H., Wolfram, H. (1979): Pathotypen von *Erysiphe graminis* DC.f.sp. *tritici Marchal* und *E. graminis* DC.f.sp. *hordei Marchal* in Europa. *Arch. Phytopathol. Plant Protect.* 15, *pp.* 391–399. doi: 10.1080/03235407909437497.
108. Gao, H., Niu, J., Li, S. (2018): Impacts of wheat powdery mildew on grain yield & quality and its prevention and control methods. *Am. J. Agricult. Forest.* 6, *pp.* 141–147. 10.11648/j.ajaf.20180605.14.
109. Gershenzon J, & Dudareva N. (2007): The function of terpene natural products in the natural world. *Nat Chem Biol.*;3(7) *pp.* 408-14. doi: 10.1038/nchembio.2007.5.
110. Gershenzon, J., Mcconkey, M. E., Croteau, R. B. (2000): Regulation of Monoterpene Accumulation in Leaves of Peppermint. Plant Physiol., 122, *pp.* 205–213. doi: 10.1104/pp.122.1.205
111. Gfeller, A., Laloux, M., Barsics, F., Kati, D.E., Haubruge E., Jardin, P., et al. (2013): Characterization of volatile organic compounds emitted by barley (*Hordeum vulgare L.*) roots and their attractiveness to wireworms. *J. Chem. Ecol.* 39, *pp.* 1129–1139. doi: 10.1007/s10886-013-0302-3.
112. Gfeller, V., Huber, M., Förster, C., Huang, W., Köllner, T. G., Erb., M. (2019): Root volatiles in plant–plant interactions I: High root sesquiterpene release is associated with increased germination and growth of plant neighbours. *Plant Cell Environ.* 42, *pp.* 1950–1963. doi: 10.1111/pce.13532
113. Gomez, G.L., Loubet, B., Lafouge, F., Ciuraru, R., Buysse, P., Durand, B., et al. (2019): Comparative study of biogenic volatile organic compounds fluxes by wheat, maize and rapeseed with dynamic chambers over a short period in northern France. *Atmos. Environ.* 214, 116855. doi: 10.1016/j.atmosenv.2019.116855.
114. Gondor, O.K., Pál, M., Janda, T., Szalai, G. (2022): The role of methyl salicylate in plant growth under stress conditions, Journal of Plant Physiology, Volume 277, 2022, 153809, ISSN 0176-1617, doi: 10.1016/j.jplph.2022.153809.

115. Griffey C.A., Das M.K., Stromberg (1993): Effectiveness of adult-plant resistance in reducing grain yield loss to powdery mildew in winter wheat. *Plant Dis.* 77 *pp.* 618–622.
116. Grira, A., Amarandei, C., Romanias, M.N., El Dib, G., Canosa, A., Arsene, C., et al. (2020): Kinetic measurements of Cl atom reactions with C5–C8 unsaturated alcohols. Atmosphere 11, *pp.* 256. doi: 10.3390/atmos11030256.
117. Gu, Y., Chu, B., Wang, C., Li, L., Zhou, Y., Luo, Y., Ma, Z. (2020): Spore concentrations of *Blumeria graminis* f. sp. *tritici* in relation to weather factors and disease development in Gansu, China. *Can. J. Plant Pathol.* 42, 52–61. *pp.* 10.1080/07060661.2019.1630011.
118. Guenther, A. (2013): Biological and chemical diversity of biogenic volatile organic emissions into the atmosphere. Intl. Schol. Res. Notices 2013, 786290. https://doi.org/10.1155/2013/786290.
119. Guinness World Records, 2020. Highest wheat yield. Available at https://www.guinnessworldrecords.com/world-records/highest-wheat-yield.Accessed 28 October 2020.
120. Gulati, S., Ballhausen, M. B., Kulkarni, P., Grosch, R., Garbeva, P. (2020): A non-invasive soil-based setup to study tomato root volatiles released by healthy and infected roots. *Sci. Rep.* 10, *pp.* 12704. doi: 10.1038/s41598-020-69468-z
121. Gutiérrez-Santa, A. A., Carrillo-Cerda, H. A., Rodriguez-Campos, J., Velázquez-Fernández, J. B., Patrón-Soberano, O. A., Contreras-Ramos, S. M. (2020): Dynamics of volatilomes emitted during cross-talking of plantgrowth-promoting bacteria and the phytopathogen, *Fusarium solani*. *World J. Microbiol. Biotechnol.* 36, *pp.* 152. doi: 10.1007/s11274-020-02928-w
122. Hacquard, S., Kracher, B., Maekawa, T., Vernaldi, S., Schulze-Lefert, P., Ver Loren van Themaat, E., (2013): Mosaic genome structure of the barley powdery mildew pathogen and conservation of transcriptional programs in divergent hosts. *Proc. Natl. Acad. Sci. USA* 110, *pp.* 2219–2228. Description: "RNA-seq during early pathogenesis (6-24 h post inoculation: conidiospore germination,haustorium formation)"
123. Halitschke, R., Keßler, A., Kahl, J., Lorenz, A., Baldwin, I. T. (2000): Ecophysiological comparison of direct and indirect defenses in *Nicotiana attenuata*. *Oecologia*, 124, *pp.* 408–417.
124. Hall, A.A., Zhang, Z., Gurr, S.J., Carver, T.L.W., (2000): Powdery mildews. In: Lederberg, J. (Ed.), Encyclopedia of Microbiology, Vol. 3, 2nd edn, Academic Press, USA: San Diego, pp. 801–808.
125. Hall, D.R., Beevor, P.S., Cork, A., Nesbitt, B.F., Vale, G.A. (1984): 1-Octen-3-ol: a potent olfactory stimulant and attractant for tsetse isolated from cattle odours. *Insect Sci. Applic.* 5, 335–339. 10.1017/S1742758400008626.
126. Hamow, K. Á., Ambrózy, Z., Puskás, K., Majláth, I., Cséplő, M., Mátyus, R., et al. (2021): Emission of novel volatile biomarkers for wheat powdery mildew. *Sci. Total Environ*. 781, 146767. doi: 10.1016/j.scitotenv.2021.146767
127. Handley, A. J., Adlard, E. R. (2001): Gas Chromatographic Techniques and Applications. Boca Raton, FL: CRC Press. *pp.* .1-337
128. Hartikainen, K., Kivimäenpää, M., Nerg, A.-M., Holopainen, T. (2012): Significance of leaf structure and emission of volatile organic compounds in ozone tolerance of oat and wheat. *Botany* 90, *pp.* 121–135. doi: 10.1139/b11-090.
129. Herrero-Garcia, E., Garzia, A., Cordobés, S., Espeso, E. A., Ugalde, U. (2011): 8-Carbon oxylipins inhibit germination and growth, and stimulate aerial conidiation in *Aspergillus nidulans*. *Fungal Biol.* 115, 4-5. *pp.* 393–400. doi: 10.1016/j.funbio.2011.02.005
130. Hiltpold, I., Erb, M., Robert, C. A. M., Turlings, T. C. J. (2011): Systemic root signalling in a belowground, volatile-mediated tritrophic interaction. *Plant Cell Environ.* 34, *pp.* 1267–1275. doi: 10.1111/j.1365-3040.2011.02327.x
131. Hoffmann, T., et al. (1997): Formation of Organic Aerosols from the Oxidation of Biogenic Hydrocarbons. *Journal of Atmospheric Chemistry* 26, *pp.* 189–222.

132. Holzinger, R., Rottenberger, S., Crutzen, P. J., Kesselmeier, J. (2000): Emissions of volatile organic compounds from *Quercus ilex* L. measured by Proton Transfer Reaction Mass Spectrometry under different environmental conditions. *J. Geophys. Res.* 105, 573–*pp.* 579.
133. Honkanen, E., Moisio, T., (1963): On the occurrence of oct-1-en-3-ol in clover plants. *Acta Chem. Scand.* 17, *pp.* 858.
134. Ho-Plágaro, T., García-Garrido, J. M. (2022a): Molecular regulation of arbuscular mycorrhizal symbiosis. *Int. J. Mol. Sci.* 23, *pp.* 5960. doi: 10.3390/ijms23115960
135. Hossain, M. A., Nakano, Y., Asada, K., Nishihara, H. (2011): Molecular characterization of the glutathione-dependent dehydroascorbate reductase gene in *Vigna aconitifolia* (moth bean*). Journal of Plant Physiology,* 168(16), *pp.* 1917-1926.
136. Hungarian Central Statistical Office (KSH); https://www.ksh.hu/stadat_files/mez/hu/mez0071.html.
137. Isman, M. B. (2006): Botanical insecticides, deterrents, and repellents in modern agriculture and an increasingly regulated world. *Annual Review of Entomology* 51, *pp.* 45-66. doi: 10.1146/annurev.ento.51.110104.151146
138. Jakobsen, H. B. (1997): The preisolation phase of in situ headspace analysis: methods and perspectives. *Modern Methods of Plant Analysis* 19, *pp.* 1–22. Springer.
139. Jalali, F., Zafari, D., Salari, H. (2017): Volatile organic compounds of some *Trichoderma* spp. increase growth and induce salt tolerance in *Arabidopsis thaliana. Fungal Ecol.* 29, *pp.* 67–75. doi: 10.1016/j.funeco.2017.06.007
140. Jansen, R. M. C., et al. (2009): Induced plant volatiles allow sensitive monitoring of plant health status in greenhouses. *Plant Signaling & Behavior* 4(9), *pp.* 824–829. doi: 10.4161/psb.4.9.9431
141. Jansen, R. M. C., Wildt, J., Hofstee, J. W., Bouwmeester, H. J., Van Henten, E. J. (2010a): Plant volatiles: useful signals to monitor crop health status in greenhouses. *Plant Communication from an Ecological Perspective, pp.* 229–247. Springer.
142. Jansen, R. M. C., Wildt, J., Kappers, I. F., Bouwmeester, H. J., Hofstee, J. W., Van Henten, E. J. (2011): Detection of Diseased Plants by Analysis of Volatile Organic Compound Emission. *Annu. Rev. Phytopathol.* 49, *pp.* 157–174. doi: 10.1146/annurev-phyto-072910-095227
143. Jansen, R. M. C., Hofstee, J. W., Wildt, J., Vanthoor, B. H. E., Verstappen, F. W. A., Takayama, K., Bouwmeester, H. J., Van Henten, E. J. (2010b): Health monitoring of plants by their emitted volatiles: A model to predict the effect of *Botrytis cinerea* on the concentration of volatiles in a large-scale greenhouse. *Biosystems Engineering* 106(1), *pp.* 37–47. doi: 10.1016/j.biosystemseng.2010.01.009
144. Jelen, H. H., Krawczyk, J., Larsen, T. O., Jarosz, A., Gołebniak, B. (2005): Main compounds responsible for off-odour of strawberries infected by *Phytophthora cactorum*. *Letters in Applied Microbiology* 40(4), *pp.* 255–259. doi: 10.1111/j.1472-765X.2005.01668.x.
145. Ju, Y., Yue, X., Zhao, X., Zhao, H., Fang, Y. (2018): Physiological, micro-morphological and metabolomic analysis of grapevine (*Vitis vinifera* l.) leaf of plants under water stress. *Plant Physiol. Biochem.* 130, *pp.* 501–510. doi: 10.1016/j.plaphy.2018.07.036
146. Junker, R. R., Tholl, D. (2013): Volatile organic compound mediated interactions at the plant-microbe interface. *J. Chem. Ecol.* 39, *pp.* 810–825. doi: 10.1007/s10886-013-0325-9
147. Jürgens, A., Dötterl, S. (2004): Chemical Composition of Anther Volatiles in Ranunculaceae: Genera - Specific Profiles in *Anemone* , *Aquilegia*, *Caltha* , *Pulsatilla* , *Ranunculus,* and *Trollus* Species. *Am. J. Bot.* 91(12), 1969–1980.
148. Jüttner, F., (1990): Monoterpenes and microbial metabolites in the soil. *Environ. Poll.* 68, *pp.* 377–382. doi: 10.1016/0269-7491(90)90039-F.
149. Kaddes, A., Fauconnier, M. L., Sassi, K., Nasraoui, B., Jijakli, M. H. (2019a): Endophytic fungal volatile compounds as solution for sustainable agriculture. *Molecules* 24(6), *pp.* 1065. doi: 10.3390/molecules24061065

150. Kaddes, A., Fauconnier, M. L., Sassi, K., Nasraoui, B., Jijakli, M. H. (2019b): Antifungal properties of two volatile organic compounds on barley pathogens and introduction to their mechanism of action. *Int. J. Environ. Res. Public Health* 16, *pp.* 2866. doi: 10.3390/ijerph16162866
151. Kaiser, R. (1991): New Volatile Constituents of the Flower Concrete of *Michelia champaca* L. *Journal of Essential Oil Research* 3, *pp.* 129–146. doi: 10.1080/10412905.1991.9700493.
152. Kalalian, C., Abis, L., Depoorter, A., Lunardelli, B., Perrier, S., George, C. (2020): Influence of indoor chemistry on the emission of mVOCs from *Aspergillus niger* molds. *Sci. Total Environ.* 741, *pp.* 140148. doi: 10.1016/j.scitotenv.2020.140148.
153. Kaminski, E., Stawicki, S., Wasowicz, E., (1974): Volatile flavor compounds produced by molds of *Aspergillus, Penicillium,* and *Fungi imperfecti*. *Appl. Microbiol.* 27, *pp.* 1001–1004. doi: 10.1128/AM.27.6.1001-1004.1974.
154. Kasal-Slavik, T., Eschweiler, J., Kleist, E., Mumm, R., Goldbach, H. E., Schouten, A., Wildt, J. (2017): Early biotic stress detection in tomato (*Solanum lycopersicum*) by BVOC emissions. *Phytochemistry* 144, *pp.* 180–188. doi: 10.1016/j.phytochem.2017.09.006
155. KEGG (Kyoto Encyclopedia of Genes and Genomes) https://www.genome.jp/kegg/
156. Kegge, W., Pierik, R. (2010): Biogenic volatile organic compounds and plant competition. *Trends Plant Sci.* 15, *pp.* 126–132. doi: 10.1016/j.tplants.2009.11.007
157. Kermasha, S., Perraud, X., Bisakowski, B., Husson, F. (2002): Production of flavor compounds by hydroperoxide lyase from enzymatic extracts of *Penicillium* sp. *J. Mol. Catal. B: Enz.* 19–20, *pp.* 479–487. doi: 10.1016/S1381-1177(02)00202-3.
158. Kesselmeier, J., Staudt, M. (1999): Biogenic Volatile Organic Compounds (VOC): An Overview on Emission, Physiology, and Ecology. Journal of Atmospheric Chemistry 33, *pp.* 23–88.
159. Kessler, A., Baldwin, I. T. (2001): Defensive Function of Herbivore-Induced Plant Volatile Emissions. *Nature* 291, *pp.* 2141–2144. doi: 10.1126/science.291.5511.2141
160. Khater, M., De Escosura-Muñiz, A., Merkoçi, A. (2017): Biosensors for plant pathogen detection. *Biosensors and Bioelectronics* 93, *pp.* 72–86. doi: 10.1016/j.bios.2016.09.091.
161. Kihara, H. (1924): Cytologische und genetische Studien bei wichtigen Getreidearten mit besonderer Rücksicht auf das Verhalten der Chromosomen und die Sterilität in den Bastarden. *Memoirs of the College of Science, Kyoto Imperial University, Series B* 1, *pp.* 1-200.
162. Kihika, R., Murungi, L. K., Coyne, D., Ng'ang'a, M., Hassanali, A., Teal, P. E. A., et al. (2017): Parasitic nematode *Meloidogyne incognita* interactions with different capsicum annum cultivars reveal the chemical constituents modulating root herbivory. *Sci. Rep.* 7 (1), 2903. doi: 10.1038/s41598-017-02379-8
163. Kindlovits, S., Sárosi, Sz., Inotai, K., Petrović, G., Stojanović, G., Németh, É. (2018): Phytochemical characteristics of root volatiles and extracts of achillea collina becker genotypes. *J. Essential Oil Res.* 30(5), *pp.* 330–340. doi: 10.1080/10412905.2018.1470581
164. Kishimoto, K., Matsui, K., Ozawa, R., Takabayashi, J. (2007): Volatile 1-octen-3-ol induces a defensive response in *Arabidopsis thaliana. Journal of General Plant Pathology* 73, *pp.* 35-37. doi: 10.1007/s10327-006-0314-8
165. Kiss, T. (2016): A Kenyérbúza (*Triticum Aestivum* L.) Környezeti Adaptációját Meghatározó Genetikai Komponensek Vizsgálata, Doctoral (PhD thesis) dissertation – *Szent István Egyetem (renamed Hungarian University of Agricultural and Life Sciences)*
166. Kline, D. L., Allan, S. A., Bernier, U. R., Welch, C. H. (2007): Evaluation of the enantiomers of 1-octen-3-ol and 1-octyn-3-ol as attractants for mosquitoes associated with a freshwater swamp in Florida, U.S.A. *Med. Vet. Entomol.* 21, *pp.* 323–331. doi: 10.1111/j.1365-2915.2007.00697.x.
167. Knudsen, J. T., Eriksson, R., Gershenzon, J., Ståhl, B. (2006): Diversity and distribution of floral scent. *The Botanical Review* **72**, 1. doi: 10.1663/0006-8101(2006)72[1:DADOFS]2.0.CO;2

168. Koch, T., Krumm, T., Jung, V., Boland, W. (1999): Differential Induction of Plant Volatile Biosynthesis in the Lima Bean by Early and Late Intermediates of the Octadecanoid-Signaling Pathway. *Plant Physiology* 121(1), *pp.* 153–162. doi: 10.1104/pp.121.1.153.
169. Köllner, T. G., Schnee, C., Gershenzon, J., Degenhardt, J. (2004): The sesquiterpene hydrocarbons of maize (Zea mays) form five groups with distinct developmental and organ-specific distributions. *Phytochemistry* 65(13), *pp.* 1895–1902. doi: 10.1016/j.phytochem.2004.05.021.
170. Komáromi, J. (2016): Lisztharmat-Rezisztenciatípusok és a Gazdagnövény–Kórokozó Kapcsolat Vizsgálata Búzában – Doctoral (PhD thesis) dissertation – *Szent István University (renamed Hungarian University of Agricultural and Life Sciences)*
171. König, G., Brunda, M., Puxbaum, H., Hewitt, C. N., Duckham, S. C., Rudolph, J. (1995): Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected Mid-European agricultural and natural plant species. *Atm. Env.* 29, *pp.* 861–874. doi: 10.1016/1352-2310(95)00026-U
172. Korpi, A., Järnberg, J., Pasanen, A.-L., (2009): Microbial volatile organic compounds. *Crit. Rev. Toxicol.* 39, *pp.* 139–193. doi: 10.1080/10408440802291497.
173. Korpi, A., Pasanen, A.-L., Pasanen, P. (1998): Volatile compounds originating from mixed microbial cultures on building materials under various humidity conditions. *Appl. Environ. Microbiol.* 64, *pp.* 2914–2919. doi: 10.1128/AEM.64.8.2914-2919.1998.
174. Kováts, E. (1958): Gas-chromatographische Charakterisierung organischer Verbindungen. Teil 1: Retentionsindices aliphatischer Halogenide, Alkohole, Aldehyde und Ketone. *Helv. Chim. Acta* 41, *pp.* 1915–1932. doi: 10.1002/hlca.19580410703.
175. Kreuzwieser, J., Kühnemann, F., Martis, A., Rennenberg, H., Urban, W. (2000): Diurnal pattern of acetaldehyde emission by flooded poplar trees. *Physiol. Plant.* 108(1), *pp.* 79–86. doi: 10.1034/j.1399-3054.2000.108001079.x
176. Lackus, N. D., Lackner, S., Gershenzon, J., Unsicker, S. B., Köllner, T. G. (2018): The occurrence and formation of monoterpenes in herbivore-damaged poplar roots. *Sci. Rep.* 8, *pp.* 17936. doi: 10.1038/s41598-018-36302-6
177. Landis, D. A., Wratten S. D., Gurr G. M. (2000): Habitat management to conserve natural enemies of arthropod pests in agriculture. *Annual Review of Entomology* 45(1), *pp.* 175-201. doi: 10.1146/annurev.ento.45.1.175.
178. Láng, L., Bedő, Z. (2006): A hazai búzanemesítés stratégiai jelentősége. *p.* 19-25 In: Dudits, D. (Ed.): A búza nemesbítésének tudománya: a funkcionális genomikától a vetőmagig. *Szeged: MTA Szegedi Biológiai Központ–Winter Fair, pp.* 334.
179. Langenheim, J. H. (1994): Higher plant terpenoids: A phytocentric overview of their ecological roles. *J. Chem. Ecol.* 20(6), *pp.* 1223–1280. doi: 10.1007/BF02059809.
180. Laothawornkitkul, J., Jansen, R. M. C., Smid, H. M., Bouwmeester, H. J., Müller, J., Van Bruggen, A. H. C. (2010): Volatile organic compounds as a diagnostic marker of late blight infected potato plants: A pilot study. *Crop Protection* 29(8), *pp.* 872–878.
181. Laothawornkitkul, J., Taylor, J. E., Paul, N. D., Hewitt, C. N. (2009): Biogenic volatile organic compounds in the Earth system. *New Phytologist* 183(1), *pp.* 27–51. doi: 10.1111/j.1469-8137.2009.02859.x
182. Large, E. C., Doling, D. A., (1962): The measurement of cereal mildew and its effect on yield. *Plant Pathol.* 11, *pp.* 47–57. doi: 10.1111/j.1365-3059.1962.tb00165.x.
183. Last, F. T., (1953): Some effects of temperature and nitrogen supply on wheat powdery mildew. *Ann. Appl. Biol.* 40, *pp.* 312–322. doi: 10.1111/j.1744-7348.1953.tb01085.x.
184. Laur, J., Ramakrishnan, G. B., Labbe, C., Lefebvre, F., Spanu, P. D., Belanger, R. R., (2018): Effectors involved in fungal–fungal interaction lead to a rare phenomenon of hyperbiotrophy in the tritrophic system biocontrol agent–powdery mildew–plant. *New Phytol.* 217, *pp.* 713–725. Description: RNA-seq during early pathogenesis (4-5 days post infection with *Blumeria graminis*)

185. Lê, S., Josse, J., Husson, F., (2008): FactoMineR: An R package for multivariate analysis. *J. Stat. Softw.* 25, *pp.* 1–18. doi: 10.18637/jss.v025.i01.
186. Lee, B., Farag, M. A., Park, H. B., Kloepper, J. W., Lee, S. H., Ryu, C. M. (2012): Induced resistance by a long-chain bacterial volatile: Elicitation of plant systemic defense by a C13 volatile produced by *Paenibacillus polymyxa. PloS One* 7, e48744. doi: 10.1371/journal.pone.0048744
187. Lee, S., Hung, R., Schink, A., Mauro, J., Bennett, J. W. (2014): *Arabidopsis thaliana* for testing the phytotoxicity of volatile organic compounds. *Plant Growth Regul.* 74, *pp.* 177–186. doi: 10.1007/s10725-014-9909-9
188. Lemfack, M. C., Gohlke, B. O., Toguem, S. M. T., Preissner, S., Piechulla, B., Preissner, R., (2018): mVOC 2.0: a database of microbial volatiles. *Nucleic Acids Res.* 46, *pp.* D1261–D1265. doi: 10.1093/nar/gkx1016.
189. Lev-Yadun, S., Gopher, A., Abbo, S. (2000): The cradle of agriculture. *Science* 288, *pp.* 1602-1603. doi: 10.1126/science.288.5471.1602
190. Li, J., Chen, B., Zhang, X., Hao, Z., Zhang, X., Zhu, Y. (2021): Arsenic transformation and volatilization by arbuscular mycorrhizal symbiosis under axenic conditions. *J. Hazard Mater.* 413, *pp.* 125390. doi: 10.1016/j.jhazmat.2021.125390
191. Li, W., Chen, Y., Tong, S., Guo, Y., Zhang, Y., Ge, M., (2018): Kinetic study of the gas-phase reaction of O3 with three unsaturated alcohols. *J. Environ. Sci.* 30, *pp.* 292–299. doi: 10.1016/j.jes.2018.04.009.
192. Li, Z., Paul, R., Tis, T.B., Saville, A.C., Hansel, J.C., Yu, T., et al. (2019): Non-invasive plant disease diagnostics enabled by smartphone-based fingerprinting of leaf volatiles. *Nat. Plants* 5, *pp.* 856–866. doi: 10.1038/s41477-019-0476-y.
193. Liang, P., Liu, S., Xu, F., Jiang, S., Yan, J., He, Q., et al. (2018): Powdery mildews are characterized by contracted carbohydrate metabolism and diverse effectors to adapt to obligate biotrophic lifestyle. *Front. Microbiol.* 9, 3160. doi: 10.3389/fmicb.2018.03160.
194. Linderman, R. G. (1988): Mycorrhizal interactions with the rhizosphere microflora – the mycorrhizosphere effect. *Phytopathology* 78, *pp.* 366–371.
195. Liu, X. M., Zhang, H. (2015): The effects of bacterial volatile emissions on plant abiotic stress tolerance. *Front. Plant Sci.* 6. doi: 10.3389/fpls.2015.00774
196. Llusià, J., Peñuelas, J. (2000): Emission of volatile organic compounds by apple trees under spider mite attack and attraction of predatory mites. *Experimental & Applied Acarology* 24(4), *pp.* 287-302.
197. Lockwood, G. B. (2001): Techniques for gas chromatography of volatile terpenoids from a range of matrices. *Journal of Chromatography A* 936, *pp.* 23–31. doi: 10.1016/s0021-9673(01)01151-7.
198. Loreto, F., Schnitzler, J. P., (2010): Abiotic stresses and induced BVOCs. *Trends in Plant Science* 15(3), *pp.* 154–166. doi: 10.1016/j.tplants.2009.12.006.
199. Loreto, F., Velikova, V. (2001): Isoprene Produced by Leaves Protects the Photosynthetic Apparatus against Ozone Damage, Quenches Ozone Products, and Reduces Lipid Peroxidation of Cellular Membranes. *Plant Physiology* 127, *pp.* 1781–1787. doi: 10.1104/pp.010497.
200. Loreto, F., Barta, C., Brilli, F., Nogues, I. (2006): On the induction of volatile organic compound emissions by plants as consequence of wounding or fluctuations of light and temperature. *Plant Cell Environment* 29(9), *pp.* 1820–1828. doi: 10.1111/j.1365-3040.2006.01561.x.
201. Loreto, F., Förster, A., Dürr, M., Csiky, O., Seufert, G. (1998): On the monoterpene emission under heat stress and on the increased thermotolerance of leaves of *Quercus ilex* L. fumigated with selected monoterpenes. *Plant, Cell & Environment* 21, *pp.* 101–107. doi: 10.1046/j.1365-3040.1998.00268.x

202. Loreto, F., Mannozzi, M., Maris, C., Nascetti, P., Ferranti, F., Pasqualini, S. (2001): Ozone Quenching Properties of Isoprene and Its Antioxidant Role in Leaves. *Plant Physiology* 126, *pp.* 993–1000. doi: 10.1104/pp.126.3.993
203. Maffei, M. E., Gertsch, J., Appendino, G. (2011): Plant volatiles: production, function and pharmacology. *Nat. Prod. Rep.* 28, *pp.* 1359–1380. doi: 10.1039/c1np00021g
204. Magan N., Evans P. (2000): Volatiles as an indicator of fungal activity and differentiation between species, and the potential use of electronic nose technology for early detection of grain spoilage. *J Stored Prod Res.* 36(4), *pp.* 319-340. doi: 10.1016/s0022-474x(99)00057-0
205. Majchrzak, T., Wojnowski, W., Lubinska- Szczygeł, M., Różańska, A., Namieśnik, J., et al. (2018): PTR-MS and GC-MS as complementary techniques for analysis of volatiles. A tutorial Rev. *Analytica Chimica Acta.* 1035, *pp.* 1–13. doi: 10.1016/j.aca.2018.06.056
206. Malik, U., Karmakar, A., Barik, A. (2016): Attraction of the potential biocontrol agent *Galerucella placida* (Coleoptera: Chrysomelidae) to the volatiles of *Polygonum orientale* (Polygonaceae) weed leaves. *Chemoecology* 26, *pp.* 45–58. doi: 10.1007/s00049-015-0206-5.
207. Marriott, P. J., Shellie, R., Cornwell, C. (2001): Gas chromatographic technologies for the analysis of essential oils. *Journal of Chromatography A.* 936, *pp.* 1–22. doi: 10.1016/s0021-9673(01)01314-0.
208. Martinelli, F., Scalenghe, R., Davino, S., Panno, S., Scuderi, G., Ruisi, P., Villa, P., Stroppiana, D., Boschetti, M., Goulart, L. R., Davis, C. E. Dandekar, A. M. (2015): Advanced methods of plant disease detection. *Agron. Sustain. Dev.* 35. *pp.* 1-25. doi: 10.1007/s13593-014-0246-1.
209. Martínez-Medina, A., Appels, F. V. W., van Wees, S. C. M. (2017b): Impact of salicylic acid- and jasmonic acid-regulated defences on root colonization by *Trichoderma harzianum* T-78. *Plant Signaling Behav.* 12, e1345404. doi: 10.1080/15592324.2017.1345404
210. Martínez-Medina, A., Van Wees, S. C. M., Pieterse, C. M. J. (2017a): Airborne signals from *Trichoderma* fungi stimulate iron uptake responses in roots resulting in priming of jasmonic acid-dependent defences in shoots of *Arabidopsis thaliana* and *Solanum lycopersicum:* fungal volatiles trigger iron uptake responses and ISR. *Plant Cell Environ.* 40, *pp.* 2691–2705. doi: 10.1111/pce.13016
211. Martín-Sánchez, L., Cristiana, A., Paolina, G., Gianpiero, V. (2020): Investigating the effect of belowground microbial volatiles on plant nutrient status: perspective and limitations. *J. Plant Interact.* 15(1), *pp.* 188–195. doi: 10.1080/17429145.2020.1776408
212. Materić, D., Bruhn, D., Turner, C., Morgan, G., Mason, N., Gauci, V. (2015): Methods in plant foliar volatile organic compounds research. *Appl. Plant Sci.* 3, doi: 10.3732/apps.1500044
213. Matsui, K., Sasahara, S., Akakabe, Y., Kajiwara, T. (2003): Linoleic acid 10-hydroperoxide as an intermediate during formation of 1-octen-3-ol from linoleic acid in *Lentinus decadetes. Biosci. Biotechnol. Biochem.* 67, *pp.* 2280–2282. doi: 10.1271/bbb.67.2280.
214. Mátyus, R. (2023): Növények és patogénjeik non-invazív illatanyag-vizsgálatának kritikai aspektusai, Debreceni Egyetem, TTK Alkalmazott Kémiai Tanszék, Diplomamunka
215. Mau, J. J., Chyau, C. C., Li, J. Y., Tseng, Y. H. (1997): Flavor compounds in straw mushroom *Volvariella volvaceae* harvested at different stages of maturity. *J. Agric. Food Chem.* 45, *pp.* 4726–4729. doi: 10.1021/jf9703314.
216. Mcgarvey, D. J., Croteau, R. (1995): Terpenoid Metabolism. *Plant Cell* 7, *pp.* 1015–1026. doi: 10.1105/tpc.7.7.1015
217. Meier, A. R., Hunter, M. D. (2019): Mycorrhizae alter constitutive and herbivore-induced volatile emissions by milkweeds. *J. Chem. Ecol.* 45, *pp.* 610–625. doi: 10.1007/s10886-019-01080-6
218. Menotta, M., Gioacchini, A., Amicucci, A., Buffalini, M., Sisti, D., Stocchi, V., et al. (2004): Headspace solidphase microextraction with gas chromatography and mass spectrometry in the

investigation of volatile organic compounds in an ectomycorrhizae synthesis system. *Rapid Commun. Mass Spectrom* 18, *pp.* 206–210. doi: 10.1002/rcm.1314
219. Merfort, I. (2002): Review of the analytical techniques for sesquiterpenes and sesquiterpene lactones. *Journal of Chromatography A* 967, *pp.* 115–130.
220. Mesdag, J., Donner, D. A. (2000): Breeding for bread-making quality in Europe. In: Donner, D. A. (Ed.), Bread-Making Quality of Wheat: A Century of Breeding in Europe. *Kluwer, the Netherlands: Dordrecht, pp.* 416.
221. Millar, J. G., Sims, J. J. (1998): Preparation, cleanup, and preliminary fractionation of extracts. In Millar, J. G., Hanes, K. F., (Eds.), Methods in Chemical Ecology. *Boston: Kluwer Academic Publishers, pp.* 1–37.
222. Mirzaie, M., Talebizadeh, A. R., Hashemipour, H. (2021): Mathematical modeling and experimental study of VOC adsorption by Pistachio shell–based activated carbon. *Environ. Sci. Pollut. Res.* 28(3), *pp.* 3737–3747. doi: 10.1007/s11356-020-10634-1
223. Moisan, K., Aragón, M., Gort, G., Dicke, M., Cordovez, V., Raaijmakers, et al. (2020b): Fungal volatiles influence plant defence against aboveground and belowground herbivory. *Funct. Ecol.* 34, *pp.* 2259–2269. doi: 10.1111/1365-2435.13633
224. Moisan, K., Cordovez, V., van de Zande, E. M., Raaijmakers, J. M., Dicke, M., Lucas-Barbosa, D. (2019): Volatiles of pathogenic and non-pathogenic soil-borne fungi affect plant development and resistance to insects. *Oecologia* 190, *pp.* 589–604. doi: 10.1007/s00442-019-04433-w
225. Moisan, K., Dicke, M., Raaijmakers, J. M., Rachmawati, E., Cordovez, V. (2021): Volatiles from the fungus *Fusarium oxysporum* affect interactions of brassica rapa plants with root herbivores. *Ecol. Entomol.* 46, *pp.* 240–248. doi: 10.1111/een.12956
226. Moisan, K., Raaijmakers, J. M., Dicke, M., Lucas-Barbosa, D., Cordovez, V. (2020a): Volatiles from soil-borne fungi affect directional growth of roots. *Plant Cell Environ.* 202144, *pp.* 339–345. doi: 10.1111/pce.13890
227. Morath, S. U., Hung, R., Bennett, J. W. (2012): Fungal volatile organic compounds: a review with emphasis on their biotechnological potential. *Fungal Biol.* 26, *pp.* 73–83. doi: 10.1016/j.fbr.2012.07.001
228. Morgounov, A., Tufan, H. A., Sharma, R., Akin, B., Bagci, A., Braun, H.-J., et al. (2012): Global incidence of wheat rusts and powdery mildew during 1969–2010 and durability of resistance of winter wheat variety *Bezostaya* 1. *Eur. J. Plant Pathol.* 132, *pp.* 323–340. doi: 10.1007/s10658-011-9879-y.
229. Moriura, N., Matsuda, Y., Oichi, W., Nakashima, S., Hirai, T., Nonomura, T., et al. (2006): An apparatus for collecting total conidia of *Blumeria graminis* f.sp. *hordei* from leaf colonies using electrostatic attraction. *Plant Pathol.* 55, *pp.* 367–374. doi: 10.1111/j.1365-3059.2006.01356.x.
230. Murahashi, S. (1936) About the fragrances of matsutake. *Bull. Inst. Phys. Chem. Res.* 30, *pp.* 263–271.
231. Murray, G. M., Brennan, J. P. (2009): The Current and Potential Costs from Diseases of Wheat in Australia. *Grains Research and Development Corporation, Australia: Kingston, pp.* 69. ISBN 978-1-875477-92-0
232. Murungi, L. K., Kirwa, H., Coyne, D., Teal, P. E. A., Beck, J. J., Torto, B. (2018): Identification of key root volatiles signaling preference of tomato over spinach by the root knot nematode *Meloidogyne incognita. J. Agric. Food Chem.* 66(28), *pp.* 7328–7336. doi: 10.1021/acs.jafc.8b03257
233. Nadal, M., Paszkowski, U. (2013): Polyphony in the rhizosphere: presymbiotic communication in arbuscular mycorrhizal symbiosis. *Curr. Opin. Plant Biol.* 16(4), *pp.* 473-479. doi: 10.1016/j.pbi.2013.06.005
234. Naves, Y. (1943): Etudes sur les matières végétales volatiles XXV. Sur la présence de l'alcool de Matsutake (n-octène-1-ol-(3)) et du méthyl-1-cyclohexanol-(3) dans l'essence de

menthe pouliot (Mentha Pulegium L.). *Helvet. Chim. Acta* 26, *pp.* 1992–2001. doi: 10.1002/hlca.19430260625.
235. Ndomo-Moualeu, A. F., Ulrichs, C., Adler, C. (2016): Behavioral responses of *Callosobruchus maculatus* to volatile organic compounds found in the headspace of dried green pea seeds. *J. Pest Sci.* 89, *pp.* 107–116. doi: 10.1007/s10340-015-0652-4.
236. Nemčovič, M., Jakubikova, J., Víden, I., Farka, V. (2008): Induction of conidiation by endogenous volatile compounds in *Trichoderma* spp. *FEMS Microbiol. Lett.* 284, *pp.* 231–236. doi: 10.1111/j.1574-6968.2008.01202.x.
237. Nover, I. (1958): Sechsjährige Beobachtungen über die physiologische Spezialisierung des echten Mehltaus (*Erysiphe graminis* DC.) von Weizen und Gerste in Deutschland. *J. Phytopathol.* 31, *pp.* 85–107. doi: 10.1111/j.1439-0434.1958.tb01766.x.
238. Oerke, E.-C. (2006): Crop losses to pests. *J. Agric. Sci.* 144, *pp.* 31–43. doi: 10.1017/S0021859605005708.
239. Oksanen, J., Blanchet, F. G., Friendly, M., Kindt, R., Legendre, P., McGlinn, D., et al. (2020): vegan: Community Ecology Package. *R package version* 2.5-7. https://CRAN.R-project.org/package=vegan.
240. Okull, D. O., Beelman, R. B., Gourama, H. (2003): Antifungal activity of 10-oxo-trans-8-decenoic acid and 1-octen-3-ol against *Penicillium expansum* in potato dextrose agar medium. *J. Food Prot.* 66, *pp.* 1503–1505
241. Ozawa, R., Shimoda, T., Kawaguchi, M., Arimura, G. I., Horiuchi, J. I., Nishioka, T., Takabayashi, J. (2000): Lotus japonicus infested with herbivorous mites emits volatile compounds that attract predatory mites. *J. Plant Res.* 113, *pp.* 427–433. doi: 10.1007/PL00013951.
242. Palma, R., Mutis, A., Manosalva, L., Ceballos, R., Quiroz, A. (2012): Behavioral and electrophysiological responses of *Hylastinus obscurus* to volatiles released from the roots of *Trifolium pratense* l. *J. Soil Sci. Plant Nutr.* 12, *pp.* 183–193. doi: 10.4067/S0718-95162012000100015
243. Park, Y. S., Dutta, S., Ann, M., Raaijmakers, J. M., Park, K. (2015): Promotion of plant growth by *Pseudomonas fluorescens* strain SS101 via novel volatile organic compounds. *Biochem. Biophys. Res. Commun.* 461, *pp.* 361–365. doi: 10.1016/j.bbrc.2015.04.039
244. Pasanen, P., Korpi, A., Kalliokoski, P., Pasanen, A.-L., (1997): Growth and volatile metabolite production of *Aspergillus versicolor* in house dust. *Environ. Int.* 23, 425–432. doi: 10.1016/S0160-4120(97)00027-5.
245. Peñuelas, J., Staudt, M. (2010): BVOCs and global change. *Trends in Plant Science* 15(3), *pp.* 133-144.
246. Penuelas, J., Asensio, D., Tholl, D., Wenke, K., Rosenkranz, M., Piechulla, B. (2014): Biogenic volatile emissions from the soil. *Plant Cell Environ.* 37, *pp.* 1866–1891. doi: 10.1111/pce.12340
247. Pichersky, E., and Gershenzon, J. (2002): The formation and function of plant volatiles: perfumes for pollinator attraction and defense. *Plant Biol.* 5, *pp.* 237–243. doi: 10.1016/s1369-5266(02)00251-0.
248. Piechulla, B., Lemfack, M. C., Kai, M. (2017): Effects of discrete bioactive microbial volatiles on plants and fungi. *Plant Cell Environ.* 40, *pp.* 2042–2067. doi: 10.1111/pce.13011
249. Pierce, A. M., Pierce, H.D., Oehlschlager, A. C., Borden, J. H. (1991): 1-Octen-3-ol, attractive semiochemical for foreign grain beetle, *Ahasverus advena* (Waltl) (Coleoptera: Cucujidae). *J. Chem. Ecol.* 17, *pp.* 567–580. doi: 10.1007/BF00982127.
250. Piesik, D., Łyszczarz, A., Tabaka, P., Lamparski, R., Bocianowski, J., Delaney, K. J. (2010) Volatile induction of three cereals: influence of mechanical injury and insect herbivory on injured plants and neighbouring uninjured plants. *Ann. Appl. Biol*. 157, *pp.* 425–434. doi: 10.1111/j.1744-7348.2010.00432.x.
251. Podhradszky J., Csuti I.-né (1962): Búza- és árpa-lisztharmatjárvány 1961. évben Magyarországon. *Növénytermelés* 11 *pp.* 249–256.

252. Pons, S., Fournier, S., Chervin, C., Be´card, G., Rochange, S., Frey, et al. (2020): Phytohormone production by the arbuscular mycorrhizal fungus *Rhizophagus irregularis. PloS One* 15(10), e0240886. doi: 10.1371/journal.pone.0240886
253. Pusztahelyi, T., Holb, I. J., Pócs, I. (2017): Plant-fungal interactions: special secondary metabolites of the biotrophic, necrotrophic, and other specific interactions. In: Mérillon, J.-M., Ramawat, K.G. (Eds.), *Fungal Metabolites. Springer, Cham, pp.* 133–190. https://doi.org/10.1007/978-3-319-19456-1_39-1.
254. Pyysalo, H. (1976): Identification of volatile compounds in seven edible mushrooms. *Acta Chem. Scand. B* 30, *pp.* 235–244. doi: 10.3891/acta.chem.scand.30b-0235.
255. R Core Team (2020): R: A language and environment for statistical computing. *R ver.* 3.6.3. R Foundation for Statistical Computing, Austria: Vienna. https://www.R-project.org/.
256. Radványi D., Szelényi, M. O., Hamow, K. Á., Ambrózy, Zs., Lukács, P., Puskás, K., Cséplő, M., Molnár, B. P. (2019): Egészséges és fertőzött mezőgazdasági növények, valamint agaricus bisporus illatanyagprofiljának feltérképezése – előtanulmány, *NÖVÉNYVÉDELEM 2019* 80 [N. S. 55]: 8. *pp.* 333-342.
257. Ragunathan, N., Krock, K. A., Klawun, C., Sasaki, T. A., Wilkins, C. L. (1999): Gas chromatography with spectroscopic detectors. *Journal of Chromatography A* 856, *pp.* 349–397. doi: 10.1016/s0021-9673(99)00819-5.
258. Raguso, R. A. (2008): Wake up and smell the roses: the ecology and evolution of floral scent. *Annual Review of Ecology, Evolution, and Systematics* 39, *pp.* 549-569.
259. Raguso, R. A., Pellmyr, O. (1998): Dynamic Headspace Analysis of Floral Volatiles: A Comparison of Methods. *Oikos* 81(2), *pp.* 238–254. doi: 10.2307/3547045.
260. Raskin, I. (1992): Role of salicylic acid in plants. *Annu. Rev. Plant Biol.* 43, *pp.* 439–463. doi: 10.1146/annurev.pp.43.060192.002255
261. Rasmann, S., Köllner, T.G., Degenhardt, J., Hiltpold, I., Toepfer, S., Kuhlmann, U., Gershenzon, J. (2005): Recruitment of entomopathogenic nematodes by insect-damaged maize roots. *Nature* 434, *pp.* 732–737.
262. Raza, W., Ling, N., Liu, D., Wei, Z., Huang, Q., Shen, Q. (2016): Volatile organic compounds produced by pseudomonas fluorescens WR-1 restrict the growth and virulence traits of ralstonia solanacearum. *Microbiol. Res.* 192, 103–113. doi: 10.1016/j.micres.2016.05.014
263. Reding, M. E., Alston, D. G., Thomson, S. V., Stark, A. V. (2001): Association of powdery mildew and spider mite populations in apple and cherry orchards. *Agr. Ecosyst. Environ.* 84, *pp.* 177–186. doi: 10.1016/S0167-8809(00)00204-8.
264. Rohloff, J., Bones, A. M. (2005): Volatile profiling of Arabidopsis thaliana – Putative olfactory compounds in plant communication. Phytochemistry 66, *pp.* 1941–1955. doi: 10.1016/j.phytochem.2005.06.021
265. Rowaished, A. K. (1980): Effect of NPK fertilizer on powdery mildew incidence in winter wheat. *Cereal Res. Commun.* 8, *pp.* 559–566.
266. Roze, L. V., Beaudry, R. M., Linz, J. E. (2012): Analysis of volatile compounds emitted by filamentous fungi using solid-phase microextraction-gas chromatography/mass spectrometry. *Methods Mol. Biol.* 944, *pp.* 133–142. doi: 10.1007/978-1-62703-122-6_9
267. Ryu, C.-M., Farag, M. A., Hu, C. H., Reddy, M. S., Kloepper, J. W., Pare, et al. (2004a): Bacterial volatiles induce systemic resistance in 115rabidopsis. *Plant Physiol.* 134, *pp.* 1017–1026. doi: 10.1104/pp.103.026583
268. Ryu, C.-M., Farag, M. A., Hu, C. H., Reddy, M. S., Wei, H. X., Pare, P. W. (2003): Bacterial volatiles promote growth in *Arabidopsis. Proc. Natl. Acad. Sci. U.S.A.* 100, *pp.* 4927–4932. doi: 10.1073/pnas.0730845100
269. Ryu, C.-M., Murphy, J. F., Mysore, K. S., Kloepper, J. W. (2004b): Plant growth-promoting rhizobacteria systemically protect Arabidopsis thaliana against Cucumber mosaic virus by a salicylic acid and NPR1-independent and jasmonic acid-dependent signaling pathway. *Plant Journal* 39(3), *pp.* 381-392. doi: 10.1111/j.1365-313X.2004.02142.x.

270. SANTE/11312/2021 (Guidance Document on Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis) https://food.ec.europa.eu/system/files/2023-11/pesticides_mrl_guidelines_wrkdoc_2021-11312.pdf
271. Saunders, P. J. W., Doodson, J. K., (1970): Periodic fluctuations in mildew intensity in cereal cultivar trials. *Trans. Brit. Mycol. Soc.* 55, *pp.* 318–321. doi: 10.1016/S0007-1536(70)80019-5.
272. Savary, S., Willocquet, L., Pethybridge, S.J., Esker, P., McRoberts, N., Nelson, A. (2019): The global burden of pathogens and pests on major food crops. *Nat. Ecol. Evol.* 3, *pp.* 430–439. doi: 10.1038/s41559-018-0793-y.
273. Scala, A., Allmann, S., Mirabella, R., Haring, M. A., Schuurink, R. C. (2013): Green leaf volatiles: a plant's multifunctional weapon against herbivores and pathogens. *International Journal of Molecular Sciences* 14(9), *pp.* 17781-17811. doi: 0.3390/ijms140917781
274. Schellenbaum, L., Berta, G., Ravolanirina, F., Tisserant, B., Gianinazzi, S., Fitter, A. H. (1991): Influence of endomycorrhizal infection on root morphology in a micropropagated woody plant species (*Vitis vinifera* l.). *Biol. J. Linne Soc.* 68(2), *pp.* 135–141. doi: 10.1093/oxfordjournals.aob.a088231
275. Schenkel, D., Lemfack, M. C., Piechulla, B., Splivallo, R. (2015): A meta-analysis approach for assessing the diversity and specificity of belowground root and microbial volatiles. *Front. Plant Sci.* 6. doi: 10.3389/fpls.2015.00707
276. Schenkel, D., Maciá-Vicente, J. G., Bissell, A., Splivallo, R. (2018): Fungi indirectly affect plant root architecture by modulating soil volatile organic compounds. *Front. Microbiol.* 9. doi: 10.3389/fmicb.2018.01847
277. Schindler, F., Seipenbusch, R. (1990): Fungal flavour by fermentation. *Food Biotechnol.* 4, *pp.* 77–85. doi: 10.1080/08905439009549724.
278. Schmidt, R., Cordovez, V., De Boer, W., Raaijmakers, J., Garbeva, P. (2015): Volatile affairs in microbial interactions. *ISME J.* 9, *pp.* 2329–2335. doi: 10.1038/ismej.2015.42
279. Schuh, G., Heiden, A. C., Hoffmann, T., Kahl, J., Rockel, P., Rudolph, J., Wildt, J. (1997): Emissions of Volatile Organic Compounds from Sunflower and Beech: Dependence on Temperature and Light Intensity. *Journal of Atmospheric Chemistry* 27(3), *pp.* 291–318. doi: 10.1023/A:1005850710257
280. Schulz, S., Dickschat, J. S. (2007): Bacterial volatiles: the smell of small organisms. *Nat. Prod. Rep.* 24, *pp.* 814–842. doi: 10.1039/b507392h
281. Schulz-Bohm, G. K. S., Hundscheid, M., Melenhorst, J., De Boer, W., Garbeva, P. (2017): Calling from distance: attraction of soil bacteria by plant root volatiles. *ISME J* 12(5), *pp.* 1252–1262. doi: 10.1038/s41396-017-0035-3
282. Sharifi, R., Jeon, J. S., Ryu, C. M. (2022): Belowground plant–microbe communications via volatile compounds. *J. Exp. Bot.* 73(2), *pp.* 463–486. doi: 10.1093/jxb/erab465
283. Sharkey, T. D., Yeh, S. (2001): Isoprene Emission from Plants. Annual Review of Plant Physiology and Plant Molecular Biology, *Annual Reviews* 52, *pp.* 407–436. doi: 10.1146/annurev.arplant.52.1.407
284. Sharkey, T. D., Chen, X., Yeh, S. (2001): Isoprene Increases Thermotolerance of Fosmidomycin-Fed Leaves. *Plant Physiology* 125(4), *pp.* 2001–2006. doi: 10.1104/pp.125.4.2001
285. Sharkey, T. D., Wiberley, A. E., Donohue, A. R. (2008): Isoprene emission from plants: why and how. *Annals of Botany* 101(1), *pp.* 5-18. doi: 10.1093/aob/mcm240.
286. Shen, S., Sha, Y., Deng, C., Zhang, X., Fu, D., Chen, J. (2004): Quality assessment of *Flos Chrysanthemi Indici* from different growing areas in China by solid-phase microextraction-gas chromatography-mass spectrometry. *J. Chromatogr. A.* 1047, *pp.* 281–287. doi: 10.1016/j.chroma.2004.06.129

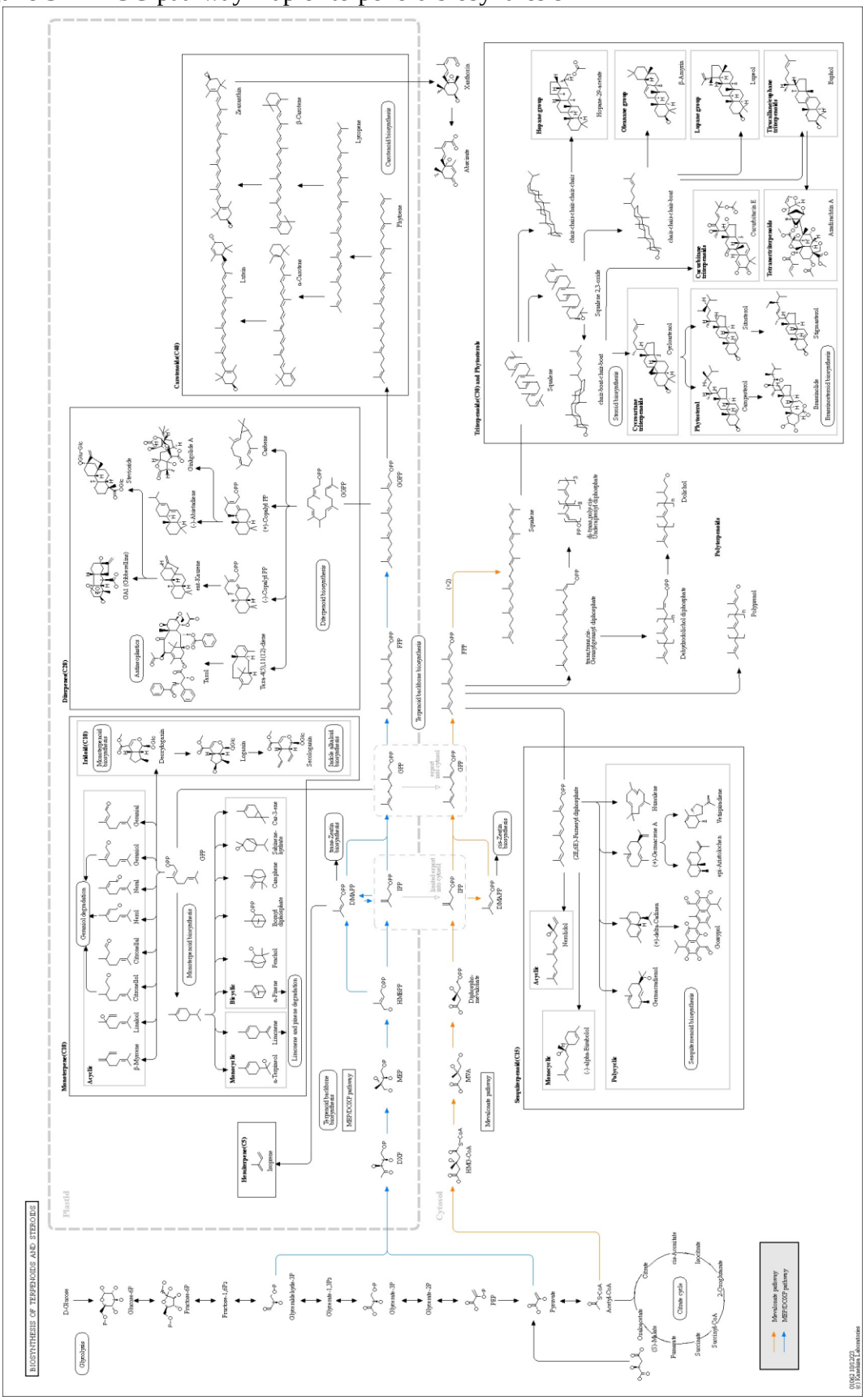
287. Sheoran, N., Nadakkakath, A. V., Munjal, V., Kundu, A., Subaharan, K., Venugopal, V., et al. (2015): Genetic analysis of plant endophytic *Pseudomonas putida* BP25 and chemo-profiling of its antimicrobial volatile organic compounds. *Microbiol. Res.* 173, *pp.* 66–78. doi: 10.1016/j.micres.2015.02.001
288. Shualev, V., Silverman, P., Raskin, I. (1997): Airborne signaling by methyl salicylate in plant pathogen resistance. *Nature* 385(6618), *pp.* 718–721. doi: 10.1038/386738a0
289. Simas, D. L. R., Silésia, H. B. M., de Amorim, F. R. V., Goulart, C. S., Alviano, D. S., Alviano, A. J. R., et al. (2017): Citrus species essential oils and their components can inhibit or stimulate fungal growth in fruit. *Industrial Crops and Products* 98, *pp.* 108–115. doi: 10.1016/j.indcrop.2017.01.026
290. Sinha, R. N., Tuma, D., Abramson, D., Muir, W. E. (1988): Fungal volatiles associated with moldy grain in ventilated and non-ventilated bin-stored wheat. *Mycopathol* 101, *pp.* 53–60. doi: 10.1007/BF00455669.
291. Song, G. C., Choi, H. K., Ryu, C. M. (2017): Gaseous 3-pentanol primes plant immunity against a bacterial speck pathogen, *Pseudomonas syringae* pv. tomato via salicylic acid and jasmonic acid-dependent signaling pathways in *Arabidopsis*. *Frontiers in Plant Science* 8, *pp.* 1807. doi: 10.3389/fpls.2015.00821.
292. Spinelli, F., Cellini, A., Marchetti, L., Nagesh, K. M., Piovene, C. (2011): Emission and function of volatile organic compounds in response to abiotic stress. In: Eds. Shanker, A. K., Venkateswarlu, B., Abiotic Stress in Plants – Mechanisms and Adaptations. *InTech, Croatia: Rijeka, pp.* 367–394. doi: 10.5772/24155.
293. Spitzer, M., Wildenhain, J., Rappsilber, J., Tyers, M., (2014): BoxPlotR: a web tool for generation of box plots. *Nat. Methods* 11, *pp.* 121–122. doi: 10.1038/nmeth.2811.
294. Splivallo, R., Novero, M., Bertea, C. M., Bossi, S., Bonfante, P. (2007): Truffle volatiles inhibit growth and induce an oxidative burst in *Arabidopsis thaliana*. *New Phytol.* 175, *pp.* 417–424. doi: 10.1111/j.14698137.2007.02141.x
295. Stevens, M. M., Wood, R. M., Mo, J. (2019): Monitoring flight activity of *Cryptolestes ferrugineus* (Coleoptera: Laemophloeidae) in outdoor environments using a commercial pheromone lure and the kairomone 1-octen-3-ol. *J. Stored Prod. Res.* 83, *pp.* 227–235. doi: 10.1016/j.jspr.2019.07.005.
296. Suinyuy, T. N., Donaldson, J. S., Johnson, S. S., (2013): Variation in the chemical composition of cone volatiles within the African cycad genus Encephalartos. Phytochemistry 85, *pp.* 82–91. doi: 10.1016/j.phytochem.2012.09.016.
297. Sun, X. G., Bonfante, P., Tang, M. (2015): Effect of volatiles versus exudates released by germinating spores of *Gigaspora margarita* on lateral root formation. *Plant Physiol. Biochem.* 97, *pp.* 1–10. doi: 10.1016/j.plaphy.2015.09.010
298. Sun, X. G., Tang, M. (2013): Effect of arbuscular mycorrhizal fungi inoculation on root traits and root volatile organic compound emissions of sorghum bicolor. *South Afr. J. Bot.* 88, *pp.* 373–379. doi: 10.1016/j.sajb.2013.09.007
299. Tabata, J., De Moraes, C.M., Mescher, M.C., (2011): Olfactory cues from plants infected by powdery mildew guide foraging by a mycophagous ladybird beetle. *PLoS ONE* 6, e23799. doi: 10.1371/journal.pone.0023799.
300. Terra, W. C., Campos, V. P., Martins, S. J., Costa, L. S. A. S., da Silva, J. C. P., Barros, A. F., et al. (2018): Volatile organic molecules from *Fusarium oxysporum* strain 21 with nematicidal activity against *Meloidogyne incognita*. *Crop Prot.* 106, *pp.* 125–131. doi: 10.1016/j.cropro.2017.12.022
301. Tholl, D., Boland, W., Hansel, A., Loreto, F., Röse, U. S. R., Schnitzler, J. P. (2006): Practical approaches to plant volatile analysis. *Plant J.* 45, *pp.* 540–560. doi: 10.1111/j.1365-313X.2005.02612.x
302. Tholl, D., Hossain, O., Weinhold, A., Röse, U. S. R., Wei, Q. (2021): Trends and applications in plant volatile sampling and analysis. *Plant J.* 106, *pp.* 314–325. doi: 10.1111/tpj.15176

303. Thompson, A. M. (1992): The Oxidizing Capacity of the Earth's Atmosphere: Probable Past and Future Changes. *Science* 256(5060), *pp.* 1157–1164.
304. Thorn, R. M. S., Greenman, J. (2012): Microbial volatile compounds in health and disease conditions. *J. Breath Res.* 6, *pp.* 24001. doi: 10.1088/1752-7155/6/2/024001
305. Timmusk, S., El-Daim, I. A. A., Copolovici, L., Tanilas, T., Kännaste, A., Behers, L., et al. (2014): Drought-tolerance of wheat improved by rhizosphere bacteria from harsh environments: enhanced biomass production and reduced emissions of stress volatiles. *PLOS ONE* 9, e96086. doi: 10.1371/journal.pone.0096086.
306. Tischner, T., Kőszegi, B., Veisz, O. (1997): Climatic programmes used in the Martonvásár phytotron most frequently in recent years. *Acta Agron. Hung.* 45, *pp.* 85–104.
307. Tomova, B. S., Waterhouse, J. S., Doberski, J. (2005): The effect of fractionated Tagetes oil volatiles on aphid reproduction. *Entomol. Exp. Appl.*, *pp.* 115, 153–159.
308. Tompkins, D. K., Wright, A. T., Fowler, D. B. (1992): Foliar disease development in no-till winter wheat: influence of agronomic practices on powdery mildew development. *Can. J. Plant Sci.* 72, *pp.* 965–972. doi: 10.4141/cjps92-121.
309. Tuma, D., Sinha, R. N., Muir, W. E., Abramson, D. (1989): Odor volatiles associated with microflora in damp ventilated and non-ventilated bin-stored bulk wheat. *Int. J. Food Microbiol.* 8, *pp.* 103–119. doi: 10.1016/0168-1605(89)90065-2.
310. Turlings, T. C., Erb, M. (2018): Tritrophic interactions mediated by herbivore-induced plant volatiles: mechanisms, ecological relevance, and application potential. *Annual Review of Entomology* 63, *pp.* 433-452. doi: 10.1146/annurev-ento-020117-043507
311. Turlings, T. C., Loughrin, J. H., McCall, P. J., Röse, P. J., Lewis, P. J., Tumlinson, J. H. (1995): How caterpillar-damaged plants protect themselves by attracting. *Proc. Natl. Acad. Sci. U. S. A* 92, no. May, pp. 4169–4174, 1995.
312. Tyagi, S., Mulla, S. I., Lee, K. J., Chae, J. C., Shukla, P. (2018): VOCs-mediated hormonal signaling and crosstalk with plant growth promoting microbes. *Crit. Rev. Biotechnol.* 38(8), *pp.* 1277–1296. doi: 10.1080/07388551.2018.1472551
313. van Dam, N. M., Weinhold, A., Garbeva, P. (2016): "Calling in the dark: The role of volatiles for communication in the rhizosphere,": *Deciphering chemical language of plant communication.* Eds. Blande, J. D., Glinwood, R. (Cham: Springer International Publishing), *pp.* 175–210.
314. Van Der Heijden, M. G. A., Martin, F., Selosse, M. A., Sanders, I. R. (2015): Mycorrhizal ecology and evolution: the past, the present, and the future. *New Phytol.* 205, *pp.* 1406–1423. doi: 10.1111/nph.13288
315. van Doan, C., Züst, T., Maurer, C., Zhang, X., Machado, R. A. R., Mateo, P., et al. (2021): Herbivore-induced plant volatiles mediate defense regulation in maize leaves but not in maize roots. *Plant Cell Environ.* 44(8), *pp.* 2672–2686. doi: 10.1111/pce.14052
316. Van Lancker, F., Adams, A., Delmulle, B., De Saeger, S., Moretti, A., Van Peteghem, C., De Kimpe, N. (2008): Use of headspace SPME-GC-MS for the analysis of the volatiles produced by indoor molds grown on different substrates. *J. Environ. Monit.* 10, *pp.* 1127–1133. doi: 10.1039/b808608g.
317. Velásquez, A., Valenzuela, M., Carvajal, M., Fiaschi, G., Avio, L., Giovannetti, M., et al. (2020b): The arbuscular mycorrhizal fungus *Funneliformis mosseae* induces changes and increases the concentration of volatile organic compounds in *Vitis vinifera* cv. sangiovese leaf tissue. *Plant Physiol. Biochem.* 155, *pp.* 437–443. doi: 10.1016/j.plaphy.2020.06.048
318. Velásquez, A., Vega-Celedón, P., Fiaschi, G., Agnolucci, M., Avio, L., Giovannetti, M., et al. (2020a): Responses of *Vitis vinifera* cv. Cabernet sauvignon roots to the arbuscular mycorrhizal fungus *Funneliformis mosseae* and the plant growth-promoting rhizobacterium *Ensifer meliloti* include changes in volatile organic compounds. *Mycorrhiza* 30(1), *pp.* 161–170. doi: 10.1007/s00572-020-00933-3

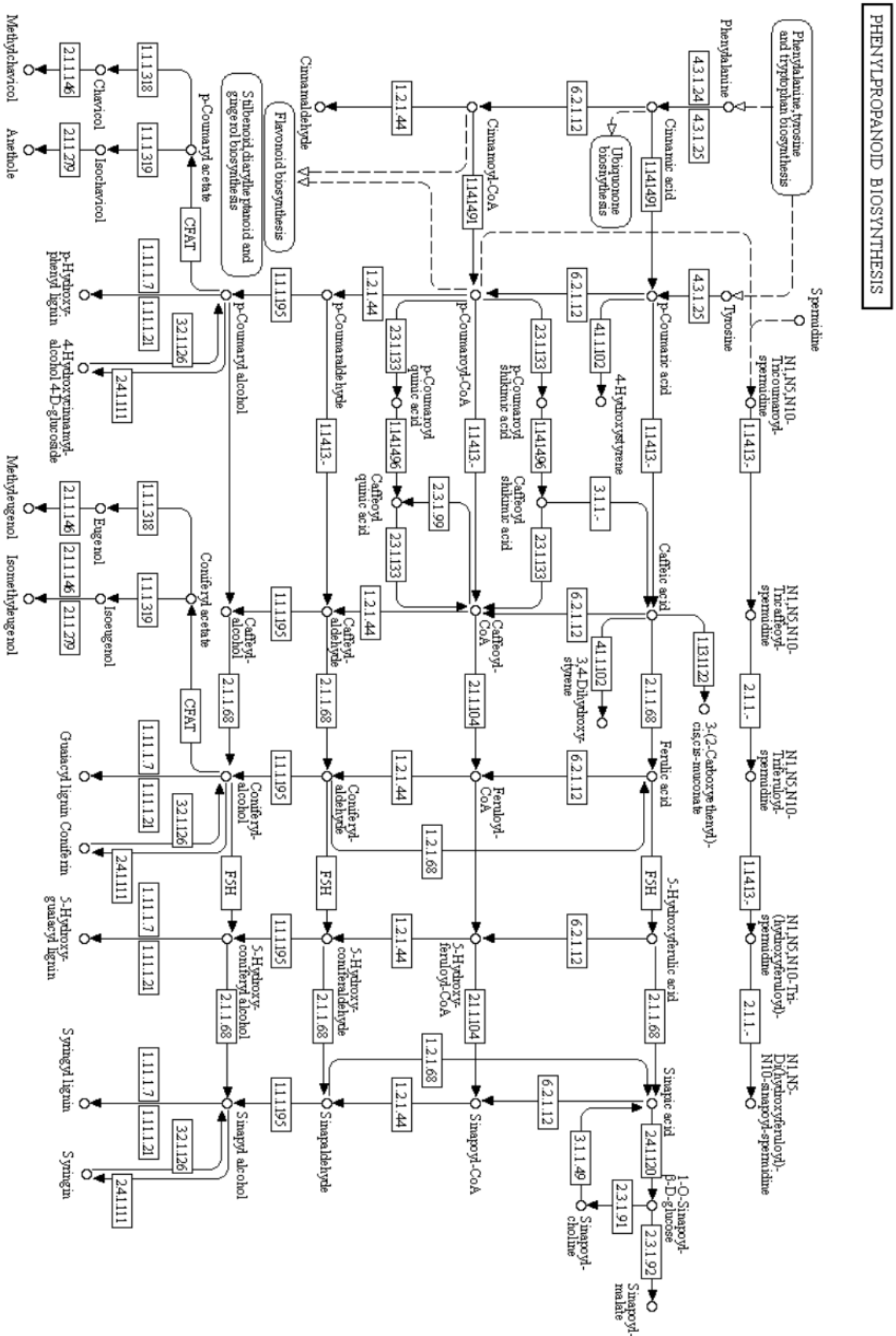
319. Vickers, C. E., Gershenzon, J., Lerdau, M. T., Loreto, F. (2009): A unified mechanism of action for volatile isoprenoids in plant abiotic stress. *Nature Chemical Biology*, 5(5), *pp.* 283-291.
320. Gershenzon, J., Dudareva, N. (2007): The function of terpene natural products in the natural world. *Nature Chemical Biology* 3(7), *pp.* 408-414.
321. Vida, G., Szunics, L., Gál, M., Veisz, O., Bedő, Z. (2002.) Comparison of two wheat powdery mildew differential sets in seedling tests. *Plant Protect. Sci.* 38(Special Issue 2), *pp.* 417–420. doi: 10.17221/10510-PPS.
322. Volpe, V., Chitarra, W., Cascone, P., Volpe, M. G., Bartolini, P., Moneti, G., et al. (2018): The association with two different arbuscular mycorrhizal fungi differently affects water stress tolerance in tomato. *Front. Plant Sci.* 9. doi: 10.3389/fpls.2018.01480
323. Vuts, J., Konczor, S., Imrei, Z., Jósvai, J. K., Lohonyai, Z., Molnár, B. P., Kárpáti, Z., Szocs, G., Tóth, M. (2018): Módszerek a kémiai ökológiában. *Növényvédelem* 79 (54)(3), *pp.* 89–109.
324. Weir, T. L., Park, S. W., Vivanco, J. M. (2004): Biochemical and physiological mechanisms mediated by allelochemicals. *Current Opinion in Plant Biology* 7(4), *pp.* 472-479.
325. Weisskopf, L. (2013): "The potential of bacterial volatiles for crop protection against phytophathogenic fungi," in Microbial pathogens and strategies for combating them: *Science, technology and education*. Ed. Méndez-Vilas, A. (Badajoz: Formatex Research Center), *pp.* 1352–1363.
326. Wenda-Piesik, A. (2011): Volatile organic compound emissions by winter wheat plants *(Triticum aestivum L.)* under *Fusarium* spp. infestation and various abiotic conditions. *Pol. J. Environ. Stud.* 20, *pp.* 1335–1342.
327. Wenda-Piesik, A., Piesik, D., Ligor, T., Buszewski, B. (2010): Volatile organic compounds (VOCs) from cereal plants infested with crown rot: their identity and their capacity for inducing production of VOCs in uninfested plants. *Int. J. Pest Management* 56, *pp.* 377–383. doi: 10.1080/09670874.2010.505668.
328. Werner, S., Andrea, P., Nicole, B. (2016): Belowground communication: impacts of volatile organic compounds (VOCs) from soil fungi on other soil-inhabiting organisms. *Appl. Microbiol. Biotechnol.* 100(20). doi: 10.1007/s00253-016-7792-1
329. Wickham, H. (2007): Reshaping Data with the reshape Package. *J. Stat. Softw.* 21, *pp.* 1–20. doi: 10.18637/jss.v021.i12.
330. Wu, S.-Y., Duncan, L. W. (2020) Recruitment of an insect and its nematode natural enemy by olfactory cues from a saprophytic fungus. *Soil Biol. Biochem.* 144, *pp.* 107781. doi: 10.1016/j.soilbio.2020.107781.
331. Wurzenberger, M., Grosch, W. (1984): The formation of 1-octen-3-ol from the 10-hydroperoxide isomer of linoleic acid by a hydroperoxide lyase in mushrooms (*Psalliota bispora*). *Biochim. Biophys. Acta* 794, *pp.* 25–30. doi: 10.1016/0005-2760(84)90293-5.
332. Xie, X., Ling, J., Mao, Z., Li, Y., Zhao, J., Yang, Y., et al. (2022): Negative regulation of root-knot nematode parasitic behavior by root-derived volatiles of wild relatives of *Cucumis metuliferus* CM3. *Horticulture Res.* 9, uhac051. doi: 10.1093/hr/uhac051
333. Xu, Y., Tong, Z., Zhang, X., Zhang, X., Luo, Z., Shao, W., et al. (2021): Plant volatile organic compound (E)-2-hexenal facilitates *Botrytis cinerea* infection of fruits by inducing sulfate assimilation. *New Phytol.* 231, *pp.* 432–446. doi: 10.1111/nph.17378
334. Yarwood, C. E. (1943): Association of thrips with powdery mildews. *Mycologia* 35, *pp.* 189–191. doi: 10.1080/00275514.1943.12017475.
335. Yerushalmy, J. (1947): Statistical problems in assessing methods of medical diagnosis, with special reference to X-ray techniques. *Public Health Rep.* 62, *pp.* 1432–1449. doi: 10.2307/4586294.
336. Zadoks, J. C., Chang, T. T., Konzak, C. F. (1974): A decimal code for the growth stages of cereals. *Weed Res.* 14, *pp.* 415–421. doi: 10.1111/j.1365-3180.1974.tb01084.x.

337. Zawirska-Wojtasiak, R. (2004): Optical purity of (R)-(-)-1-octen-3-ol in the aroma of various species of edible mushrooms. *Food Chem.* 86, *pp.* 113–118. doi: 10.1016/j.foodchem.2003.08.016.
338. Zeng, F.-S., Menardo, F., Xue, M.-F., Zhang, X.-J., Gong, S.-J., Yang, L.-J., Shi, W.-Q., Yu, D.-Z. (2017): Transcriptome analyses shed new insights into primary metabolism and regulation of *Blumeria graminis* f. sp. *tritici* during conidiation. *Front. Plant Sci.* 8, *pp.* 1146. doi: 10.3389/fpls.2017.01146
339. Zhang, J., Zhi, J.-R., Yang, G.-M. (2015): Behavioral responses of *Frankliniella occidentalis* to kidney bean plants and their volatiles under different treatments. *Chinese J. Ecol.* 34, *pp.* 425–430.
340. Zhang, Q., Gao, X., Ren, Y., Ding, X., Qiu, J., Li, N., et al. (2018): Improvement of *Verticillium* wilt resistance by applying arbuscular mycorrhizal fungi to a cotton variety with high symbiotic efficiency under field conditions. *Int. J. Mol. Sci.* 19(1), 241. doi: 10.3390/ijms19010241
341. Zhang, W., Yu, L., Han, B., Liu, K., Shao, X. (2022): Mycorrhizal inoculation enhances nutrient absorption and induces insect-resistant defense of *Elymus nutans. Front. Plant Sci.* 13, doi: 10.3389/fpls.2022.898969
342. Zhao, G., Yin, G., Inamdar, A.A., Luo, J., Zhang, N., Yang, I., Buckley, B., Bennett, J.W. (2017): Volatile organic compounds emitted by filamentous fungi isolated from flooded homes after Hurricane Sandy show toxicity in a *Drosophila* bioassay. *Indoor Air* 27, *pp.* 518–528. doi: 10.1111/ina.12350.

9.2 Figure S1 KEGG pathway map of terpenoid biosynthesis



9.3 Figure S2 KEGG pathway map of phenylpropanoid biosynthesis



9.4 Table S1 Chemical compounds of plant root VOCs, collected in cited literature published between 2016-2022

Chemical compounds of plant root VOCs, collected during 2016-2022 yy.							
Plant	Functional groups	VOC compounds	Molecular Formula	InChIKey	CAS	Properties	References
Barley	Aldehydes	(2E)-hex-2-enal	$C_6H_{10}O$	MBDOYVRWFFCFHM-SNAWJCMRSA-N	6728-26-3	not given	Delory et al., 2016a
Barley		(2E,6Z)-nona-2,6-dienal	C9H14O	HZYHMHHBBBSGHB-ODYTWBPASA-N	557-48-2	not given	Delory et al., 2016a
Barley		(E)-non-2-enal	C9H16O	BSAIUMLZVGUGKX-BQYQJAHWSA-N	18829-56-6	not given	Delory et al., 2016a
Cucumber line Xintaimici		2,6-Octadienal, 3,7-dimethyl-, (E)-	C10H16O	WTEVQBCEXWBHNA-JXMROGBWSA-N	141-27-5	not given	Xie at al., 2022
Cucumber line Xintaimici		1-Cyclohexene-1-carboxaldehyde, 4-(1-	C10H14O	RUMOYJJNUMEFDD-UHFFFAOYSA-N	2111-75-3	not given	Xie at al., 2022
Arabidopsis thaliana		Furfural	C5H4O2	HYBBIBNJHNGZAN-UHFFFAOYSA-N	98-01-1	not given	Schenkel et al., 2018
Arabidopsis thaliana		5-methyl-2-furancarboxaldehyde	C6H6O2	OUDFNZMQXZILJD-UHFFFAOYSA-N	620-02-0	not given	Schenkel et al., 2018
Arabidopsis thaliana		Octanal	C8H16O	NUJGJRNETVAIRJ-UHFFFAOYSA-N	124-13-0	not given	Schenkel et al., 2018
Arabidopsis thaliana, Cucumber line *Xintaimici*,		Nonanal	C9H18O	GYHFUZHODSMOHU-UHFFFAOYSA-N	124-19-6	not given	Schenkel et al., 2018; Xie et al., 2022
Arabidopsis thaliana, Cucumber line *Xintaimici*,		Decanal	C10H20O	KSMVZQYAVGTKIV-UHFFFAOYSA-N	112-31-2	not given	Schenkel et al., 2018; Gulati et al., 2020; Xie et al., 2022
Arabidopsis thaliana		Benzaldehyde	C7H6O	HUMNYLRZRPPJDN-UHFFFAOYSA-N	100-52-7	not given	Schenkel et al., 2018
Arabidopsis thaliana		Benzeneactealdehyde	C8H8O	DTUQWGWMVIHBKE-UHFFFAOYSA-N	122-78-1	not given	Schenkel et al., 2018
Cucumis metuliferus CM3		Butanal, 3-methyl-	C5H10O	YGHRJJRRZDOVPD-UHFFFAOYSA-N	590-86-3	not given	Xie at al., 2022
Cucumis metuliferus CM3		2-Isopropylidene-3-methylhexa-3,5-dienal	C10H14O	NIEPGDUXTWPJLS-RMKNXTFCSA-N	1000191-76-5	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Pentadecanal-	C15H30O	XGQJZNCFDLXSIJ-UHFFFAOYSA-N	2765-11-9	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Hexadecanal	C16H32O	NIOYUNMRJMEDGI-UHFFFAOYSA-N	629-80-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		cis,cis-7,10,-Hexadecadienal	C16H28O	WIWVOAOSGQCJSL-HZJYTTRNSA-N	56829-23-3	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		cis-9-Hexadecenal	C16H30O	QFPVVMKZTVQDTL-FPLPWBNLSA-N	56219-04-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Heptadecanal	C17H34O	PIYDVAYKYBWPPY-UHFFFAOYSA-N	1000376-70-0	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Dodecenal, (E)-	C12H22O	SSNZFFBDIMUILS-ZHACJKMWSA-N	20407-84-5	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Tridecanal	C13H26O	BGEHHAVMRVXCGR-UHFFFAOYSA-N	10486-19-8	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		(E)-Tetradec-2-enal	C14H26O	WHOZNOZYMBRCBL-OUKQBFOZSA-N	51534-36-2	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Tetradecanal	C14H28O	UHUFTBALEZWWIH-UHFFFAOYSA-N	124-25-4	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Tridecenal, (E)-	C13H24O	VMUNAKQXJLHODT-VAWYXSNFSA-N	7069-41-2	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Dodecanal	C12H24O	HFJRKMMYBMWEAD-UHFFFAOYSA-N	112-54-9	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Undecenal	C11H20O	PANBRUWVURLWGY-MDZDMXLPSA-N	2463-77-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Undecanal	C11H22O	KMPQYAYAQWNLME-UHFFFAOYSA-N	112-44-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Formamide, N,N-dibutyl-	C9H19NO	NZMAJUHVSZBJHL-UHFFFAOYSA-N	761-65-9	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Benzaldehyde, 4-methoxy-	C8H8O2	ZRSNZINYAWTAHE-UHFFFAOYSA-N	123-11-5	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2,6-Nonadienal, (E,Z)-	C9H14O	HZYHMHHBBBSGHB-ODYTWBPASA-N	557-48-2	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		6-Nonenal, (Z)-	C9H16O	RTNPCOBSXBGDMO-ARJAWSKDSA-N	2277-19-2	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2,4-Heptadienal, (E,E)-	C7H10O	SATICYYAWWYRAM-VNKDHWASSA-N	4313-03-5	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3;		Benzaldehyde	C7H6O	HUMNYLRZRPPJDN-UHFFFAOYSA-N	100-52-7	not given	Xie at al., 2022; Schenkel et al., 2018; Lackus et al., 2018
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Heptanal	C7H14O	FXHGMKSSBGDXIY-UHFFFAOYSA-N	111-71-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Hexenal, (E)-	C6H10O	MBDOYVRWFFCFHM-SNAWJCMRSA-N	6728-26-3	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Hexenal	C6H10O	MBDOYVRWFFCFHM-UHFFFAOYSA-N	505-57-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Hexanal	C6H12O	JARKCYVAAOWBJS-UHFFFAOYSA-N	66-25-1	not given	Delory et al., 2016a; Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Pentenal, (E)-	C5H8O	DTCCTIQRPGSLPT-ONEGZZNKSA-N	1576-87-0	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Pentanal	C5H10O	HGBOYTHUEUWSSQ-UHFFFAOYSA-N	110-62-3	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Acetaldehyde	C2H4O	IKHGUXGNUITLKF-UHFFFAOYSA-N	75-07-0	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Methacrolein	C4H6O	STNJBCKSHOAVAJ-UHFFFAOYSA-N	78-85-3	not given	Xie at al., 2022

9.4 Table S1 continued Chemical compounds of plant root VOCs, collected in cited literature published between 2016-2022

Chemical compounds of plant root VOCs, collected during 2016-2022 yy.							
Plant	Functional groups	VOC compounds	Molecular Formula	InChIKey	CAS	Properties	References
Cucumis metuliferus CM3	Ketones	2(3H)-Benzofuranone, 3a,4,5,7a-tetrahydro-3a,6-	C10H14O2	NQWBFQXRASPNLB-UHFFFAOYSA-N	33722-72-4	not given	Xie at al., 2022
Cucumis metuliferus CM3		2-Pentadecanone, 6,10,14-trimethyl-	C18H36O	WHWDWIHXSPCOKZ-UHFFFAOYSA-N	502-69-2	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		trans-.beta.-Ionone	C13H20O	PSQYTAPXSHCGMF-BQYQJAHWSA-N	79-77-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-	C14H20O2	RDQSIADLBQFVMY-UHFFFAOYSA-N	719-22-2	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		5,9-Undecadien-2-one, 6,10-dimethyl-, (Z)-	C13H22O	HNZUNIKWNYHEJJ-XFXZXTDPSA-N	3879-26-3	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Ethanone, 1-(4-hydroxy-3,5-dimethoxyphenyl)-	C10H12O4	OJOBTAOGJIWAGB-UHFFFAOYSA-N	2478-38-8	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		(R,S)-5-Ethyl-6-methyl-3E-hepten-2-one	C10H18O	BCYUENXUQILNAA-VOTSOKGWSA-N	57283-79-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		3,5-Octadien-2-one	C8H12O	LWRKMRFJEUFXIB-UHFFFAOYSA-N	38284-27-4	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		1-Penten-3-one	C5H8O	JLIDVCMBCGBIEY-UHFFFAOYSA-N	1629-58-9	not given	Xie at al., 2022
Arabidopsis thaliana; pepper		camphor	C10H16O	DSSYKIVIOFKYAU-UHFFFAOYSA-N	21368-68-3	not given	Schenkel et al., 2018; Kihika et al., 2017
Arabidopsis thaliana	Alcohols	2-ethylhexan-1-ol	C8H18O	YIWUKEYIRIRTPP-UHFFFAOYSA-N	104-76-7	not given	Schenkel et al., 2018
Cucumis metuliferus CM3		2-Propanol, 1,1,1-trichloro-	C3H5Cl3O	HCMBPASAOZIEDZ-UHFFFAOYSA-N	76-00-6	not given	Xie at al., 2022
Cucumis metuliferus CM3		2-Penten-1-ol, (Z)-	C5H10O	BTSIZIIPFNVMHF-ARJAWSKDSA-N	1576-95-0	attract and kill *M. inc*	Xie at al., 2022
Cucumis metuliferus CM3		hexan-1-ol	C6H14O	ZSIAUFGUXNUGDI-UHFFFAOYSA-N	111-27-3	not given	Xie at al., 2022
Cucumber line Xintaimici; poplar		Benzyl alcohol	C7H8O	WVDDGKGOMKODPV-UHFFFAOYSA-N	100-51-6	not given	Xie at al., 2022; Lackus et al., 2018
Cucumber line Xintaimici		Bicyclo[3.1.1]hept-2-ene-2-methanol, 6,6-dimethyl-	C10H16O	RXBQNMWIQKOSCS-UHFFFAOYSA-N	515-00-4	not given	Xie at al., 2022
Cucumber line Xintaimici		Bicyclo[3.1.1]heptan-3-ol, 6,6-dimethyl-2-methylene-	C10H16O	LCYXQUJDODZYIJ-HACHORDNSA-N	547-61-5	not given	Xie at al., 2022
Cucumber line Xintaimici		4,8-Decadien-3-ol, 5,9-dimethyl-	C12H22O	PQUSMVMWVMGVGN-UHFFFAOYSA-N	67845-54-9	not given	Xie at al., 2022
Cucumber line Xintaimici		2-Octyn-1-ol	C8H14O	TTWYFVOMGMBZCF-UHFFFAOYSA-N	20739-58-6	not given	Xie at al., 2022
Cucumber line Xintaimici		Bicyclo[2.2.1]heptane-2,5-diol, 1,7,7-trimethyl-, (2-	C10H18O2	HLVIHBJQDKVEAL-LCFZEIEZSA-N	10359-41-8	not given	Xie at al., 2022
Cucumber line Xintaimici		Bicyclo[2.1.1]hexan-2-ol, 2-ethenyl-	C8H12O	YSGFFYIGUOYNID-UHFFFAOYSA-N	1000221-37-2	not given	Xie at al., 2022
Cucumber line Xintaimici		endo-Borneol	C10H18O	DTGKSKDOIYIVQL-CCNFQMFXSA-N	507-70-0	not given	Xie at al., 2022
Cucumber line Xintaimici		Cyclohexanol, 2,2-dimethyl-	C8H16O	BYBYZPFVXFPCND-UHFFFAOYSA-N	1193-46-0	not given	Xie at al., 2022
Cucumber line Xintaimici		11-Tridecyn-1-ol	C13H24O	QBYUWRZJJAYBJR-UHFFFAOYSA-N	33925-75-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2-Pentadecyn-1-ol	C15H28O	PFHRFJSUAGQBFE-UHFFFAOYSA-N	2834-00-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		p-Mentha-1(7),8(10)-dien-9-ol	C10H16O	SDDQNZKSVASSFO-UHFFFAOYSA-N	29548-13-8	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Neral	C10H16O	WTEVQBCEXWBHNA-YFHOEESVSA-N	106-26-3	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		alpha -Terpineol	C10H18O	WUOACPNHFRMFPN-SECBINFHSA-N	98-55-5	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		1-Ethynyl-1-cyclooctanol	C10H16O	DHAPUKCAOFQTIT-UHFFFAOYSA-N	55373-76-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		1-Hexanol, 2-ethyl-	C8H18O	YIWUKEYIRIRTPP-UHFFFAOYSA-N	104-76-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Eucalyptol	C10H18O	WEEGYLXZBRQIMU-UHFFFAOYSA-N	470-82-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		4-Ethylcyclohexanol	C8H16O	RVTKUJWGFBADIN-UHFFFAOYSA-N	4534-74-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		4-Penten-1-ol, 3-methyl-	C6H12O	VTCQTYOGWYLVES-UHFFFAOYSA-N	51174-44-8	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		1-Butanol, 3-methyl-	C5H12O	PHTQWCKDNZKARW-UHFFFAOYSA-N	123-51-3	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		1-Penten-3-ol	C5H10O	VHVMXWZXFBOANQ-UHFFFAOYSA-N	616-25-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		4-Penten-1-ol	C5H10O	LQAVWYMTUMSFBE-UHFFFAOYSA-N	821-09-0	not given	Xie at al., 2022
Achillea collina		sterols	C17H28O	FPXSXMFOYWRHDX-UHFFFAOYSA-N		not given	Kindlovits et al., 2018
Tomato	Organic acid	formic acid	CH2O2	BDAGIHXWWSANSR-UHFFFAOYSA-N	64-18-6	not given	Gulati et al., 2020
Arabidopsis thaliana		1-methyl ester dodecanoic acid	C13H26O2	UQDUPQYQJKYHQI-UHFFFAOYSA-N	111-82-0	not given	Schenkel et al., 2018
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Hexadecanoic acid, methyl ester	C17H34O2	FLIACVVOZYBSBS-UHFFFAOYSA-N	112-39-0	not given	Xie at al., 2022

9.4 Table S1 continued Chemical compounds of plant root VOCs, collected in cited literature published between 2016-2022

Chemical compounds of plant root VOCs, collected during 2016-2022 yy.							
Plant	Functional groups	VOC compounds	Molecular Formula	InChIKey	CAS	Properties	References
Cucumber line Xintaimici, *Cucumis metuliferus* CM3	Esters	1,2-Benzenedicarboxylic acid, bis(2-methylpropyl)	C16H22O4	MGWAVDBGNNKXQV-UHFFFAOYSA-N	84-69-5	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Propanoic acid, 2-methyl-, 3-hydroxy-2,2,4-	C12H24O3	DAFHKNAQFPVRKR-UHFFFAOYSA-N	77-68-9	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		2,2,4-Trimethyl-1,3-pentanediol diisobutyrate	C16H30O4	OMVSWZDEEGIJJI-UHFFFAOYSA-N	6846-50-0	not given	Xie at al., 2022
Cucumber line Xintaimici; pepper; tomato		Methyl salicylate	C8H8O3	OSWPMRLSEDHDFF-UHFFFAOYSA-N	119-36-8	attract second-stage larvae (J2) of *M.*	Xie at al., 2022; Murungi et at., 2018; Kihika et al., 2017
Cucumis metuliferus CM3		11-Dodecyn-1-ol acetate	C14H24O2	ANBOMSJGDBBKMR-UHFFFAOYSA-N	53596-78-4	undetected	Xie at al., 2022
Carex arenaria		γ-capro	not given	not given	not given	attract benefit bacteria from bulk soil	Schulz-Bohm et al., 2017
Carex arenaria		γ-deca	not given	not given	not given		Schulz-Bohm et al., 2017
Carex arenaria		γ-nonalactone	C9H16O2	OALYTRUKMRCXNH-UHFFFAOYSA-N	104-61-0		Schulz-Bohm et al., 2017
Achillea collina		Neryl esters	$C_{12}H_{20}O_2$	HIGQPQRQIQDZMP-FLIBITNWSA-N	141-12-8	not given	Kindlovits et al., 2018
Tomato	Aromatic compounds	Benzothiazol	C7H5NS	IOJUPLGTWVMSFF-UHFFFAOYSA-N	95-16-9	antifungal activity	Gulati et al., 2020
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Dibutyl phthalate	C16H22O4	DOIRQSBPFJWKBE-UHFFFAOYSA-N	84-74-2		Xie at al., 2022
Cucumis metuliferus CM3		Creosol	C8H10O2	PETRWTHZSKVLRE-UHFFFAOYSA-N	93-51-6	attract and kill *M. inco*	Xie at al., 2022
Poplar		salicylaldehyde	C7H6O2	SMQUZDBALVYZAC-UHFFFAOYSA-N	90-02-8	play a role as a nemati	Lackus et al., 2018
Cucumber line Xintaimici		Benzene, 1-ethenyl-4-methoxy-	C9H10O	UAJRSHJHFRVGMG-UHFFFAOYSA-N	637-69-4	not given	Xie at al., 2022
Cucumis metuliferus CM3		Benzene, (methoxymethyl)-	C8H10O	GQKZBCPTCWJTAS-UHFFFAOYSA-N	538-86-3	repel *M. incognita*	Xie at al., 2022
Carex arenaria		Benzofuran	C8H6O	IANQTJSKSUMEQM-UHFFFAOYSA-N	25086-73-1	antifungal activity	Schulz-Bohm et al., 2017
Pepper		Thymol	C10H14O	MGSRCZKZVOBKFT-UHFFFAOYSA-N	89-83-8	repel root-knot, cyst, and stubby root	Kihika et al., 2017
Centaurea stoebe ; tomato	Terpenes	(E)-β-caryophyllene	C15H24	NPNUFJAVOOONJE-IOMPXFEGSA-N	87-44-5	effect on the germination and growth of different sympatric neighbours	Gfeller et al., 2019; Gulati et al., 2020
Centaurea stoebe ; tomato		daucadiene	C15H24	CSLLMNDHZGLWRB-ZRNAQANOSA-N	not given		Gfeller et al., 2019; Gulati et al., 2020
Centaurea stoebe ; tomato		(E)-α-bergamotene	C15H24	YMBFCQPIMVLNIU-GRKKQISMSA-N	not given		Gfeller et al., 2019; Gulati et al., 2020
Centaurea stoebe ; tomato		humulene	C15H24	FAMPSKZZVDUYOS-HRGUGZIWSA-N	6753-98-6		Gfeller et al., 2019; Gulati et al., 2020
Centaurea stoebe ; tomato		(E)-β-farnesene	C15H24	JSNRRGGBADWTMC-NTCAYCPXSA-N			Gfeller et al., 2019; Gulati et al., 2020
Centaurea stoebe ; tomato		petasitene 1–3	C15H24	ZGKPBXWQOYDEMA-UHFFFAOYSA-N	443124-67-2		Gfeller et al., 2019; Gulati et al., 2020
Centaurea stoebe ; tomato; spinach; pepper; poplar		α-pinene	C10H16	GRWFGVWFFZKLTI-UHFFFAOYSA-N	80-56-8		Gfeller et al., 2019; Gulati et al., 2020; Murungi et at., 2018; Lackus et al., 2018; Kihika et al., 2017
Centaurea stoebe; tomato		β-myrcene	C10H16	UAHWPYUMFXYFJY-UHFFFAOYSA-N	123-35-3		Gfeller et al., 2019; Gulati et al., 2020
Achillea collina		β-sesquiphellandrene	C15H24	PHWISBHSBNDZDX-YSSOQSIOSA-N	20307-83-9	not given	Kindlovits et al., 2018
Achillea collina		albene	C12H18	HKLBEHRJWPWLOB-UHFFFAOYSA-N	38451-64-8	not given	Kindlovits et al., 2018
Achillea collina; poplar		β –pinene	C10H16	WTARULDDTDQWMU-UHFFFAOYSA-N	127-91-3	not given	Kindlovits et al., 2018; Lackus et al., 2018
Tomato; Pepper		p-cymene	C10H14	HFPZCAJZSCWRBC-UHFFFAOYSA-N	99-87-6	attract second-stage larvae (J2) of M.	Gulati et al., 2020; Kihika et al., 2017
Tomato		3-carene	C10H16	BQOFWKZOCNGFEC-DTWKUNHWSA-N	13466-78-9	not given	Gulati et al., 2020
Tomato		δ-3-carene	C10H16	BQOFWKZOCNGFEC-DTWKUNHWSA-N	13466-78-9	not given	Murungi et at., 2018
Tomato		Sabinene	C10H16	NDVASEGYNIMXJL-UHFFFAOYSA-N	3387-41-5	attract second-stage larvae (J2) of *M.*	Murungi et at., 2018
Tomato, spinach, poplar		Camphene	C10H16	CRPUJAZIXJMDBK-UHFFFAOYSA-N	79-92-5	not given	Murungi et at., 2018; Lackus et al., 2018
Tomato, spinach		Myrcene	C10H16	UAHWPYUMFXYFJY-UHFFFAOYSA-N	123-35-3	not given	Murungi et at., 2018
Tomato, spinach; pepper		β-ocimene	C10H16	IHPKGUQCSIINRJ-UHFFFAOYSA-N	13877-91-3	not given	Murungi et at., 2018; Kihika et al., 2017
Tomato, spinach		α-cedrene	C15H24	IRAQOCYXUMOFCW-YKURLNKLSA-N	11028-42-5	not given	Murungi et at., 2018
Tomato, spinach		β-cedrene	C15H24	DYLPEFGBWGEFBB-OSFYFWSMSA-N	546-28-1	not given	Murungi et at., 2018
Tomato, spinach; pepper		limonene	C10H16	XMGQYMWWDOXHJM-UHFFFAOYSA-N	138-86-3	attract second-stage larvae (J2) of *M.*	Murungi et at., 2018; Kihika et al., 2017
Cucumber line Xintaimici, Cucumis metuliferus CM3;		D-limonene	C10H16	XMGQYMWWDOXHJM-SNVBAGLBSA-N	5989-27-5	not given	Xie at al., 2022; Kihika et al., 2017;
Pepper		γ - Himachalene	C15H24	PUWNTRHCKNHSAT-UHFFFAOYSA-N	53111-25-4	not given	Kihika et al., 2017
Pepper		Allo-aromadendrene	C15H24	ITYNGVSTWVVPIC-OOAQSJESSA-N	25246-27-9	not given	Kihika et al., 2017
Pepper		Alpha-Muurolene	C15H24	QMAYBMKBYCGXDH-ZNMIVQPWSA-N	31983-22-9	not given	Kihika et al., 2017
Pepper		4,5-Di-epi-aristolochene	C15H24	YONHOSLUBQJXPR-JHIQODARSA-N		not given	Kihika et al., 2017
Pepper		γ - Gurjunene	C15H24	DUYRYUZIBGFLDD-UHFFFAOYSA-N	22567-17-5	not given	Kihika et al., 2017
Poplar		1,8- cineole	C10H18O	WEEGYLXZBRQIMU-UHFFFAOYSA-N	470-82-6		Lackus et al., 2018

9.4 Table S1 continued Chemical compounds of plant root VOCs, collected in cited literature published between 2016-2022

Chemical compounds of plant root VOCs, collected during 2016-2022 yy.							
Plant	Functional groups	VOC compounds	Molecular Formula	InChIKey	CAS	Properties	References
Tomato, spinach	Pyrazines	2-isopropyl-3-methoxypyrazine	C8H12N2O	NTOPKICPEQUPPH-UHFFFAOYSA-N	25773-40-4	attract second-stage larvae (J2) of *M.*	Murungi et at., 2018
Tomato, spinach; pepper; pepper		2-(methoxy)-3-(1-methylpropyl)pyrazine	C9H14N2O	QMQDJVIJVPEQHE-UHFFFAOYSA-N	24168-70-5	attract second-stage larvae (J2) of *M.*	Murungi et at., 2018; Kihika et al., 2017
Cucumis metuliferus CM3	Alkynes	1-Nonyne	C9H16	OSSQSXOTMIGBCF-UHFFFAOYSA-N	3452-09-3	might have ability of improvement plant	Xie at al., 2022
Cucumis metuliferus CM3		1-Octadecyne	C18H34	IYDNQWWOZQLMRH-UHFFFAOYSA-N	629-89-0	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		9-Eicosyne	C20H38	ARULVMGJDAAVBD-UHFFFAOYSA-N	71899-38-2	not given	Xie at al., 2022
Cucumis metuliferus CM3		4-Tetradecyne	C14H26	QWZXVDGVISCHQH-UHFFFAOYSA-N	60212-33-1	not given	Xie at al., 2022
Cucumis metuliferus CM3	Other hydrocarbones	Cyclohexene, 2,4-dimethyl-1-(1-	C11H18	DJNBXADZJNAMQR-UHFFFAOYSA-N	56763-60-1	not given	Xie at al., 2022
Cucumis metuliferus CM3		Cyclooctene, 3-(1-methylethenyl)-	C11H18	MZCVHZHOSLNLTO-VURMDHGXSA-N	61233-78-1	not given	Xie at al., 2022
Cucumis metuliferus CM3		Trans-β-ocimene	C10H16	IHPKGUQCSIINRJ-CSKARUKUSA-N	3779-61-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		1,1'-Biphenyl, 3,4-diethyl-	C16H18	ZTLWBQOFTIFRHI-UHFFFAOYSA-N	61141-66-0	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		(S,1Z,6Z)-8-Isopropyl-1-methyl-5-	C15H24	GAIBLDCXCZKKJE-ACWLMNNXSA-N	317819-80-0	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		3-Undecen-5-yne, (Z)-	C11H18	RVNPFAOWVMGBBF-ALCCZGGFSA-N	74744-27-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		exo-7-(trans-1-Propenyl)bicyclo[4.2.0]oc	C11H16		107983-42-6	not given	Xie at al., 2022
Cucumber line Xintaimici, Cucumis metuliferus CM3		p-Xylene	C8H10	URLKBWYHVLBVBO-UHFFFAOYSA-N	106-42-3	attractant to natural enemies of	Xie at al., 2022; Li et al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Cyclohexane, 2-ethenyl-1,1-dimethyl-3-methylene-	C11H18	YRBXRKRLOGXJAN-UHFFFAOYSA-N	95452-08-7	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3	Alkenes	1-Tetradecene	C14H28	HFDVRLIODXPAHB-UHFFFAOYSA-N	1120-36-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Cyclohexane, 1,1,3-trimethyl-2-(3-	C15H30	UDBAOHWDISNFAQ-UHFFFAOYSA-N	54965-05-8	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3	Alkanes	Hexane, 2,3,4-trimethyl-	C9H20	RUTNOQHQISEBGT-UHFFFAOYSA-N	921-47-1	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3,		Tetradecane	C14H30	BGHCVCJVXZWKCC-UHFFFAOYSA-N	629-59-4	not given	Xie at al., 2022; Kihika et al., 2017
Tomato		n-alkanes	(CH4)n	–	–	not given	Gulati et al., 2020
Cucumber line Xintaimici, Tomato, spinach; pepper		Tridecane	C13H28	IIYFAKIEWZDVMP-UHFFFAOYSA-N	629-50-5	attract second-stage larvae (J2) of *M.*	Murungi et at., 2018; Xie at al., 2022; Kihika et al., 2017
Pepper		Decane	C10H22	DIOQZVSQGTUSAI-UHFFFAOYSA-N	124-18-5	not given	Kihika et al., 2017
Pepper		Undecane	C11H24	RSJKGSCJYJTIGS-UHFFFAOYSA-N	1120-21-4	not given	Kihika et al., 2017
Pepper		Dodecane	C12H26	SNRUBQQJIBEYMU-UHFFFAOYSA-N	112-40-3	not given	Kihika et al., 2017
Cucumber line Xintaimici, *Cucumis metuliferus* CM3	Unidentify groups	7-Oxabicyclo[4.1.0]heptane	C8H12O2	AVROMNDRDNRBOK-UHFFFAOYSA-N	106-87-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Oxime-, methoxy-phenyl	C8H9NO2	HUYDCTLGGLCUTE-HJWRWDBZSA-N	1000222-86-6	not given	Xie at al., 2022
Cucumber line Xintaimici, *Cucumis metuliferus* CM3		Borane, compd. with dimethylamine (1:1)	C2H10BN	RUOMFVPJBOADHA-UHFFFAOYSA-N	74-94-2	not given	Xie at al., 2022
Tomato	Sulfur compounds	dimethyl trisulfide	C2H6S3	YWHLKYXPLRWGSE-UHFFFAOYSA-N	3658-80-8	antifungal activity	Gulati et al., 2020
Cucumber line Xintaimici, *Cucumis metuliferus* CM3	Nitrogen compounds	Cyclohexene, 1-(2-nitro-2-propenyl)-	C9H13NO2	QOKFSIOIZAOVBW-UHFFFAOYSA-N	80255-20-5	not given	Xie at al., 2022
Tomato; *Carex arenaria*		Benzonitrile	C6H5(CN)	JFDZBHWFFUWGJE-UHFFFAOYSA-N	100-47-0	antifungal activity	Gulati et al., 2020; Schulz-Bohm et al., 2017
Cucumber line Xintaimici, *Cucumis metuliferus* CM3	Chloro compounds	Hexane, 1-chloro-5-methyl-	C7H15Cl	YESHSLGUAPTMLI-UHFFFAOYSA-N	33240-56-1	not given	Xie at al., 2022
Tomato		beclomethasone dipropionate	C28H37ClO7	KUVIULQEHSCUHY-XYWKZLDCSA-N	5534_09_8	not given	Gulati et al., 2020

9.5 Table S2 – VOC components in healthy and P. teres infected barley samples

				start		after 12 days				start				after 14 days			
		0309_marpa_kez	0309_marpa_Ctr	0307_Harrington_kez_seb	0307Harrington_kez_intact	0320Harpa1	0320Harpa2	0322Harpak1	0322Harpak2	0322árpakez1	0322árpakez2	0322árpa_control1	(soil+pot)	0405 Árpa Hunor1	0405 Árpa Hunor3	0405Árpa_Ctr	(soil+pot)
		Initium_treated	Initium_control	Harrington_treated0_WOUNDED	Harrington_treated0	Harrington_treated1	Harrington_treated2	Harrington_control1	Harrington_control2	Hunor_treated1	Hunor_treated2	Hunor_kontrol1	blank	Hunor_treated1	Hunor_treated2	Hunor_control2	blank
RT (min)	Component name	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area
3.12	Pentane, 2,3-dimethyl-	10315	19014	10184	9608	8131	6923	-	5931	1714	-	-	2086	6234	2395	2384	2120
3.307	toluene	4187	40089	6488	2466	58803	47160	15384	53968	1714	-	4661	2086	-	-	-	-
3.459	3-hexanone	7134	28132	10325	3582	29266	23538	14246	13770	5272	1633	3098	13295	3143	3092	-	2032
3.505	2-hexanone	2713.53	2935.42	7237	1716.03	34375	28772	18980	15596	6661	5719	5731	12838	4353	4192	-	2327
3.556	3-hexanol	2992	13352	21504	4957	20600	17608	12397	14081	12243	4750	3360	8775	6769	2922	-	-
3.607	2-hexanol	3161	33674	-	-	26390.16	18229	10990.46	28854	13409	21598	2411	3425	-	-	-	-
3.628	octane	17177	121388	291954	239808	142519.11	143856	95801.74	67122	3889	12415	7825	46126	147133	128197	101831	109170
4.28	Guanidine	113119.04	-	-	-	-	-	-	-	28335	101032	2683.31	-	4702.48	15502.01	10968.19	-
4.3	2-hexenal, (E)-	190823	4940.62	4182	5634.65	14661	18690	8438	35552	28765	67547	8369	1500	6180	23993	13366	935
4.324	3-hexen-1-ol	108178	14688	15167	18333	11819.24	-	-	-	36743	31748	-	-	11717	-	-	-
4.43	heptane,2,4-dimethyl-	-	-	-	-	-	-	-	-	-	-	-	-	9569	11722	12783	8183
4.46	Ethylbenzene	30808	120584	97750	90244	156536	95460	26267	95580	-	-	16083	16816	17721	16379	-	-
4.489	1-hexanol	12433.53	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
4.569	p-xylene	36109	257526	222496	193621	356525	249345	73859	256388	24452	17067	25034	31306	25080	16561	26562	12795
4.666	octatriene, 1,3-trans-5-trans-	9080	21305	7780	11183	10428	9970	3867.88	5693.03	8574	11366	8836	1472	8373	9113	5994	2058
4.827	Dimethyl-3,5 heptene-3*	3006.54	8291.28	9486.41	8599.69	11560.81	5419.83	1068.85	2831.49	3607	3192	2216	3295	1080	2271	1297	441
4.874	styrene	2134.76	19720.3	-	-	56844.97	26566.55	8739.41	3953.17	-	-	-	-	-	-	-	-
4.912	Benzene, 1,3-dimethyl-*	16194.9	135931	120072.3	92185.15	122017.91	81915.75	18351.14	93327.78	11981	6697	6173	9391	2776	2696	6936	614
4.954	nonane	16403.04	4702.71	36139.17	29318.58	42391.31	31930.61	8355.66	4634.97	1926	1169	1896	4658	17094	15106	12181	12587
4.975	heptanal	2172.84	4007.36	2372	2324.55	47077.11	25684.56	2125.1	2098.12	2001	3564	2659	1368	-	-	-	-
5.11	1-Ethyl-3-methylcyclohexane (c,t)*	1572.37	13143.4	13176.63	13050.68	3552.72	3922.44	-	1488.29	1205	-	-	2444	-	-	-	-
5.372	7,7-Dimethylcycloheptatriene	6700.93	20665.3	27554.68	21419.48	24259.08	14935.3	1781.82	9569.63	523.1	1412.96	-	1898.39	-	-	-	-
5.456	Cyclopentane, 1-methyl-2-propyl-	4957.43	18693	7831.72	8066.2	15778.33	9555.42	632.25	2624.91	339	-	1335	1171.1	3882	2545.92	6488	-
5.52	(+)-alpha-Pinene (((1R,5R)-2,6,6-Trimethylbicyclo[3.1.1]hept-2-ene))	26920.4	96242.6	53500.09	53197.94	159972.9	101637.86	1451.86	43308.3	-	-	10614	1454	16732.37	31404.12	26461.32	15879.82
5.57	2-propanol, 1-butoxy-	3339312.5	81624.6	17376.57	15745.33	8394.49	6963.82	-	20764.48	215051	391022	822.57	-	460575.8	790555.4	5070.88	-
5.77	2-pentanol,4,4-dimethyl-	-	22263.3	15039.92	15339.26	38845.46	21977.85	1303.26	7487.82	8326.8	15384.4	2472.12	-	19798.27	29927.46	5478.24	-
5.811	Benzene, propyl-	-	42857.3	37735.88	25922.1	45082.78	21965.82	2632.5	13555.88	-	-	2904	3131	-	-	-	-
5.785	Butane, 1-(1-methylpropoxy)-	84653.46	-	-	-	-	-	-	-	3556	8338	2472	2333	16747	28419	5478	1426.95
5.929	benzene, 1-ethyl-3-methyl-*	5252.49	67237.5	152683.49	104790.55	137464.44	70298.3	17721.29	40990.73	1784	3575	2000	5414	3188	4201	9730	1757
5.95	benzene, 1-ethyl-2-methyl-	-	54956.4	31807.15	24548.78	54205.98	35577.54	6267.51	15149.01	-	-	1416	1166	-	-	1904	-
6.034	1,2,4-Trimethylbenzene*	-	8432.81	29496.95	23259.06	41122.63	19470.44	2244.61	9274.88	-	-	-	-	-	-	-	-
6.06	2-hexene,3,5,5-trimethyl	94224.43	178325	-	-	-	-	-	-	118948	118415	161087	-	113471	126467	31301	5452
6.132	1-Octen-3-ol	53585.77	96616.2	4381.52	3687.31	4645.37	2431.92	-	2656.53	88292	99403.7	124655.05	-	53164.42	64698.56	23916.12	-
6.216	2 /3/ 4-Ethyltoluene	11046.54	59303.4	115358.68	100623.17	54972.97	34580.16	4263.77	35229.45	-	-	-	-	-	-	-	-
6.263	5-Hepten-2-one, 6-methyl-	17334.51	16349.6	7406.53	4082.24	31584.59	26281.66	2822.74	2264.1	12674	19788	14176.8	-	71811	88882	18162	-
6.355	Heptane, 2,2,4,6,6-pentamethyl-	38309.43	103904	55772.08	43004.29	15559.21	15905.69	-	23154.51	-	-	-	-	-	-	-	-
6.427	Mesitylene	-	161022	170975.74	107565.3	154856.95	80703.03	13139.79	57631.66	-	-	-	-	-	-	-	-
6.516	octanal	6637.35	4505.19	3651.09	4218.04	34748.3	38248.37	992.99	8580.45	10471	12689	8713	10659	7932	11707	6379.84	10116
6.558	3-Hexen-1-ol, acetate, (Z)-	708151.96	340909	84612.56	-	2890.74	1442.73	-	1509.45	116696	129267	86057.24	-	3466.88	8407.02	912.9	-
6.69	(+)-3-Carene	10399.7	94107.2	57540.74	41264.3	48333.4	25081.38	1827.37	15326.16	4911	1761	4541	14001	8611	10393	11227.79	5494
6.892	Benzene, 1,3,5-trimethyl-*	41838.88	82821.7	105307.41	83823.38	106944.97	53579.09	10780.72	34681.18	9442	8186	15493	7953	21863	31929.8	19531.22	10204
6.972	D-Limonene	24888.83	117700	32741.57	34869.93	92244.93	52505.41	5784.23	19633.63	6185	6927	23844	3382	17297	30367.6	12005	9869.96
7.06	nona-3,5-dien-2-ol	-	-	-	-	-	-	-	-	3509.1	6793.73	7553.58	-	7711.96	7895.52	893.14	-
7.103	Indane	-	21740.1	42638.01	30095.36	24722.84	13161.72	1386.9	8479.64	-	-	-	-	-	-	-	-
7.124	levomenthol	-	-	-	-	-	-	-	-	-	-	-	-	8434.08	11146.35	-	-
7.229	β-ocimene (Z)- (1,3,6-Octatriene, 3,7-dimethyl-, (Z)-)	9135.39	15002.7	15834.14	11818.89	3986.67	3398.16	-	1516.49	25565	216766	55122.87	-	60873.9	8624.44	13497.3	-
7.365	?Pentatriacontane	4576.01	18983	8525.4	11036.99	7290.92	2255.33	538.89	3039.16	2939.5	8533.33	21749.83	14163.84	18327	14532	15384	10728.83
7.635	1,2-oxolinalool (.alpha.-Methyl-.alpha.-[4-methyl-3-pentenyl]oxiranemethanol)	3405	4895	1540	3145	617	378	-	-	28505	33578	83938.1	-	12997.57	17569.87	-	35882
7.69	Trichloroacetic acid, 6-ethyl-3-octyl ester	-	-	-	-	-	-	-	-	-	-	-	-	7505.42	8393.97	-	-
7.75	2-Piperidinone, N-[4-bromo-n-butyl]-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
7.82	1-Phenyl-1-butene	9240.68	19943.5	22910.68	16900.53	16182.02	7753.65	1106.44	4118.27	-	-	-	-	12500.29	33314	21647	8321
7.86	5-tridecane	-	-	-	-	-	-	-	-	-	-	-	-	14648	27148	759.97	18908
7.94	Benzene, 1-ethenyl-4-ethyl-	-	-	-	-	-	-	-	-	653	1779	1469	3404	16055	30533	20772	11333
8.01	Linalool (1,6-Octadien-3-ol, 3,7-dimethyl-)*	13518.96	63928.3	3281.74	1598.69	41544.32	19416.61	-	-	389102	228579	2737866.6	-	24911.03	19399.78	11532.31	-
8.04	1-Octanol, 2-butyl-	1415.75	18596.8	5980.12	8072.83	-	-	-	-	-	-	-	8232.48	-	-	-	-
8.08	nonanal	17932.77	25019.7	19754.83	13645.3	201558.95	252540.6	8966.25	21291.37	46235	41381.5	55349.7	-	12511.12	28263.9	13320.83	-
8.188	1-Butoxy-2-propanol acetate	14463.52	1938.68	4433.16	2270.53	2658.3	1109.19	-	-	-	-	-	-	-	-	-	-
8.209	Cyclohexanol, 2,6-dimethyl-	15620.07	1528.83	1741.25	-	1563.57	1087.34	-	1024.85	-	12237.7	-	-	16973.69	12954.92	-	-
8.32	Benzene, 1,2,3,4-tetramethyl- *	-	10712.1	16786.75	14351.85	9936.06	5015.13	-	3198.9	-	-	-	-	3213	2524	4925	-
8.39	Benzene, methyl(1-methylethyl)-	-	8606.23	11400.75	8293.32	12218.74	4991.93	-	2299.75	-	-	-	-	3308	2410	3375	-
8.973	Azulene	38972.5	52762.8	40777.9	47091.29	7289.94	9175.93	1530.04	11995.93	10195	9151.16	13345	1991	22083	33377.77	21414.47	17738
9.019	benzaldehyde, 4-ethyl	-	-	-	-	-	-	-	-	6108	4542	5532	2229.62	24194	49971.91	34294.77	32114
9.032	3-Ethylbenzaldehyde	51534.31	57700.4	60616.07	58163.53	47705.76	20421.5	7517.05	14219.1	827	1173	554	671	15783	24515	-	-
9.34	4-tert-Butylanisole (Benzene, 1-(1,1-dimethylethyl)-4-methoxy-)	-	-	-	-	-	-	-	-	-	-	-	-	80412.21	48549.14	-	-
9.4	Naphthalene	7443.92	57157.9	15440.64	11535.01	294366.55	123210.9	25312.58	18146.7	-	-	-	-	-	-	-	-
9.488	tetradecane*	5810.43	16052.5	14885.55	12399.32	38879.85	18248.7	2255.27	3541.88	1924	5503	6819.24	8611	13348	14607	15553	15428
9.585	decanal	20895.25	38582	39010.99	19537.62	189955.47	274224.9	6769.02	16822.51	63614	52391	37629.8	8376	9095.94	69763.54	8735	6069
9.75	2-Pinen-4-one (bicyclo[3.1.1]hept-3-en-2-one, 4,6,6-trimethyl-)	16309.25	36216.5	44109.91	19437.46	21583.47	16033.49	3202.07	21441.56	-	-	-	-	-	-	-	-
9.902	?exo-2-Hydroxycineole	23782.04	18996	17891.01	15396.23	15450.54	10764.8	1766.13	9482.86	937	8155	2824	9707	15113	17718	5664	6432
9.991	?2,6-Dimethyldecalin (Naphthalene, decahydro-2,6-dimethyl-)*	9363.6	19783.9	13994.87	17239.7	9749.15	3786.53	412.44	1538.3	-	-	-	16836	15546.49	27281	13373	13069.79
10.206	3,5-Heptadienal, 2-ethylidene-6-methyl- *	43870.19	47879.3	41097.91	30231.07	20440.5	12768.48	3772.3	15859.39	14783	14159	10540	13336	50389.71	70629.68	42308.93	50551
10.489	m-Ethylacetophenone*	214462.78	242212	217447.67	233108.01	105071.78	68649.3	14244.08	65106.69	56783	48151	49064	31705	178412	279805	161501	168729
10.641	Pentatriacontane*	14758.79	48901.6	39330.03	33039.27	32655.71	28053.47	2030.1	8482.93	9061	10784.3	34752	30881	22548	38888	29968	12399.54
10.759	Ethanone, 1-(4-ethylphenyl)-	100753.04	116989	100608.45	105330.36	47859.87	23778.71	4478	21461.22	17256	11968.5	17103	14318	73232	94729	67002	55727
10.899	Tridecane	61270.06	86340.7	54282.97	66958.74	103632.04	65671.24	4529.81	29119.35	13036	32274	21141	9458	120178	234351	106720	82589
11.532	triacetin	17505.65	29379.6	32917.41	15465.51	107536.44	98445.53	3156.22	123882.2	4139.8	22293	37683.99	19817	31900	105019	35646	35868
11.76	eugenol	175517.88	10387.5	6650.54	9780.31	2981.29	3321.97	0	2874.44	-	-	-	-	40110	15179.69	14018	11916
12.233	tridecane, 6-methyl-	66545.27	126104	126843.43	111551.2	64971.47	65467.44	7992.86	34916.71	15079	37787	69208	42515.43	156503	282304	146174	143432
12.414	2-Dodecen-1-yl(-)succinic anhydride	-	-	-	-	-	-	-	-	-	-	-	-	16024.46	35555	4841	7649.69

9.5 Table S2 continued – VOC components in healthy and *P. teres* infected barley samples

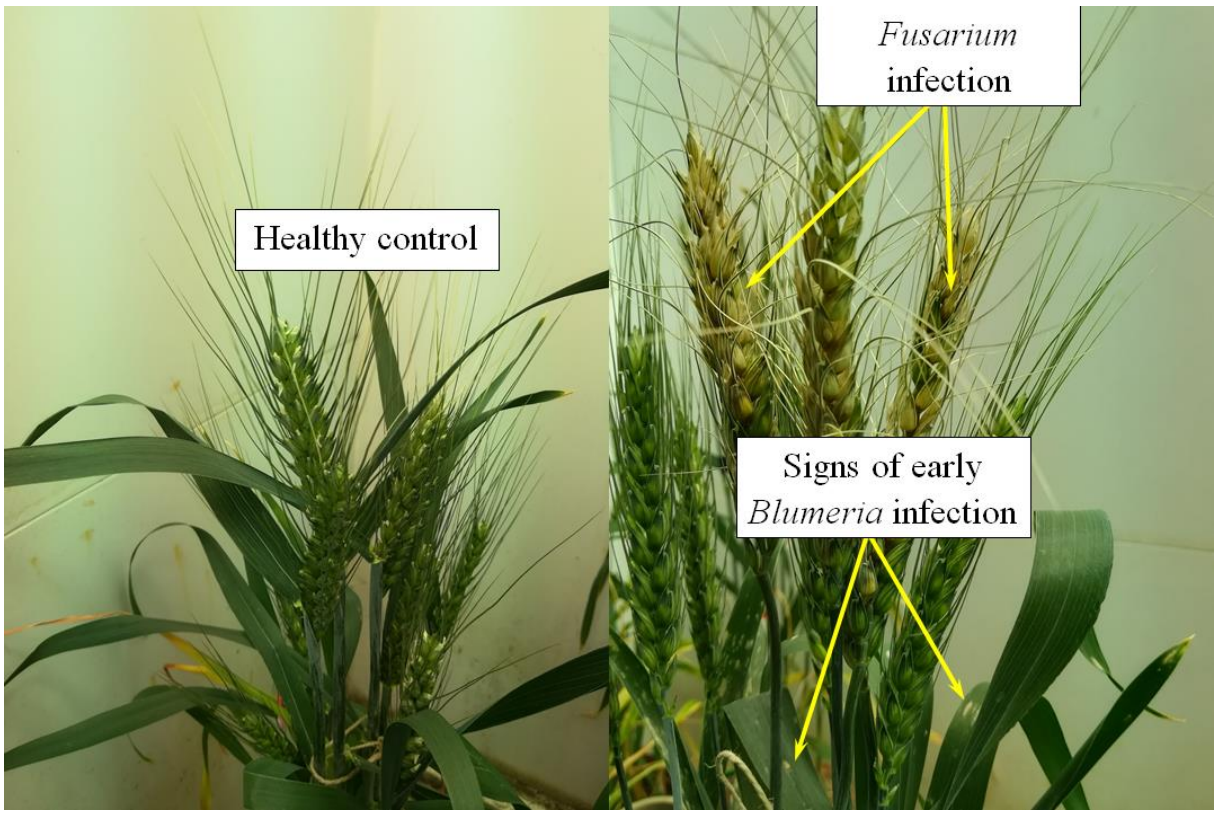
				start		after 12 days				start	after 14 days						
		0309_marpa_kez	0309_marpa_Ctr	0307_Harrington_kez_seb	0307Harrington_kez_intact	0320Harpa1	0320Harpa2	0322Harpak1	0322Harpak2	0322árpakez1	0322árpakez2	0322árpa_control1	(soil+pot)	0405 Árpa Hunor1	0405 Árpa Hunor3	0405Árpa_Ctr	(soil+pot)
		Initium_treated	Initium_control	Harrington_treated0_WOUNDED	Harrington_treated0	Harrington_treated1	Harrington_treated2	Harrington_control1	Harrington_control2	Hunor_treated1	Hunor_treated2	Hunor_kontrol1	blank	Hunor_treated1	Hunor_treated2	Hunor_control2	blank
RT (min)	Component name	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area
12.554	Junipene*	6782.88	15549.6	11523.72	28716.71	27928.01	15573.54	1134.08	10168.89					12321	25144	11789.54	16211
12.697	caryophyllene	24830.21	40032.5	-	-	-	-	-	-	29619	102401	95974.71	-	-	-	-	-
14.015	1-Iodododecane	21945.32	16300.2	38368.39	21102.13	12009.21	10238.78	1582.19	9638.46	8979	18579.7	29809.94	11527	19531	17409.53	23106	9272
14.25	hexadecane, 2-methyl-*	6391.43	7561.87	12475.67	7734.35	6424.77	6654.21	1077.45	2175.49	1809	1774	7586	-	10013.61	14705	9983	9116.98
14.69	hexacosane*	26624.11	40376.3	42748.62	25839.19	27767.7	30351.84	2743.8	10589.96	11573	39394	44071	14497	47646	55962	83631	59721.72
14.745	Propanoic acid, 2-methyl-, 2-(hydroxymethyl)-1-propylbutyl ester*	30167.67	27458.2	43279.48	21677.92	58295.54	45822	10362.46	35529.01	6997	152929	84760	5017	17649.53	46765.65	12785	36436
14.939	4,4-Dimethyl-1,1-bis(1-methyl-1H-imidazol-2-yl)pentan-3-one	8872.39	9860.22	11168.84	6514.16	5814.01	5097.6	-	3655.08	1812	4419	7673	-	-	-	-	-
15.433	Octane, 1,1'-oxybis-	-	31926	-	-	4405.46	-	-	-	6167	-	-	-	657	-	-	-
15.526	butyl dodecyl ether	59473.55	37283.1	95586.35	46813.01	4342.4	2866.27	-	2261.39	-	-	-	-	-	-	-	-
15.632	??1-(4-ISOPROPYLPHENYL)-2-METHYLPROPYL ACETATE	26072.06	14601.9	11639.42	4435.99	7842.63	4669.67	1044.81	4967.55	-	7717	8732	-	-	-	-	-
15.817	Pentadecane*	23466.17	18530.8	21353.54	16928.86	27956.37	18536.9	3129.76	8646.07	19202	31957	26594	1902	22228	34169	30041	38163
15.885	?n-cetyl thiocyanate	6796.9	4875.18	8359.52	7119.91	9690.66	11839.89	1930.82	3308.15	-	-	-	-	-	-	-	-
15.969	?tricosane	14466.76	6874.81	17679.22	13936.91	9071.37	7099.19	0	6053.05	6324	5480	7321	5031	9095	12225	27541	3468
16.012	?pentadecanal	2530.16	8562.97	3292.06	2208.8	1682.49	2095.5	971.84	1975.4	-	-	-	-	-	-	-	-
16.434	tricosane	19879.16	14480.5	22189.54	17525.03	10493.46	12830.45	1941.4	15029.28	5729	12709	9456	4530	21659.97	14355	36691	6922
16.856	Benzenesulfonamide, N-butyl-	729576.37	353645	342772.31	252619.99	444453.53	417271.6	201953.1	225920.11	27388	21832.5	148209.86	122632	389315	260242	267726	279199
17.164	Isopropyl myristate	7474.71	6139.26	8843.59	3771.61	71210.08	50204.44	-	66803.64	26570	1402428	723376	13852	18851	43211	8012	11757
17.392	2-Pentadecanone, 6,10,14-trimethyl-	616255.1	28225.3	12311.24	11808.63	259353.56	104518.35	8456.76	10813.83	130866	255286	31542.08	-	9864090	10335639	50665.17	-
17.557	2-Hexadecen-1-ol, 3,7,11,15-tetramethyl-, acetate, [R-[R*,R*-(E)]]- (??phytol, acetate)	-	-	-	-	-	-	-	-	-	-	-	-	109888	162046.4	-	-
17.743	Z,E-2,13-Octadecadien-1-ol	9691.85	2844.85	3668.48	2000.44	4313.53	3034.24	-	2753.21	-	-	-	-	17976	19606.54	-	-
17.962	homosalate	4971.03	1388.17	4557.97	1268.03	20143.68	21837.98	677.9	17515.59	2702	31500	2626314	21558	-	-	-	-
18.241	?Methyl 3-[[(1,1-Dimethylethoxy)carbonyl]methylamino]methyl]-6-chloro-2-hexenoate	8841.69	3863.32	6984.06	3742.76	4128.02	4925	2689.44	4215.76	-	-	-	-	-	-	-	-
18.41	Dodecyl isobutyl carbonate	118927.12	36908.4	28737.44	19277.1	19580.09	18374.62	-	17263.84	29922	81819	122248	-	439	620	-	-
18.621	1,2-Benzenedicarboxylic acid, dibutyl ester*	94000.18	45823.7	43239.57	33636.46	58239.46	46250.96	10436.22	53044.45	27279	72789.1	83913	11510.17	28284.52	50391.94	27891	32553
18.9	?Neopentyl 2,2-dimethylpropanoate	8440.02	8059.01	10791.56	6930.93	9280.93	4607.79	905.74	3776.85	3386	13448	6657	-	-	-	-	-
20.732	?Neopentyl 2,2-dimethylpropanoate*	11180.75	5800.56	6742.53	9831.83	7188.43	7676.13	2434.75	22478.77	2797	42613	25165	2083	5655	9244	3264	3264
21.593	??Octadecanoic acid	18216.62	11406.9	4967.39	13111.35	5857.29	2782.74	1867.29	35674.48	7696	98188.4	46740.43	3453	4100	15339	11312	6647
23.308	??1,2-Benzenedicarboxylic acid, bis(2-ethylhexyl) ester	45691.94	1367.11	72609.2	66416.89	157725.9	161546.72	101759	72554.21	-	-	-	51501	432679.8	251908	256622.5	321728

9.6 Table S3 English common names, retention times, calculated and literature retention index for semi-standard non-polar column, CAS numbers and InCHI keys, quantitative ion m/z, compound class and solvent used for stock solutions (1 mg/ml) of components and their submixtures (100 µg/ml)

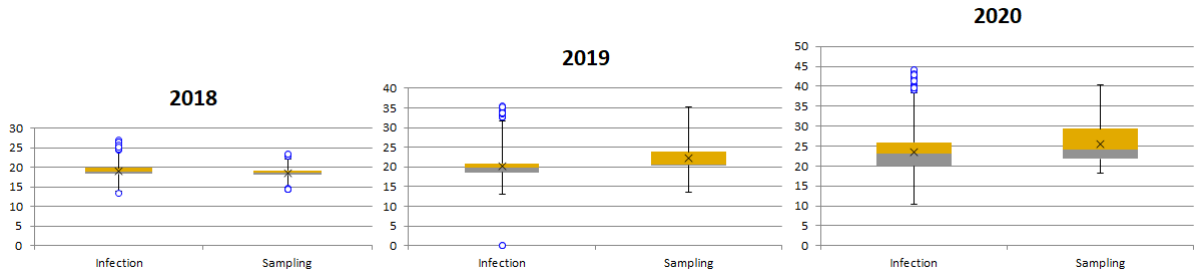
Submix number	English common name	Retention time (minutes)	Retention index calculated	Retention index from NIST17 library or other sources as indicated (values in parentheses indicates number of records)	CAS number	InchiKey	quant. m/z	Compound class	Solvent used
MIX1	2-Hexenal, (E)-	6.894	851.69	851±5 (53)	6728-26-3	MBDOYVRWFFCFHM-SNAWJCMRSA-N	83	Aldehyde	Ethanol
	p-Xylene	7.319	868.67	865±7 (178)	106-42-3	URLKBWYHVLBVBO-UHFFFAOYSA-N	106	Aromatic hydrocarbon	
	2-Heptenal, (E)-	9.506	956.16	958±4 (74)	18829-55-5	NDFKTBCGKNOHPJ-AATRIKPKSA-N	83	Aldehyde	
	1-Octen-3-ol	10.095	979.30	980±2 (355)	3391-86-4	VSMOENVRRABVKN-UHFFFAOYSA-N	72	Alcohol	
	3-Carene	10.851	1010.86	1011±2 (336)	13466-78-9	BQOFWKZOCNGFEC-UHFFFAOYSA-N	93	Terpene	
	α-Terpinolene	12.709	1089.91	1088±2 (607)	586-62-9	MOYAFQVGZZPNRA-UHFFFAOYSA-N	93	Terpene	
	Isopulegol	13.993	1148.62	1146±3 (32)	89-79-2	ZYTMANIQRDEHIO-UHFFFAOYSA-N	93	Terpene	
	Pulegone	16.011	1243.98	1237±3 (81)	89-82-7	NZGWDASTMWDZIW-UHFFFAOYSA-N	152	Terpene	
	Caryophyllene	19.258	1423.78	1419±13 (983) 1432 on HP-5MS	87-44-5	NPNUFJAVOOONJE-WDZFZDKYSA-N	93	Sesquiterpene	
	trans-Farnesol	21.844	1726.75	1722±3 (76)	106-28-5	CRDAMVZIKSXKFV-YFVJMOTDSA-N	81	Sesquiterpene	
MIX2	3-Hexen-1-ol, (E)-	6.899	850.80	852±3 (41)	928-97-2	UFLHIIWVXFIJGU-ONEGZZNKSA-N	82	Alcohol	Ethanol
	o-Xylene	7.901	892.02	887±8 (178)	95-47-6	CTQNGGLPUBDAKN-UHFFFAOYSA-N	91	Aromatic hydrocarbon	
	α-Pinene	8.952	934.12	937±3 (995)	80-56-8	GRWFGVWFFZKLTI-UHFFFAOYSA-N	93	Terpene	
	1-Heptanol	9.866	969.89	970±2 (68)	111-70-6	BBMCTIGTTCKYKF-UHFFFAOYSA-N	70	Alcohol	
	Phenol	10.141	980.47	980±4 (94)	108-95-2	ISWSIDIOOBJBQZ-UHFFFAOYSA-N	94	Phenol	
	3-Hexen-1-ol, acetate, (Z)-	10.776	1007.05	1005±2 (74)	3681-71-8	NPFVOOAXDOBMCE-PLNGDYQASA-N	82	Ester	
	R-(+)-Limonene	11.297	1029.85	1030±2 (1004)	138-86-3	XMGQYMWWDOXHJM-UHFFFAOYSA-N	93	Terpene	
	Nonanal	13.046	1104.54	1104±2 (556)	124-19-6	GYHFUZHODSMOHU-UHFFFAOYSA-N	70	Aldehyde	
	Decanal	15.264	1206.09	1206±2 (406)	112-31-2	KSMVZQYAVGTKIV-UHFFFAOYSA-N	82	Aldehyde	
	Longifolene	19.093	1420.69	1405±5 (89) 1413.4 on HP-5MS	475-20-7	PDSNLYSELAIEBU-UHFFFAOYSA-N	93	Sesquiterpene	
MIX3	Hexanal	5.602	797.71	800±2 (453)	66-25-1	JARKCYVAAOWBJS-UHFFFAOYSA-N	82	Aldehyde	Ethanol
	m-Xylene	7.313	867.26	866±7 (170)	108-38-3	IVSZLXZYQVIEFR-UHFFFAOYSA-N	91	Aromatic hydrocarbon	
	Benzaldehyde	9.592	959.33	962±3 (416)	100-52-7	HUMNYLRZRPPJDN-UHFFFAOYSA-N	105	Aldehyde	
	5-Hepten-2-one, 6-methyl-	10.279	986.79	986±2 (222)	110-93-0	UHEPJGULSIKKTP-UHFFFAOYSA-N	108	Ketone	
	α-Phellandrene	10.709	1004.74	1005±2 (509)	99-83-2	OGLDWXZKYODSOB-UHFFFAOYSA-N	93	Terpene	
	p-Cymene	11.204	1025.52	1025±2 (820)	99-87-6	HFPZCAJZSCWRBC-UHFFFAOYSA-N	119	Aromatic hydrocarbon	
	Phenol, 4-ethyl-2-methoxy-	16.788	1281.67	1282±4 (46)	2785-89-9	CHWNEIVBYREQRF-UHFFFAOYSA-N	137	Phenol/Ether	
	trans-β-Ionone	19.962	1494.76	1486±4 (211)	79-77-6	PSQYTAPXSHCGMF-BQYQJAHWSA-N	177	Sesquiterpene	
MIX4	2-Hexanol	5.624	798.91	801±10 (19)	626-93-7	QNVRIHYSUZMSGM-UHFFFAOYSA-N	69	Alcohol	Ethanol
	2-Heptanone	7.855	889.80	891±2 (212)	110-43-0	CATSNJVOTSVZJV-UHFFFAOYSA-N	71	Ketone	
	(5Z)-Octa-1,5-dien-3-ol	9.952	973.83	975+-2 PUBCHEM	50306-18-8	APFBWMGEGSELQP-WAYWQWQTSA-N	57	Alcohol	
	3-Octanone	10.27	986.58	986±3 (101)	106-68-3	RHLVCLIPMVJYKS-UHFFFAOYSA-N	72	Ketone	
	2-methylphenol (o-cresol)	11.886	1054.13	1054±9 (53)	95-48-7	QWVGKYWNOKOFNN-UHFFFAOYSA-N	108	Phenol	
	3-methylphenol (m-cresol)	12.371	1074.96	1075±5 (40)	108-39-4	RLSSMJSEOOYNOY-UHFFFAOYSA-N	108	Phenol	
	Linalool	12.951	1099.62	1099±2 (976)	78-70-6	CDOSHBSSFJOMGT-UHFFFAOYSA-N	93	Terpene alcohol	
	Phenylethyl Alcohol	13.245	1113.30	1116±5 (262)	60-12-8	WRMNZCZEMHIOCP-UHFFFAOYSA-N	91	Alcohol	
	β-Citronellol	15.717	1228.52	1228±3 (181)	106-22-9	QMVPMAAFGQKVCJ-UHFFFAOYSA-N	69	Terpene	
MIX5	2-Hexanone	5.372	789.93	790±3 (106)	591-78-6	QQZOPKMRPOGIEB-UHFFFAOYSA-N	58	Ketone	Ethanol
	3-Hexanol	5.496	794.86	797±7 (12)	623-37-0	ZOCHHNOQQHDWHG-UHFFFAOYSA-N	59	Alcohol	
	1-Hexanol	7.31	868.02	868±4 (223)	111-27-3	ZSIAUFGUXNUGDI-UHFFFAOYSA-N	56	Alcohol	
	2-Heptanol	8.105	899.48	900±4 (53)	543-49-7	CETWDUZRCINIHU-UHFFFAOYSA-N	45	Alcohol	
	3-Octanol	10.487	995.14	994±3 (124)	589-98-0	NMRPBPVERJPACX-UHFFFAOYSA-N	83	Alcohol	
	Benzyl alcohol	11.397	1033.70	1036±4 (174)	100-51-6	WVDDGKGOMKODPV-UHFFFAOYSA-N	79	Aromatic alcohol	
	1-Nonanol	14.832	1171.28	1173±2 (61)	143-08-8	ZWRUINPWMLAQRD-UHFFFAOYSA-N	70	Alcohol	
	2-Undecanone	17.05	1294.01	1294±2 (160)	112-12-9	KYWIYKKSMDLRDC-UHFFFAOYSA-N	71	Ketone	

9.6 Table S3 continued English common names, retention times, calculated and literature retention index for semi-standard non-polar column, CAS numbers and InCHI keys, quantitative ion m/z, compound class and solvent used for stock solutions (1 mg/ml) of components and their submixtures (100 µg/ml)

Submix number	English common name	Retention time (minutes)	Retention index calculated	Retention index from NIST17 library or other sources as indicated (values in parentheses indicates number of records)	CAS number	InchiKey	quant. m/z	Compound class	Solvent used
MIX6	Isopentyl acetate	7.539	877.31	876±2 (100)	123-92-2	MLFHJEHSLIIPHL-UHFFFAOYSA-N	70	Ester	n-Hexane
	Acetic acid, pentyl ester	8.486	915.33	911±6 (40)	628-63-7	PGMYKACGEOXYJE-UHFFFAOYSA-N	70	Ester	
	β-Myrcene	10.395	991.59	991±2 (840)	123-35-3	UAHWPYUMFXYFJY-UHFFFAOYSA-N	93	Terpene	
	Acetophenone	12.165	1066.26	1065±4 (134)	98-86-2	KWOLFJPFCHCOCG-UHFFFAOYSA-N	105	Aromatic ketone	
	(-)-Bornyl acetate	16.968	1289.48	1284±2 (8)	5655-61-8	KGEKLUUHTZCSIP-UHFFFAOYSA-N	93	Ester	
	Decane, 1-bromo-	18.142	1356.25	1337±3 (3)	112-29-8	MYMSJFSOOQERIO-UHFFFAOYSA-N	135	Halogenated hydrocarbon	
	α-Cedrene	19.177	1425.48	1411±3 (93)	469-61-4	IRAQOCYXUMOFCW-UHFFFAOYSA-N	93	Sesquiterpene	
	α-Humulene	19.663	1467.76	1454±3 (792)	6753-98-6	FAMPSKZZVDUYOS-HRGUGZIWSA-N	93	Sesquiterpene	
MIX7	Butanoic acid, ethyl ester	5.668	802.57	802±2 (154)	105-54-4	OBNCKNCVKJNDBV-UHFFFAOYSA-N	88	Ester	n-Hexane
	(-)-β-Pinene	10.022	976.82	N/A	18172-67-3	WTARULDDTDQWMU-UHFFFAOYSA-N	93	Terpene	
	cis-β-Ocimene	11.519	1039.02	1037±7 (20)	13877-91-3	IHPKGUQCSIINRJ-CSKARUKUSA-N	93	Aromatic hydrocarbon	
	trans-β-Ocimene	11.765	1049.51	1037±7 (20)	13877-91-3	IHPKGUQCSIINRJ-CSKARUKUSA-N	93	Aromatic hydrocarbon	
	cis-Limonene oxide	13.722	1135.35	1136±N/A (1)	13837-75-7	CCEFMUBVSUDRLG-AEJSXWLSSA-N	93	Terpene	
	trans-Limonene oxide	13.825	1140.06	1138±3 (36)	203719-54-4	CCEFMUBVSUDRLG-BBBLOLIVSA-N	93	Terpene	
	1-Dodecene	14.966	1192.12	1190±3 (40)	112-41-4	CRSBERNSMYQZNG-UHFFFAOYSA-N	83	Unsaturated hydrocarbon	
	Valencene	20.081	1504.34	1492±3 (152)	4630-07-3	QEBNYNLSCGVZOH-UHFFFAOYSA-N	93	Sesquiterpene	
	trans-Nerolidol	20.664	1554.12	1564±2 (277)	40716-66-3	FQTLCLSUCSAZDY-SDNWHVSQSA-N	93	Sesquiterpene alcohol	
	Methyl jasmonate	21.351	1648.20	1638±17 (7)	1211-29-6	GEWDNTWNSAZUDX-SNAWJCMRSA-N	83	Ester	
MIX8	3(2H)-Furanone, dihydro-2-methyl-	5.755	805.99	809±3 (22)	3188-00-9	FCWYQRVIQDNGBI-UHFFFAOYSA-N	72	Oxygen-containing heterocyclic compound	n-Hexane
	Styrene	7.852	889.75	893±5 (91)	100-42-5	PPBRXRYQALVLMV-UHFFFAOYSA-N	104	Aromatic hydrocarbon with an unsaturated side chain	
	Butanoic acid, 3-hydroxy-, ethyl ester	8.961	933.97	944±6 (22)	5405-41-4	OMSUIQOIVADKIM-UHFFFAOYSA-N	88	Ester	
	Hexanoic acid, ethyl ester	10.598	1007.89	1000±2 (157)	123-66-0	SHZIWNPUGXLXDT-UHFFFAOYSA-N	88	Ester	
	Benzoic acid, methyl ester	12.844	1095.37	1094±3 (86)	93-58-3	QPJVMBTYPHYUOC-UHFFFAOYSA-N	105	Ester	
	Benzene, 1,3-dimethoxy-	14.448	1168.47	1166±13 (8)	151-10-0	DPZNOMCNRMUKPS-UHFFFAOYSA-N	138	Ether	
	α-Terpineol	14.986	1192.68	1189±2 (811)	98-55-5	WUOACPNHFRMFPN-UHFFFAOYSA-N	93	Terpene	
	(S)-(+)-Carvone	16.092	1247.08	1246±7 (14)	2244-16-8	ULDHMXUKGWMISQ-VIFPVBQESA-N	82	Terpene	
	Methyl eugenol	18.956	1406.33	1402±2 (165)	93-15-2	ZYEMGPIYFIJGTP-UHFFFAOYSA-N	178	Ether	
	Dodecane, 1-bromo-	20.757	1549.73	1549±N/A (1)	143-15-7	PBLNBZIONSLZBU-UHFFFAOYSA-N	135	Halogenated hydrocarbon	
MIX9	Propanoic acid, butyl ester	8.343	909.58	908±4 (28)	590-01-2	BTMVHUNTONAYDX-UHFFFAOYSA-N	75	Ester	n-Hexane
	Anisole	8.520	916.75	920±4 (26)	100-66-3	RDOXTESZEPMUJZ-UHFFFAOYSA-N	108	Ether	
	Acetic acid, hexyl ester	10.933	1013.90	1011±4 (112)	142-92-7	AOGQPLXWSUTHQB-UHFFFAOYSA-N	61	Ester	
	Benzoic acid, ethyl ester	14.533	1172.39	1171±2 (58)	93-89-0	MTZQAGJQAFMTAQ-UHFFFAOYSA-N	105	Ester	
	Methyl salicylate	15.062	1196.48	1192±2 (145)	119-36-8	OSWPMRLSEDHDFF-UHFFFAOYSA-N	120	Ester	
	Citral	16.603	1272.06	1276±N/A (1)	5392-40-5	WTEVQBCEXWBHNA-JXMROGBWSA-N	84	Terpene	
	Eugenol	18.287	1365.38	1357±3 (355)	97-53-0	RRAFCDWBNXTKKO-UHFFFAOYSA-N	164	Allylbenzene	
	Geranyl acetate	18.653	1386.62	1382±3 (206)	105-87-3	HIGQPQRQIQDZMP-DHZHZOJOSA-N	93	Ester	
	β-Cedrene	19.286	1435.27	1421±3 (63)	546-28-1	DYLPEFGBWGEFBB-UHFFFAOYSA-N	93	Sesquiterpene	
	Caryophyllene oxide	20.933	1601.24	1581±2 (669) 1593 on HP-5MS	1139-30-6	NVEQFIOZRFFVFW-UHFFFAOYSA-N	93	Sesquiterpene oxide	
MIX10	Octane	5.619	800.00	800	111-65-9	TVMXDCGIABBOFY-UHFFFAOYSA-N	71	open-chain, saturated hydrocarbon	n-Hexane
	Nonane	8.110	900.00	900	111-84-2	BKIMMITUMNQMOS-UHFFFAOYSA-N	71		
	Decane	10.607	1000.00	1000	124-18-5	DIOQZVSQGTUSAI-UHFFFAOYSA-N	71		
	Undecane	12.960	1100.00	1100	1120-21-4	RSJKGSCJYJTIGS-UHFFFAOYSA-N	71		
	Dodecane	15.145	1200.00	1200	112-40-3	SNRUBQQJIBEYMU-UHFFFAOYSA-N	71		
	Tridecane	17.179	1300.00	1300	629-50-5	IIYFAKIEWZDVMP-UHFFFAOYSA-N	71		
	Tetradecane	18.885	1400.00	1400	629-59-4	BGHCVCJVXZWKCC-UHFFFAOYSA-N	71		
	Pentadecane	20.039	1500.00	1500	629-62-9	YCOZIPAWZNQLMR-UHFFFAOYSA-N	71		
	Hexadecane	20.925	1600.00	1600	544-76-3	DCAYPVUWAIABOU-UHFFFAOYSA-N	71		
	Heptadecane	21.660	1700.00	1700	629-78-7	NDJKXXJCMXVBJW-UHFFFAOYSA-N	85		
	Octadecane	22.296	1800.00	1800	593-45-3	RZJRJXONCZWCBN-UHFFFAOYSA-N	85		
	Nonadecane	22.870	1900.00	1900	629-92-5	LQERIDTXQFOHKA-UHFFFAOYSA-N	85		
	Eicosane	23.395	2000.00	2000	112-95-8	CBFCDTFDPHXCNY-UHFFFAOYSA-N	85		
	Heneicosane	23.886	2100.00	2100	629-94-7	FNAZRRHPUDJQCJ-UHFFFAOYSA-N	85		
	Docosane	24.352	2200.00	2200	629-97-0	HOWGUJZVBDQJKV-UHFFFAOYSA-N	85		



9.7 Figure S3 Powdery mildew symptoms on wheat plants weakened by *Fusarium* disease.



9.8 Figure S4 Comparative boxplots of temperature conditions during the incubation period (left) and the sampling day (right) in three experimental years.

9.9 Supplementary Method Artificial inoculation and pathotype determination of *Blumeria graminis* f.sp. *tritici* (Hamow et al. 2021).

The systematic study of pathotype specification of the wheat powdery mildew pathogen (*Blumeria graminis* f.sp. *tritici*) population in Hungary goes back to almost 50 years. The survey inspects the alterations in the composition of pathotypes and their corresponding virulence genes in this dynamically changing fungal pathogen. The collection and propagation of monosporic cultures on seedlings differ from year to year, depending on weather conditions, with an average number of tested monosporic isolates of 190-200 in a winter season.

For the initial collection step, 14 susceptible 'trap' wheat cultivars with different genetic backgrounds are sown in outdoor pots. Monosporic colonies still growing separately are picked and inoculated on 7-days-old susceptible plants of 'Carsten V' (no known *Pm* resistance gene). The plants serving for the propagation of monosporic inocula are grown from sowing until application in a greenhouse (16 °C, 14 h light) under isolated circumstances in pots covered with glass bells. During the 3 weeks of propagation occasional gentle hitting ensures that the quantity of conidiospores becomes sufficient for artificial inoculation of a differential genotype set based on the description of Frauenstein et al. (1979).

The differential set (see Table below) consists of genotypes carrying the following *Pm* resistance genes: *Pm1a*, *Pm2*, *Pm2+Mld*, *Pm3b*, *Pm4b*, *Pm5a* and *Pm8*. The genotypes are arranged in rows containing approximately 12 seedlings each and grown under isolated circumstances in wooden cases covered with glass boxes. When the first leaves of plants are about 8 cm in size, the glass lid is opened for the time of inoculation and spores are scattered over the leaves. Each pot covered with glass bell serves as inoculum for one box only. In 7-10 days, the reaction type and severity of infection is evaluated based on visible powdery mildew symptoms on the leaves. Information is gained about the composition of the collected population according to the pathotype reactions described by Frauenstein et al. (1979). Selected isolates are maintained on plants under glass bell for further examination.

In the present study, prevalent pathotypes of the powdery mildew population were chosen in each greenhouse season (2018-2020). Pathotype 51 is the most aggressive one as it is virulent on all eight wheat genotypes of the differential set, the colonies on the leaves are abundant and spore production is not hampered by plant defence mechanisms. The presence of pathotype 51 was expected, as it has had the highest incidence in Martonvásár throughout 30 years (an average of 21.6% in the period of 1990-2020), with an increasing tendency. In the last five years, the mean frequency of pathotype 51 was 41.6%, with values of 37.7%, 37.4% and 61.7% in the three consecutive greenhouse seasons of the present study. Although pathotype 71 occurred only sporadically in the past, it had precipitous emergence in the last two years with frequencies of

59.2% and 35.2%, respectively. Pathotype 71 is avirulent on wheat genotypes carrying the *Pm3b* allele (see Figure below). These two pathotypes were the most abundant, altogether representing approximately 97% in the powdery mildew population during the seasons 2018/2019 and 2019/2020.

Differential set of cultivars with corresponding powdery mildew (*Pm*) resistance genes (adapted from Frauenstein et al. 1979)

No.	Test cultivar	*Pm* gene
1	'Carsten V'	none
2	'Salzmünde 14/44'	*Pm8*
3	'Red Fern'	*Pm2*
4	'Axminster'	*Pm1a*
5	Halle Stamm 13471	*Pm2+Mld*
6	'Weihenstephaner M1'	*Pm4b*
7	'Hope'	*Pm5a*
8	'Chul'	*Pm3b*

Representative reaction of the differential tester set to inoculation of *Blumeria graminis* f.sp. *tritici*. Inoculation was applied by manually shaking conidiospores of pathotype 71 onto single leaves of 7-days-old tester plants (stages 11-12 at the Zadoks scale, Zadoks et al. 1974).

Experimental setup and numbers of independent replicate samples from headspaces of *Bgt*-inoculated wheat plants in the greenhouse ('Carsten V') in three consecutive years (2018-2020) and in a growth chamber ('Mv Suba' and 'Mv Kolompos', 2020)

		Greenhouse					Growth chamber	**Grand**
Treatment	DAI	2018	2019	2020	Subtotal	Treatment total	2020	**total**
Control	7	4+4	-	4+4	16	40	8+8	**56**
	14	4+4	4+4	4+4	24			
Inoculated	7	4+4	-	4+6*	18	48	8+8	**64**
	14	4+4	6*+6*	4+6*	30			
Subtotal		16+16	10+10	16+20	88	88	16+16	**120**
Total (Year)		32	20	36			32	
Analysis type		untargeted	untargeted	targeted			untargeted	
(VOC no.)		(48)	(48)	(6)				

DAI: days after inoculation; *four replicate inoculations by pathotype 51 + two replicates by pathotype 71

References

Frauenstein, K., Meyer, H., Wolfram, H., (1979): Pathotypen von *Erysiphe graminis* DC.f.sp. *tritici* Marchal und *E. graminis* DC.f.sp. *hordei* Marchal in Europa. Arch. Phytopathol. Plant Protect. 15, 391–399. https://doi.org/10.1080/03235407909437497.

Zadoks, J.C., Chang, T.T., Konzak, C.F., (1974): A decimal code for the growth stages of cereals. Weed Res. 14, 415–421. https://doi.org/10.1111/j.1365-3180.1974.tb01084.x.

9.10 Table S4 Detailed characterization and reported occurrence of the identified VOCs

No.	NAME[a]	CAS No.[b]	InChIKey[c]	ChEBI[d]	PubChem CID[e]	KEGG[f]	KNApSAcK[g]	Wheat plant[h]	Blumeria[h]	Literature	RT min[i]	RI calc.[j]	RI lit. (NIST17 / PubChem)[k]	*m/z* quant.[l]	Scan event	Compound class
1	Octane	111-65-9	TVMXDCGIABBOFY-UHFFFAOYSA-N	17590	356	C01387	C00035857	ND	ND	-	5.91	800	800	71	Scan	aliphatic hydrocarbon
2	Heptane, 2,4-dimethyl-	2213-23-2	AUKVIBNBLXQNIZ-UHFFFAOYSA-N		16656			ND	ND	-	6.45	821.2	821±1 (41)	85	Scan	acyclic hydrocarbon
3	**1,3-Octadiene**	**1002-33-1**	**QTYUSOHYEPOHLV-FNORWQNLSA-**	**89638**	**517653**			**ND**	**ND**	**-**	**6.54**	**824.9**	**827±1 (9)**	**54**	**Scan**	**acyclic hydrocarbon**
4	Ethylbenzene	100-41-4	YNQLUTRBYVCPMQ-UHFFFAOYSA-N	16101	7500	C07111		ND	ND	-	7.43	860.3	855	91	Scan	aromatic hydrocarbon
5	Octane, 4-methyl-	2216-34-4	DOGIHOCMZJUJNR-UHFFFAOYSA-N		16665			ND	ND	-	7.53	864.2	863	85	Scan	acyclic hydrocarbon
6	*m*-Xylene	108-38-3	IVSZLXZYQVIEFR-UHFFFAOYSA-N	28488	7929	C07208	C00035778	ND	ND	-	7.63	868.2	866±7 (170	91	Scan	aromatic hydrocarbon
7	**1,3-*cis*,5-*cis*-Octatriene**	**40087-62-5**	**HOXGZVUCAYFWGR-SFECMWDFSA-N**		**5367394**			**ND**	**ND**	**-**	**7.9**	**878.7**	**879**	**79**	**Scan**	**acyclic hydrocarbon**
8	3-Heptanone	106-35-4	NGAZZOYFWWSOGK-UHFFFAOYSA-N	50139	7802			ND	ND	-	8.09	886.5	887±3 (33)	85	Scan	ketone
9	Styrene	100-42-5	PPBRXRYQALVLMV-UHFFFAOYSA-N	27452	7501	C07083	C00037855	ND	ND	-	8.18	890.1	893±5 (91)	104	Scan	aromatic hydrocarbon
10	*o*-Xylene	95-47-6	CTQNGGLPUBDAKN-UHFFFAOYSA-N	28063	7237	C07212		ND	ND	-	8.22	891.7	887±8 (178)	91	Scan	aromatic hydrocarbon
11	Nonane	111-84-2	BKIMMITUMNQMOS-UHFFFAOYSA-N	32892	8141		C00034882	ND	ND	-	8.43	900	900	71	Scan	aliphatic hydrocarbon
12	α-Pinene	80-56-8	GRWFGVWFFZKLTI-UHFFFAOYSA-N	36740	440968	C06308	C00035786	+	ND	3,9,12	9.3	934.6	935+-7	93	SIM	monoterpene
13	Benzaldehyde	100-52-7	HUMNYLRZRPPJDN-UHFFFAOYSA-N	17169	240	D02314	C00034452	+	ND	1,12	9.95	960.5	962±3 (416)	106	Scan	aldehyde
14	Benzene, 1-ethyl-3-methyl-	620-14-4	ZLCSFXXPPANWQY-UHFFFAOYSA-N	77512	12100	C14522		ND	ND	-	9.98	961.9	957±8 (67)	105	Scan	aromatic hydrocarbon
15	Benzene, 1,3,5-trimethyl- (Mesytilene)	108-67-8	AUHZEENZYGFFBQ-UHFFFAOYSA-N	34833	7947	C14508		ND	ND	-	10.16	969.1	972±9	105	Scan	aromatic hydrocarbon
16	**1-Heptanol**	**111-70-6**	**BBMCTIGTTCKYKF-UHFFFAOYSA-N**	**43003**	**8129**		**C00035700**	**ND**	**ND**	**-**	**10.19**	**970.2**	**970±2 (68)**	**70**	**SIM**	**alcohol/ fatty alcohol**
17	**(5Z)-Octa-1,5-dien-3-ol**	**50306-18-8**	**APFBWMGEGSELQP-WAYWQWQTSA-N**		**6430307**			**ND**	**ND**	**-**	**10.3**	**974.5**	**975±2**	**57**	**SIM**	**alcohol/ fatty alcohol**
18	β-Pinene	127-91-3	WTARULDDTDQWMU-UHFFFAOYSA-N	50025	14896	C09882	C00000816	+	ND	5,12	10.37	977.3	979, 974	93	SIM	monoterpene
19	**1-Octen-3-ol**	**3391-86-4**	**VSMOENVRRABVKN-UHFFFAOYSA-**	**34118**	**18827**	**C14272**	**C00029423**	**+**	**ND**	**1,3,4,9,11,13**	**10.43**	**979.8**	**980±2 (355)**	**72**	**SIM**	**alcohol/ fatty alcohol**
20	**3-Octanone**	**106-68-3**	**RHLVCLIPMVJYKS-UHFFFAOYSA-N**	**80946**	**246728**	**C17145**	**C00034765**	**ND**	**ND**	**-**	**10.62**	**987.4**	**986±3 (101)**	**72**	**SIM**	**ketone**
21	β-Myrcene	123-35-3	UAHWPYUMFXYFJY-UHFFFAOYSA-N	17221	31253	C06074	C00000853	+	ND	1,3,5,9	10.73	991.8	991	93	SIM	monoterpene
22	Benzene, 1,2,4-trimethyl- (pseudo-Cumene	95-63-6	GWHJZXXIDMPWGX-UHFFFAOYSA-N	34039	7247	C14533		ND	ND	-	10.78	993.7	990±6 (83)	105	Scan	aromatic hydrocarbon
23	Decane	124-18-5	DIOQZVSQGTUSAI-UHFFFAOYSA-N	41808	15600			ND	ND	-	10.94	1000	1000	71	Scan	aliphatic hydrocarbon
24	3-Carene	13466-78-9	BQOFWKZOCNGFEC-UHFFFAOYSA-N	7	26049	C11382	C00011044	+	ND	4	11.21	1011.5	1011±2 (336)	93	SIM	monoterpene
25	*p*-Cymene	99-87-6	HFPZCAJZSCWRBC-UHFFFAOYSA-N	28768	7463	C06575	C00003040	+	ND	12	11.54	1025.6	1025±2 (820)	119	Scan	monoterpene
26	(+)- Limonene	138-86-3	XMGQYMWWDOXHJM-UHFFFAOYSA-	15384	22311	D00194	C00000823	+	ND	1,3,9,12	11.63	1029.6	1030±2 (1004)	93	SIM	monoterpene
27	Indane	496-11-7	PQNFLJBBNBOBRQ-UHFFFAOYSA-N	37911	10326			ND	ND	-	11.8	1036.7	1029±11 (36)	117	Scan	policyclic aromatic hydrocarbon
28	Benzene, 1,2-diethyl-	135-01-3	KVNYPFKFSJPBJ-UHFFFAOYSA-N		8657			ND	ND	-	12.14	1050.9	1045±8 (22)	105	Scan	aromatic hydrocarbon
29	Acetophenone	98-86-2	KWOLFJPFCHCOCG-UHFFFAOYSA-N	27632	7410	C07113	C00002685	+	ND	4	12.51	1067	1065±4 (134)	105	Scan	ketone
30	Benzene, 2-ethyl-1,3-dimethyl-	2870-04-4	CHIKRULMSSADAF-UHFFFAOYSA-N		17877			ND	ND	-	12.83	1080.3	1080±20 (12)	119	Scan	aromatic hydrocarbon
31	3-Octanol, 3,7-dimethyl-	78-69-3	DLHQZZUEERVIGQ-UHFFFAOYSA-N	84242	6548			ND	ND	-	13.25	1098	1100±13 (8)	73	Scan	alcohol/ fatty alcohol
32	Undecane	1120-21-4	RSJKGSCJYJTIGS-UHFFFAOYSA-N	46342	14257		C00032443	ND	ND	-	13.29	1100	1100	71	Scan	aliphatic hydrocarbon
33	Nonanal	124-19-6	GYHFUZHODSMOHU-UHFFFAOYSA-N		31289		C00030828	+	ND	1,2,9	13.39	1104.3	1104±2 (556)	70	Scan	aldehyde/ fatty aldehyde
34	Benzene, 1,2,3,4-tetramethyl-	488-23-3	UOHMMEJUHBCKEE-UHFFFAOYSA-N		10263			ND	ND	-	13.68	1117.8	1116±9 (32)	119	Scan	aromatic hydrocarbon
35	Benzene, 1,2,3,5-tetramethyl-	527-53-7	BFIMMTCNYPIMRN-UHFFFAOYSA-N		10695			ND	ND	-	13.76	1121.5	1117±9 (24)	119	Scan	aromatic hydrocarbon
36	Benzaldehyde, 3-ethyl-	34246-54-3	LLYXUFQXCNIGDG-UHFFFAOYSA-N		118623			ND	ND	-	14.73	1165.7	1168±N/A (1)	134	Scan	aldehyde
37	Benzaldehyde, 4-ethyl-	4748-78-1	QNGNSVIICDLXHT-UHFFFAOYSA-N		20861			ND	ND	-	15.04	1180	1180±16 (5)	134	Scan	aldehyde
38	Naphthalene	91-20-3	UFWIBTONFRDIAS-UHFFFAOYSA-N	16482	931	C00829	C00001259	+	ND	8	15.18	1186.4	1182±8 (183)	128	Scan	policyclic aromatic hydrocarbon
39	Dodecane	112-40-3	SNRUBQQJIBEYMU-UHFFFAOYSA-N	28817	8182	C08374	C00001248	ND	ND	-	15.48	1200	1200	71	Scan	aliphatic hydrocarbon
40	Decanal	112-31-2	KSMVZQYAVGTKIV-UHFFFAOYSA-N	31457	8175	C12307	C00030099	ND	ND	-	15.6	1206	1206±2 (406)	70	Scan	aldehyde
41	Undecane, 2,6-dimethyl-	17301-23-4	MFUPKUZLTKVMFM-UHFFFAOYSA-N		28453			ND	ND	-	15.76	1214.1	1210±3 (18)	71	Scan	acyclic hydrocarbon
42	Ethanone, 1-(4-ethylphenyl)-	937-30-4	NODGRWCMFMEGJH-UHFFFAOYSA-N		13642			ND	ND	-	17.21	1284.8	1277±4 (8)	133	Scan	ketone
43	Tridecane	629-50-5	IIYFAKIEWZDVMP-UHFFFAOYSA-N	35998	12388	C13834	C00048561	ND	ND	-	17.52	1300	1300	71	Scan	aliphatic hydrocarbon
44	Tridecane, 3-methyl-	6418-41-3	NLHRRMKILFRDGV-UHFFFAOYSA-N		110848			ND	ND	-	18.72	1374.4	1371±1 (15)	71	Scan	acyclic hydrocarbon
45	Tetradecane	629-59-4	BGHCVCJVXZWKCC-UHFFFAOYSA-N	41253	12389		C00035879	ND	ND	-	19.14	1400	1400	71	Scan	aliphatic hydrocarbon
46	Longifolene	475-20-7	PDSNLYSELAIEBU-GUIRCDHDSA-N	6530	289151	C09699	C00003162	ND	ND	-	19.35	1418.7	1413±5	93	SIM	sesquiterpene
47	β-Caryophyllene	87-44-5	NPNUFJAVOOONJE-GFUGXAQUSA-N	10357	5281515	C09629	C00003110	+	ND	1,2,5.6,7,10	19.52	1434.2	1423-1442	93	SIM	sesquiterpene
48	Pentadecane	629-62-9	YCOZIPAWZNQLMR-UHFFFAOYSA-N	28897	12391	C08388	C00001265	+	ND	5	20.25	1500	1500	71	Scan	aliphatic hydrocarbon

In the order of elution; bold, identified marker VOC — 13 +, 35 ND; 48 ND

[a] according to the NIST/EPA/NIH Mass Spectral Library v17 and the Wiley Registry of Mass Spectral Data, 10th edn

[b] Chemical Abstracts Service registry number

[c] the IUPAC International Chemical Identifier format (27 characters)

[d] Chemical Entities of Biological Interest database Identifier

[e] PubChem Compound ID

[f] Kyoto Encyclopedia of Genes and Genomes database identifier

[g] KNApSAcK family database identifier

[h] absence or presence (+) in wheat plants or Blumeria in databases and literature; ND, not detected

[i] Retention Time in min

[j] Retention Index calculated, experimentally determined using *n*-alkane retention indices

[k] Retention Index literature, from corresponding data in NIST v17 and the PubChem repository

[l] selected fragment ion (*m/z*) for quantitation

Literature (see next sheet)	Development
[1]Buttery et al. 1982	(20-30 cm oat)
[2]Buttery et al. 1985	(15-20 cm wheat)
[3]König et al. 1995	(flowering wheat and rye)
[4]Birkett et al. 2004	(flowering wheat)
[5]Piesik et al. 2010	(5-6 weeks old wheat, barley, oat)
[6]Wenda-Piesik et al. 2010	(5-6 weeks old wheat)
[7]Wenda-Piesik 2011	(6 weeks old wheat)
[8]Cruz et al. 2012	(12 weeks old wheat)
[9]Hartikainen et al. 2012	(2 and 4 weeks old wheat and oat)
[10]Delaney et al. 2013	(6 weeks old wheat and barley)
[11]Gfeller et al. 2013	(1 and 3 weeks old barley)
[12]Timmusk et al. 2014	(2-3 weeks old wheat)

9.11 Table S5 QC data for injection PM *B. graminis* BVOC related reference mixture

Two year follow up on chromatographic stability, sensitivity, linearity and reproducibility (0.05-5 µg/ml)

		1-heptanol (SIM - *m/z* 70)				**1-octen-3-ol (SIM - *m/z* 72)**				**3-octanone (SIM - *m/z* 72)**			
		AVG RT (min)	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 3 years	**AVG RT**	**SD of RT**	**CV% of RT**	RT drift in 3 years	**AVG RT**	**SD of RT**	**CV% of RT**	RT drift in 3 years
		10.15	**0.019**	**0.19**	-0.057	**10.38**	**0.018**	**0.17**	-0.061	**10.57**	**0.019**	**0.18**	-0.063
		AVG accuracy%	**SD of accuracy%**	**CV% of accuracy**	Accuracy %	**AVG Accuracy**	**SD of accuracy**	**CV% of accuracy**	Accuracy %	**AVG Accuracy**	**SD of accuracy**	**CV% of accuracy**	Accuracy %
		103.73	**6.33**	**6.1**		**103.15**	**7.56**	**7.3**		**98.83**	**9.67**	**9.8**	
Date and concentration	**Exp. Conc ng/ul**	**RT(min)**	**Response**	**Final Conc ng/ul**		**RT(min)**	**Response**	**Final Conc ng/ul**		**RT(min)**	**Response**	**Final Conc ng/ul**	
190404_2.5ng/ul	2.5	10.18	629528	2.629	105.1	10.42	275827	2.635	105.4	10.60	520750	2.100	84.0
190404_1ng/ul	1.0	10.18	224795	1.108	110.8	10.42	101997	1.115	111.5	10.60	193950	0.819	81.9
190404_0.5ng/ul	0.5	10.18	92407	0.501	100.2	10.42	37673	0.455	91.1	10.61	92369	0.406	81.2
190404_0.1ng/ul	0.1	10.19	12998	0.0943	94.3	10.42	5616	0.0977	97.7	10.61	14211	0.0832	83.2
200309_0.5ng/ul	0.5	10.15	90132	0.490	98.0	10.38	38389	0.463	92.6	10.57	103275	0.451	90.1
200309_1ng/ul	1.0	10.15	214083	1.062	106.2	10.38	92402	1.021	102.1	10.56	237896	0.995	99.5
200309_2.5ng/ul	2.5	10.14	630238	2.631	105.2	10.38	271023	2.597	103.9	10.56	620437	2.478	99.1
200309_5ng/ul	5.0	10.14	1377477	4.773	95.5	10.38	590830	4.834	96.7	10.56	1238273	4.704	94.1
2003011_0.05ng/ul	0.05	10.18	5486	0.0537	107.4	10.40	2134	0.0574	114.8	10.58	7253	0.0542	108.4
2003011_0.05ng/ul - CAL	0.05	10.18	5830	0.0556	111.1	10.40	2070	0.0567	113.3	10.58	6914	0.0528	105.6
2003011_0.5ng/ul - CAL	0.5	10.15	82373	0.452	90.3	10.38	35825	0.435	87.1	10.57	108654	0.473	94.5
2003011_1ng/ul - CAL	1.0	10.15	188060	0.947	94.7	10.38	85028	0.948	94.8	10.56	232232	0.973	97.3
2003011_2.5ng/ul - CAL	2.5	10.14	626015	2.617	104.7	10.38	276982	2.644	105.8	10.56	647896	2.581	103.3
2003011_5ng/ul - CAL	5.0	10.14	1454994	4.966	99.3	10.38	610296	4.955	99.1	10.56	1315528	4.970	99.4
2003011_1ng/ul	1.0	10.14	212559	1.055	105.5	10.38	96438	1.061	106.1	10.56	251293	1.049	104.9
2003011_1ng/ul	1.0	10.14	204711	1.021	102.1	10.38	92744	1.024	102.4	10.56	245637	1.026	102.6
2003011_1ng/ul	1.0	10.14	202360	1.010	101.0	10.38	90909	1.006	100.6	10.56	244445	1.021	102.1
2003012_1ng/ul	1.0	10.15	216711	1.073	107.3	10.38	97612	1.072	107.2	10.56	254805	1.063	106.3
2003012_1ng/ul	1.0	10.15	208220	1.036	103.6	10.38	97174	1.068	106.8	10.56	259645	1.082	108.2
2003012_1ng/ul	1.0	10.15	233669	1.146	114.6	10.38	106657	1.161	116.1	10.56	286325	1.188	118.8
2003020_1ng/ul	1.0	10.14	217921	1.078	107.8	10.38	93026	1.027	102.7	10.56	230397	0.965	96.5
20210202_1ng/ul	1.0	10.12	230659	1.133	113.3	10.36	100413	1.100	110.0	10.54	255538	1.066	106.6
20210202_1ng/ul	1.0	10.12	217500	1.076	107.6	10.36	95066	1.047	104.7	10.54	253275	1.057	105.7

9.12 Table S6 System suitability reference mix injections from year 2019-2020 for precision, sensitivity and reproducibility - an early (styrene), a mid (1,3-dimethoxy-benzene) and a late eluting (longifolene) component, for the latter comparing data quality of extracted ion chromatogram (EIC) and selective ion monitoring (SIM) channels (concentration range 0.05-2.5 µg/ml)

		Styrene - EIC *m/z* 104				**1,3-Dimethoxybenzene - EIC *m/z* 138**				**Longifolene - EIC *m/z* 161**				**Longifolene - SIM *m/z* 93**			
		AVG RT (min)	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years	**AVG RT (min)**	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years	**AVG RT (min)**	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years	**AVG RT (min)**	**SD of RT (min)**	**CV% of RT**	RT drift (min) in 2 years
		8.15	**0.011**	**0.14**	-0.017	**14.75**	**0.013**	**0.09**	-0.056	**19.32**	**0.008**	**0.04**	-0.026	**19.32**	**0.009**	**0.05**	-0.031
		AVG accuracy%	**SD of accuracy%**	**CV% of accuracy**	Accuracy %	**AVG Accuracy**	**SD of accuracy**	**CV% of accuracy**	Accuracy %	**AVG Accuracy**	**SD of accuracy**	**CV% of accuracy**	Accuracy %	**AVG Accuracy**	**SD of accuracy**	**CV% of accuracy**	Accuracy %
		110.37	**9.05**	**8.2**		**109.25**	**8.35**	**7.6**		**106.51**	**7.38**	**6.9**		**110.03**	**9.74**	**8.8**	
Date and concentration	**Exp. Conc ng/ul**	**RT(min)**	**Response**	**Final Conc ng/ul**		**RT(min)**	**Response**	**Final Conc ng/ul**		**RT(min)**	**Response**	**Final Conc ng/ul**		**RT(min)**	**Response**	**Final Conc ng/ul**	
19_SST_0_05ng - CAL	0.05	8.16	3704	0.0561	112.3	14.78	5577	0.0544	108.8	19.33	2440	0.0558	111.6	19.34	2561	0.0594	118.9
19_SST_0_1ng - CAL	0.10	8.16	22112	0.119	118.8	14.77	13700	0.0983	98.3	19.34	5155	0.101	101.0	19.34	4858	0.0967	96.7
19_SST_0_5ng - CAL	0.50	8.15	122650	0.461	92.2	14.76	82676	0.469	93.7	19.33	25925	0.447	89.4	19.33	25337	0.429	85.9
19_SST_1ng - CAL	1.00	8.15	263383	0.940	94.0	14.76	176266	0.962	96.2	19.34	55364	0.937	93.7	19.34	56330	0.9325	93.3
19_SST_2_5ng - CAL	2.50	8.15	731116	2.531	101.2	14.76	494885	2.576	103.0	19.34	155771	2.609	104.4	19.34	160997	2.632	105.3
19_SST_10ng	10.00	8.16	3319639	11.34	113.4	14.76	2207813	9.989	99.9	19.34	716898	11.954	119.5	19.34	722369	11.747	117.5
20200108_SST_1ppm_1	1.00	8.15	304239	1.079	107.9	14.75	195185	1.061	106.1	19.32	58124	0.983	98.3	19.33	66529	1.098	109.8
20200108_SST_1ppm_2	1.00	8.15	314912	1.115	111.5	14.75	196656	1.069	106.9	19.32	56382	0.954	95.4	19.32	66962	1.105	110.5
20200108_SST_1ppm_3	1.00	8.15	311877	1.105	110.5	14.75	189624	1.032	103.2	19.32	56951	0.9636	96.4	19.32	66307	1.095	109.5
20200108_SST_1ppm_4	1.00	8.15	308692	1.094	109.4	14.75	199468	1.083	108.3	19.32	60700	1.026	102.6	19.32	66785	1.102	110.2
20200120_SST_1ppm_2	1.00	8.15	338014	1.194	119.4	14.74	218758	1.183	118.3	19.32	65728	1.110	111.0	19.32	72368	1.193	119.3
20200120_SST_1ppm_3	1.00	8.15	333168	1.177	117.7	14.74	211185	1.144	114.4	19.32	65357	1.104	110.4	19.32	69993	1.154	115.4
20200120_SST_1ppm_4	1.00	8.15	334152	1.180	118.0	14.74	220936	1.195	119.5	19.32	68536	1.156	115.6	19.32	71851	1.185	118.5
20200122_SSTmix	1.00	8.12	297710	1.056	105.6	14.75	191498	1.042	104.2	19.32	59196	1.001	100.1	19.32	64394	1.063	106.3
20200123_SSTmix2	1.00	8.14	309713	1.097	109.7	14.74	203367	1.103	110.3	19.32	61227	1.035	103.5	19.32	66691	1.101	110.1
20200124_SST1	1.00	8.12	316303	1.120	112.0	14.74	213030	1.154	115.4	19.32	67407	1.138	113.8	19.32	69853	1.152	115.2
20200206_1ppmSST1	1.00	8.12	314085	1.112	111.2	14.74	212434	1.151	115.1	19.32	67218	1.135	113.5	19.32	70776	1.167	116.7
20200206_1ppmSST2	1.00	8.15	337182	1.191	119.1	14.74	218410	1.182	118.2	19.32	65240	1.102	110.2	19.32	72089	1.188	118.8
20200206_1ppmSST3	1.00	8.15	320886	1.135	113.5	14.74	220374	1.192	119.2	19.32	66751	1.127	112.7	19.32	71370	1.177	117.7
20200206_1ppmSST4	1.00	8.15	339816	1.200	120.0	14.74	220332	1.191	119.1	19.32	62486	1.056	105.6	19.32	71018	1.171	117.1
20200306_1ppmSST1	1.00	8.13	318323	1.127	112.7	14.74	208424	1.130	113.0	19.32	64397	1.088	108.8	19.32	70609	1.164	116.4
20200306_1ppmSST2	1.00	8.15	337588	1.192	119.2	14.74	219655	1.188	118.8	19.32	67162	1.134	113.4	19.32	71706	1.182	118.2
20200306_1ppmSST3	1.00	8.15	338529	1.195	119.5	14.74	219183	1.186	118.6	19.32	64793	1.094	109.4	19.32	70927	1.170	117.0
20200306_1ppmSST4	1.00	8.15	337343	1.191	119.1	14.74	220633	1.193	119.3	19.32	66078	1.116	111.6	19.32	71298	1.176	117.6
20200604_SST_2ppm	2.00	8.14	628427	2.182	109.1	14.73	387724	2.044	102.2	19.32	128073	2.148	107.4	19.32	123164	2.018	100.9
20201120_SST_1_5ppm	1.50	8.14	394806	1.387	92.5	14.73	280305	1.500	100.0	19.30	97771	1.643	109.6	19.30	87072	1.432	95.4
20201120_SST_1_5ppm2	1.50	8.14	386834	1.360	90.6	14.72	279696	1.497	99.8	19.30	95748	1.610	107.3	19.31	84561	1.391	92.7

9.13 Table S7 retention times from year 2019-2021 for n-alkanes (C8-26) used for calculation of retention index (RI)

Kováts' RI value	**800**	**900**	**1000**	**1100**	**1200**	**1300**	**1400**	**1500**	**1600**	**1700**	**1800**	**1900**	**2000**	**2100**	**2200**	**2300**	**2400**	**2500**	**2600**
Date of n-alkane mix measured	RT (min) **C8**	RT (min) **C9**	RT (min) **C10**	RT (min) **C11**	RT (min) **C12**	RT (min) **C13**	RT (min) **C14**	RT (min) **C15**	RT (min) **C16**	RT (min) **C17**	RT (min) **C18**	RT (min) **C19**	RT (min) **C20**	RT (min) **C21**	RT (min) **C22**	RT (min) **C23**	RT (min) **C24**	RT (min) **C25**	RT (min) **C26**
20190318 C7-30	5.91	8.43	10.94	13.29	15.48	17.52	19.14	20.25	21.12	21.85	22.48	23.05	23.58	24.07	24.53	24.53	24.98	25.96	26.55
20190321 C7-30	5.91	8.43	10.93	13.29	15.48	17.51	19.14	20.25	21.12	21.85	22.48	23.05	23.57	24.06	24.53	24.53	24.98	25.96	26.55
190325 C7-30	5.91	8.42	10.93	13.29	15.48	17.51	19.14	20.25	21.12	21.85	22.48	23.05	23.58	24.07	24.53	24.53	24.98	25.97	26.55
20200123 C7-30	5.89	8.39	10.89	13.24	15.42	17.46	19.09	20.22	21.09	21.82	22.45	23.02	23.55	24.04	24.50	24.50	24.94	25.92	26.49
20200122 C7-30	5.92	8.41	10.90	13.24	15.43	17.46	19.10	20.22	21.09	21.82	22.45	23.02	23.55	24.04	24.50	24.50	24.94	25.92	26.50
20200309 C7-30	5.91	8.40	10.89	13.24	15.42	17.45	19.09	20.21	21.09	21.81	22.45	23.02	23.55	24.04	24.50	24.50	24.94	25.92	26.49
20200311 C7-30	5.91	8.40	10.89	13.23	15.42	17.45	19.09	20.21	21.09	21.81	22.45	23.02	23.54	24.03	24.50	24.50	24.94	25.91	26.49
20200312 C7-30	5.92	8.40	10.89	13.24	15.42	17.45	19.09	20.21	21.09	21.81	22.45	23.02	23.54	24.03	24.50	24.50	24.94	25.92	26.49
20200320 C7-30	5.91	8.40	10.89	13.24	15.42	17.45	19.09	20.21	21.09	21.81	22.45	23.02	23.54	24.03	24.50	24.50	24.94	25.91	26.49
20200323 C7-30	5.91	8.40	10.89	13.24	15.42	17.45	19.09	20.21	21.09	21.81	22.45	23.02	23.54	24.03	24.50	24.50	24.94	25.91	26.49
20200604 C7-30	5.90	8.39	10.88	13.23	15.41	17.45	19.09	20.21	21.08	21.81	22.45	23.02	23.54	24.03	24.50	24.50	24.94	25.92	26.49
20200729 C7-30	5.89	8.39	10.88	13.23	15.41	17.44	19.08	20.20	21.08	21.81	22.44	23.01	23.54	24.03	24.49	24.49	24.93	25.90	26.48
20201006 c7-30	5.90	8.38	10.88	13.22	15.40	17.44	19.08	20.20	21.08	21.81	22.44	23.01	23.53	24.02	24.49	24.49	24.93	25.90	26.48
20201120 C7-30	5.90	8.39	10.88	13.22	15.40	17.44	19.08	20.20	21.08	21.80	22.44	23.01	23.53	24.03	24.49	24.49	24.93	25.90	26.48
20210202 C7-30	5.89	8.38	10.87	13.22	15.40	17.43	19.08	20.20	21.08	21.80	22.44	23.01	23.54	24.03	24.49	24.49	24.93	25.90	26.48
RT AVERAGES	**AVG C8**	**AVG C9**	**AVG C10**	**AVG C11**	**AVG C12**	**AVG C13**	**AVG C14**	**AVG C15**	**AVG C16**	**AVG C17**	**AVG C18**	**AVG C19**	**AVG C20**	**AVG C21**	**AVG C22**	**AVG C23**	**AVG C24**	**AVG C25**	**AVG C26**
	5.9	8.4	10.9	13.2	15.4	17.5	19.1	20.2	21.1	21.8	22.5	23.0	23.5	24.0	24.5	24.5	24.9	25.9	26.5
SD of RT-s	**SD C8**	**SD C9**	**SD C10**	**SD C11**	**SD C12**	**SD C13**	**SD C14**	**SD C15**	**SD C16**	**SD C17**	**SD C18**	**SD C19**	**SD C20**	**SD C21**	**SD C22**	**SD C23**	**SD C24**	**SD C25**	**SD C26**
	0.009	0.016	0.021	0.025	0.027	0.029	0.022	0.018	0.016	0.015	0.015	0.014	0.015	0.015	0.015	0.015	0.016	0.022	0.027
CV% of RT-s	**CV% C8**	**CV% C9**	**CV% C10**	**CV% C11**	**CV% C12**	**CV% C13**	**CV% C14**	**CV% C15**	**CV% C16**	**CV% C17**	**CV% C18**	**CV% C19**	**CV% C20**	**CV% C21**	**CV% C22**	**CV% C23**	**CV% C24**	**CV% C25**	**CV% C26**
	0.15	0.20	0.20	0.19	0.18	0.16	0.11	0.09	0.08	0.07	0.06	0.06	0.06	0.06	0.06	0.06	0.06	0.09	0.10
TOTAL RT DRIFT in 2 years: 19.03-21.02 on HP-5MS UI 30m*0.25mm*0.25um used	**RT drift** (min) **C8**	**RT drift** (min) **C9**	**RT drift** (min) **C10**	**RT drift** (min) **C11**	**RT drift** (min) **C12**	**RT drift** (min) **C13**	**RT drift** (min) **C14**	**RT drift** (min) **C15**	**RT drift** (min) **C16**	**RT drift** (min) **C17**	**RT drift** (min) **C18**	**RT drift** (min) **C19**	**RT drift** (min) **C20**	**RT drift** (min) **C21**	**RT drift** (min) **C22**	**RT drift** (min) **C23**	**RT drift** (min) **C24**	**RT drift** (min) **C25**	**RT drift** (min) **C26**
	0.025	0.054	0.066	0.072	0.077	0.081	0.062	0.048	0.047	0.042	0.042	0.039	0.039	0.041	0.039	0.039	0.042	0.062	0.075

9.14 Table S8 Comparison of binding during direct administration of submixes and the complete mix - at a concentration of 1 µg/ml with respect to elution volume, characterization of mean recovery (%) and standard deviation, relative standard deviation (RSD%) and confidence interval (CI), with at least three-point external bracketing using calibration (linear regression, R2>0.99), using 1-bromodecane internal standard correction (Legend: 0-20% - red, 20-40% - orange, 40-60% - yellow, 60%< - green)

			recovery % from submixes with internal standard correction (n=5)				recovery % from complete mixture direct spiking corrected for internal standard (n=2)			
Component english common name	**Retention time (min)**	**Submix number**	**AVG recovery (%) at 1 µg/ml conc. level**	**SD**	**RSD%**	**CI**	**AVG recovery (%) at 1 µg/ml conc. level**	**Szórás**	**RSD%**	**CI**
2-hexanone	5.372	MIX5	99.0	7.3	7.4	9.1	67.7	3.9	5.7	34.6
3-hexanol	5.496	MIX5	99.6	6.8	6.8	8.4	55.0	0.8	1.5	7.2
hexanal	5.602	MIX3	93.2	11.1	11.9	13.7	67.6	0.5	0.7	4.1
2-hexanol	5.624	MIX4	66.1	5.6	8.5	6.9	47.6	6.3	13.3	56.6
butanoic acid, ethyl ester	5.668	MIX7	95.7	9.9	10.3	12.3	65.0	2.8	4.3	25.0
3(2H)-furanone, dihydro-2-methyl-	5.755	MIX8	43.2	7.4	17.2	9.2	55.7	2.1	3.8	19.0
2-hexenal, (E)-	6.894	MIX1	81.4	7.6	9.3	9.4	59.7	1.1	1.8	9.8
3-hexen-1-ol, (E)-	6.899	MIX2	73.2	6.3	8.6	7.8	50.1	1.3	2.6	11.9
1-hexanol	7.31	MIX5	77.8	3.5	4.5	4.4	49.8	0.8	1.7	7.4
m-xylene	7.313	MIX3	87.3	8.3	9.5	10.3	69.4	0.2	0.2	1.4
p-xylene	7.319	MIX1	84.0	6.6	7.8	8.1	71.8	0.8	1.1	7.1
isopentyl acetate	7.539	MIX6	97.6	14.3	14.6	17.7	71.0	0.6	0.8	5.0
styrene	7.852	MIX8	72.1	15.1	20.9	18.8	68.1	0.8	1.2	7.6
o-xylene	7.901	MIX2	93.9	5.0	5.3	6.2	69.1	0.6	0.8	5.1
2-heptanol	8.105	MIX5	92.3	6.1	6.6	7.6	68.4	0.4	0.6	3.9
2-heptanone	8.124	MIX4	86.6	6.1	7.1	7.6	54.7	3.3	6.1	29.7
propanoic acid, butyl ester	8.343	MIX9	92.6	6.3	6.9	7.9	72.8	0.5	0.6	4.2
acetic acid, pentyl ester	8.486	MIX6	98.0	15.3	15.6	19.0	71.8	0.6	0.9	5.8
anisole	8.520	MIX9	74.2	6.6	8.9	8.2	62.5	1.3	2.1	11.9
α-pinene	8.952	MIX2	103.9	2.5	2.4	3.1	77.3	1.2	1.5	10.7
butanoic acid, 3-hydroxy-, ethyl ester	8.961	MIX8	27.9	16.9	60.5	20.9	55.2	0.9	1.7	8.4
2-heptenal, (E)-	9.506	MIX1	84.6	7.3	8.7	9.1	65.8	1.1	1.7	10.0
benzaldehyde	9.592	MIX3	66.1	7.6	11.5	9.4	49.6	3.5	7.1	31.5
1-heptanol	9.866	MIX2	75.6	2.3	3.0	2.9	42.2	1.6	3.9	14.8
(5Z)-octa-1,5-dien-3-ol	9.952	MIX4	79.7	7.3	9.2	9.1	63.5	1.8	2.8	16.0
(-)-β-pinene	10.022	MIX7	99.6	12.3	12.4	15.3	77.0	0.3	0.4	3.1
1-octen-3-ol	10.095	MIX1	71.9	8.1	11.3	10.1	57.6	1.4	2.5	12.9
phenol	10.141	MIX2	81.4	2.9	3.6	3.6	48.3	0.1	0.3	1.3
5-hepten-2-one, 6-methyl-	10.279	MIX3	88.5	9.8	11.1	12.2	74.2	0.3	0.5	3.1
β-myrcene	10.395	MIX6	107.5	15.6	14.5	19.4	67.9	0.8	1.2	7.6
3-octanol	10.487	MIX5	104.5	6.5	6.2	8.1	78.6	0.2	0.2	1.5
3-octanone	10.531	MIX4	86.4	5.8	6.7	7.2	54.0	0.3	0.5	2.6
hexanoic acid, ethyl ester	10.598	MIX8	79.2	17.9	22.6	22.2	74.7	0.4	0.6	3.8
α-phellandrene	10.709	MIX3	98.1	9.0	9.2	11.2	78.0	0.1	0.2	1.2
3-hexen-1-ol, acetate, (Z)-	10.776	MIX2	98.8	4.9	4.9	6.0	72.0	0.7	1.0	6.2
3-carene	10.851	MIX1	90.4	6.6	7.3	8.2	78.5	0.5	0.7	4.6
acetic acid, hexyl ester	10.933	MIX9	90.1	7.3	8.1	9.1	73.8	0.4	0.5	3.6
p-cymene	11.204	MIX3	94.0	8.3	8.8	10.3	76.9	0.6	0.8	5.7
R-(+)-limonene	11.297	MIX2	106.6	3.6	3.4	4.5	76.7	0.4	0.5	3.5
benzyl alcohol	11.397	MIX5	88.9	4.7	5.3	5.8	37.8	2.0	5.2	17.6

9.14 Table S8 continued Comparison of binding during direct administration of submixes and the complete mix at a concentration of 1 µg/ml with respect to elution volume, characterization of mean recovery (%) and standard deviation, relative standard deviation (RSD%) and confidence interval (CI), with at least three-point external bracketing using calibration (linear regression, R2>0.99), using 1-bromodecane internal standard correction (Legend: 0-20% - red, 20-40% - orange, 40-60% - yellow, 60%< - green).

			recovery % from submixes with internal standard correction (n=5)				recovery % from complete mixture direct spiking corrected for internal standard (n=2)			
Component english common name	**Retention time (min)**	**Submix number**	**AVG recovery (%) at 1 µg/ml conc. level**	**SD**	**RSD%**	**CI**	**AVG recovery (%) at 1 µg/ml conc. level**	**Szórás**	**RSD%**	**CI**
cis-β-ocimene	11.519	MIX7	101.2	12.4	12.3	15.4	78.7	0.9	1.1	8.1
trans-β-ocimene	11.765	MIX7	101.8	12.2	11.9	15.1	79.3	0.8	1.1	7.6
2-methylphenol (o-cresol)	11.886	MIX4	75.2	4.1	5.5	5.1	49.1	0.4	0.9	3.8
acetophenone	12.165	MIX6	62.1	11.8	19.0	14.6	52.1	3.4	6.6	30.7
3-methylphenol (m-cresol)	12.371	MIX4	73.2	5.1	7.0	6.4	48.8	0.4	0.8	3.7
α-terpinolene	12.709	MIX1	89.5	7.0	7.8	8.6	76.5	0.8	1.0	6.9
benzoic acid, methyl ester	12.844	MIX8	51.5	8.5	16.5	10.5	58.3	3.3	5.7	29.9
linalool	12.951	MIX4	87.2	6.1	7.0	7.6	66.7	1.6	2.4	14.4
nonanal	13.046	MIX2	94.4	4.9	5.2	6.1	70.6	0.9	1.2	7.7
phenylethyl Alcohol	13.245	MIX4	75.6	5.9	7.8	7.4	51.9	2.9	5.5	25.7
cis-limonene oxide	13.722	MIX7	91.7	12.3	13.4	15.3	71.2	1.3	1.9	11.9
trans-limonene oxide	13.825	MIX7	93.9	12.9	13.8	16.1	71.0	1.5	2.1	13.6
isopulegol	13.993	MIX1	86.2	9.2	10.7	11.4	66.3	1.2	1.8	10.8
benzene, 1,3-dimethoxy-	14.448	MIX8	45.0	7.7	17.1	9.5	50.7	4.3	8.5	38.8
benzoic acid, ethyl ester	14.533	MIX9	69.4	5.9	8.6	7.4	60.6	2.9	4.8	26.0
1-nonanol	14.832	MIX5	86.2	10.1	11.7	12.6	78.1	1.0	1.3	9.3
1-dodecene	14.966	MIX7	102.4	12.3	12.0	15.3	82.0	0.1	0.1	1.0
α-terpineol	14.986	MIX8	53.7	15.1	28.1	18.7	65.9	0.6	0.9	5.4
methyl salicylate	15.062	MIX9	69.0	6.7	9.8	8.3	57.2	3.4	5.9	30.2
decanal	15.264	MIX2	101.4	3.6	3.5	4.4	69.3	0.7	0.9	5.9
β-citronellol	15.717	MIX4	83.6	6.2	7.4	7.7	55.2	7.0	12.7	63.2
pulegone	16.011	MIX1	82.8	8.4	10.2	10.4	66.1	1.4	2.2	13.0
(S)-(+)-carvone	16.092	MIX8	56.7	11.6	20.4	14.4	61.4	1.1	1.8	9.8
citral	16.603	MIX9	66.7	6.9	10.4	8.6	60.2	1.9	3.1	17.0
phenol, 4-ethyl-2-methoxy-	16.788	MIX3	82.0	9.5	11.6	11.8	52.3	1.2	2.2	10.4
(-)-bornyl acetate	16.968	MIX6	91.9	16.3	17.8	20.3	69.7	0.6	0.8	5.2
2-undecanone	17.05	MIX5	111.6	5.7	5.1	7.1	71.7	1.2	1.6	10.5
eugenol	18.287	MIX9	58.8	7.7	13.2	9.6	55.8	1.2	2.2	11.2
geranyl acetate	18.653	MIX9	83.0	6.9	8.3	8.6	68.9	1.6	2.3	14.0
methyl eugenol	18.956	MIX8	46.0	14.0	30.5	17.4	51.4	3.3	6.4	29.3
longifolene	19.093	MIX2	105.1	4.1	3.9	5.1	75.0	0.8	1.1	7.4
α-cedrene	19.177	MIX6	100.0	17.1	17.1	21.3	76.2	1.1	1.4	9.6
caryophyllene	19.258	MIX1	90.1	7.8	8.7	9.7	76.6	0.5	0.7	4.6
β-cedrene	19.286	MIX9	96.5	8.7	9.0	10.8	67.4	1.4	2.0	12.1
α-humulene	19.663	MIX6	98.3	16.5	16.8	20.5	73.7	1.0	1.3	8.9
trans-β-Ionone	19.962	MIX3	93.4	9.9	10.6	12.3	65.3	1.3	1.9	11.4
valencene	20.081	MIX7	94.5	11.1	11.7	13.8	78.4	1.6	2.0	14.0
trans-nerolidol	20.664	MIX7	92.0	11.7	12.7	14.6	74.4	0.8	1.1	7.5
caryophyllene oxide	20.933	MIX9	78.6	6.4	8.1	7.9	70.0	1.5	2.2	13.7
methyl jasmonate	21.351	MIX7	20.6	11.0	53.5	13.7	54.1	2.5	4.6	22.2
trans-farnesol	21.844	MIX1	87.3	10.7	12.2	13.3	67.8	3.1	4.6	27.8

9.15 Table S9 Recovery test results using submix 10 containing normal alkanes (C7-30, C8-22 evaluated), in case of direct addition, followed by periodic and continuous DHS sampling – representation of the measured recovery (% - corrected by internal standard 1-bromodecane) at 1 µg/ml concentration with repsect to elution volume (legend: 0-20% - red, 20-40% - orange , 40-60% - yellow, 60% < - green)

	DHS mode	periodic DHS (n=3)				continuous DHS (n=3)				direct spiking with complete reference mixture (n=2)			
	DHS settings	0.8 L/min, 5 min flow "on", 10 min flow "off" cyclic		for 6 hours, at 26°C		0.8 L/min		for 6 hours, at 26°C					
Retention time (min)	Component english common name	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI
5.613	octane	51.4	40.9	79.5	101.6	9.6	5.2	53.6	12.8	79.0	14.7	18.5	131.6
8.101	nonane	89.2	21.2	23.7	52.6	79.1	36.6	46.2	90.9	87.2	13.7	15.7	122.8
10.602	decane	98.3	14.5	14.7	36.0	90.5	26.7	29.5	66.3	89.2	15.3	17.1	137.5
12.955	undecane	101.5	12.8	12.6	31.7	94.4	22.3	23.6	55.3	90.4	16.0	17.7	144.0
15.139	dodecane	101.9	12.6	12.4	31.3	93.7	20.9	22.3	52.0	90.7	15.3	16.9	137.4
17.175	tridecane	101.4	12.7	12.5	31.6	92.7	18.7	20.2	46.5	90.1	15.7	17.4	140.7
18.882	tetradecane	101.3	11.5	11.4	28.6	92.4	18.9	20.4	46.9	89.7	15.8	17.6	141.8
20.036	pentadecane	102.2	12.0	11.8	29.9	94.5	20.9	22.2	52.0	89.8	16.5	18.4	148.6
20.926	hexadecane	101.0	11.4	11.2	28.2	95.5	19.2	20.1	47.7	89.6	15.3	17.1	137.9
21.657	heptadecane	98.5	11.9	12.1	29.5	91.9	20.4	22.2	50.7	89.7	13.8	15.4	123.9
22.301	octadecane	97.3	12.8	13.1	31.7	90.5	21.0	23.2	52.2	90.4	15.4	17.0	138.1
22.868	nonadecane	94.4	12.1	12.9	30.2	89.4	21.2	23.7	52.6	90.0	15.2	16.9	136.5
23.395	eicosane	94.2	12.1	12.8	30.0	88.5	21.0	23.8	52.3	89.8	14.4	16.1	129.5
23.884	heneicosane	95.0	11.9	12.5	29.6	87.5	21.3	24.4	53.0	90.3	13.9	15.4	125.2
24.349	docosane	97.2	11.5	11.8	28.6	88.6	19.5	22.0	48.5	89.8	14.1	15.7	126.4

9.16 Table S10 Recovery test results using complete mixture (sum of submix 1-9), in case of direct addition, followed by periodic and continuous DHS sampling
representation of the measured recovery (% - corrected by internal standard 1-bromodecane) at 1 µg/ml concentration with repsect to elution volume (legend: 0-20% - red, 20-40% - orange , 40-60% - yellow, 60% < - green).

	DHS mode	periodic DHS (n=3)				continuos DHS (n=3)				direct spiking with complete reference mixture (n=2)			
	DHS settings	0.8 L/min, 5 min flow "on", 10 min flow "off" cyclic		for 6 hours, at 26°C		0.8 L/min		for 6 hours, at 26°C					
Component english common name	Retention time (min)	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI
2-hexanone	5.37	6.4	1.2	18.5	2.9	3.6	2.0	56.5	5.1	67.7	3.9	5.7	34.6
3-hexanol	5.50	15.7	2.1	13.1	5.1	14.6	14.4	98.9	35.7	55.0	0.8	1.5	7.2
hexanal	5.60	20.4	19.6	96.0	48.6	7.1	3.1	44.0	7.7	67.6	0.5	0.7	4.1
2-hexanol	5.62	20.6	1.3	6.5	3.3	18.4	15.1	82.0	37.6	47.6	6.3	13.3	56.6
butanoic acid, ethyl ester	5.67	7.4	2.7	35.9	6.6	3.5	3.5	100.0	8.7	65.0	2.8	4.3	25.0
3(2H)-furanone, dihydro-2-methyl-	5.76	1.5	0.0	3.0	0.1	1.3	0.4	27.9	0.9	55.7	2.1	3.8	19.0
2-hexenal, (E)-	6.89	13.6	2.5	18.4	6.2	10.0	9.4	94.4	23.4	59.7	1.1	1.8	9.8
3-hexen-1-ol, (E)-	6.90	23.4	1.7	7.2	4.2	20.1	12.8	63.6	31.7	50.1	1.3	2.6	11.9
1-hexanol	7.31	34.9	4.7	13.3	11.6	30.1	9.1	30.1	22.6	49.8	0.8	1.7	7.4
m-xylene	7.31	22.1	5.6	25.2	13.9	12.5	8.1	65.1	20.2	69.4	0.2	0.2	1.4
p-xylene	7.32	23.2	6.0	26.0	15.0	12.7	8.8	69.5	22.0	71.8	0.8	1.1	7.1
isopentyl acetate	7.54	47.1	5.4	11.4	13.4	44.2	11.2	25.2	27.7	71.0	0.6	0.8	5.0
styrene	7.85	26.4	7.9	29.9	19.6	15.5	10.2	65.8	25.3	68.1	0.8	1.2	7.6
o-xylene	7.86	46.2	5.1	11.1	12.8	42.4	10.0	23.5	24.8	69.1	0.6	0.8	5.1
2-heptanol	7.90	23.9	5.7	23.9	14.2	14.4	8.7	60.3	21.5	68.4	0.4	0.6	3.9
2-heptanone	8.11	45.8	6.7	14.7	16.7	39.9	5.2	12.9	12.8	54.7	3.3	6.1	29.7
propanoic acid, butyl ester	8.34	52.2	6.0	11.5	14.9	49.1	8.1	16.5	20.2	72.8	0.5	0.6	4.2
acetic acid, pentyl ester	8.49	53.1	6.2	11.6	15.4	49.4	6.5	13.1	16.0	71.8	0.6	0.9	5.8
anisole	8.52	24.3	3.9	16.1	9.7	16.0	10.6	65.8	26.2	62.5	1.3	2.1	11.9
α-pinene	8.95	59.6	18.5	31.1	46.0	51.1	11.5	22.5	28.5	77.3	1.2	1.5	10.7
butanoic acid, 3-hydroxy-, ethyl ester	8.96	16.1	5.3	33.0	13.1	14.1	7.3	51.6	18.1	55.2	0.9	1.7	8.4
2-heptenal, (E)-	9.51	49.2	6.2	12.5	15.3	43.3	4.0	9.3	10.0	65.8	1.1	1.7	10.0
benzaldehyde	9.59	29.1	4.5	15.3	11.1	23.8	9.8	41.2	24.4	49.6	3.5	7.1	31.5
1-heptanol	9.87	45.6	7.5	16.4	18.5	38.2	6.9	18.2	17.2	42.2	1.6	3.9	14.8
(5Z)-octa-1,5-dien-3-ol	9.95	49.4	6.7	13.5	16.6	42.7	6.6	15.5	16.4	63.5	1.8	2.8	16.0
(-)-β-pinene	10.02	59.3	9.5	16.0	23.5	55.2	8.1	14.6	20.0	77.0	0.3	0.4	3.1
1-octen-3-ol	10.10	52.2	7.1	13.7	17.7	45.4	6.0	13.2	14.9	57.6	1.4	2.5	12.9
phenol	10.14	10.8	2.9	27.2	7.3	7.2	1.0	13.7	2.5	48.3	0.1	0.3	1.3
5-hepten-2-one, 6-methyl-	10.27	60.3	7.7	12.7	19.0	54.4	5.0	9.2	12.5	74.2	0.3	0.5	3.1
β-myrcene	10.28	54.8	7.7	14.1	19.2	48.1	4.9	10.2	12.2	67.9	0.8	1.2	7.6
3-octanol	10.40	65.3	6.9	10.6	17.2	61.6	5.2	8.4	12.8	78.6	0.2	0.2	1.5
3-octanone	10.49	57.7	8.5	14.7	21.1	49.2	7.6	15.4	18.9	54.0	0.3	0.5	2.6
hexanoic acid, ethyl ester	10.60	62.1	7.6	12.2	18.9	56.9	4.8	8.4	11.9	74.7	0.4	0.6	3.8
α-phellandrene	10.71	58.7	4.2	7.1	10.4	56.3	4.7	8.4	11.8	78.0	0.1	0.2	1.2
3-hexen-1-ol, acetate, (Z)-	10.78	59.4	7.6	12.8	18.9	53.4	4.7	8.8	11.6	72.0	0.7	1.0	6.2
3-carene	10.85	64.6	10.1	15.7	25.2	60.6	6.8	11.2	16.9	78.5	0.5	0.7	4.6
acetic acid, hexyl ester	10.93	61.6	8.0	13.1	20.0	55.7	4.5	8.0	11.1	73.8	0.4	0.5	3.6
p-cymene	11.20	65.9	9.1	13.8	22.6	60.8	5.6	9.2	13.9	76.9	0.6	0.8	5.7
R-(+)-limonene	11.30	72.7	19.4	26.7	48.2	63.4	5.8	9.2	14.4	76.7	0.4	0.5	3.5
benzyl alcohol	11.40	22.3	5.4	24.4	13.5	16.8	5.6	33.4	13.9	37.8	2.0	5.2	17.6

9.16 Table S10 continued Recovery test results using complete mixture (sum of submix 1-9), in case of direct addition, followed by periodic and continuous DHS sampling, representation of the measured recovery (% - corrected by internal standard 1-bromodecane) at 1 µg/ml concentration with repsect to elution volume (legend: 0-20% - red, 20-40% - orange , 40-60% - yellow, 60% < - green).

		periodic DHS (n=3)				continuos DHS (n=3)				direct spiking with complete reference mixture (n=2)			
	DHS mode	0.8 L/min, 5 min flow "on", 10 min flow "off" cyclic		for 6 hours, at 26°C		0.8 L/min		for 6 hours, at 26°C					
Component english common name	Retention time (min)	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI	AVG recovery (%) at 1 µg/ml conc. level	SD	RSD %	CI
cis-β-ocimene	11.52	63.4	5.9	9.4	14.7	59.8	4.3	7.3	10.8	78.7	0.9	1.1	8.1
trans-β-ocimene	11.77	64.0	6.1	9.5	15.0	60.1	4.5	7.4	11.1	79.3	0.8	1.1	2.1
2-methylphenol (o-cresol)	11.89	20.2	4.2	20.9	10.5	14.8	5.9	40.2	14.8	49.1	0.4	0.9	1.1
acetophenone	12.17	42.7	7.5	17.7	18.7	33.9	5.8	17.1	14.4	52.1	3.4	6.6	8.5
3-methylphenol (m-cresol)	12.37	15.6	3.7	23.5	9.1	11.0	5.0	45.1	12.4	48.8	0.4	0.8	1.0
α-terpinolene	12.71	60.5	6.1	10.0	15.0	56.4	4.6	8.1	11.4	76.5	0.8	1.0	1.9
benzoic acid, methyl ester	12.84	48.1	7.5	15.7	18.7	39.8	4.9	12.3	12.1	58.3	3.3	5.7	8.3
linalool	12.95	53.6	8.0	14.9	19.9	46.5	5.1	10.9	12.6	66.7	1.6	2.4	4.0
nonanal	13.05	59.7	13.5	22.6	33.6	50.6	3.0	6.0	7.5	70.6	0.9	1.2	2.1
phenylethyl Alcohol	13.25	27.4	6.1	22.3	15.2	19.0	8.4	44.0	20.8	51.9	2.9	5.5	7.1
cis-limonene oxide	13.72	57.3	7.9	13.7	19.6	50.3	4.1	8.2	10.2	71.2	1.3	1.9	3.3
trans-limonene oxide	13.83	58.4	7.2	12.3	17.9	52.1	4.1	7.8	10.1	71.0	1.5	2.1	3.8
isopulegol	13.99	58.2	8.8	15.2	21.9	50.7	4.9	9.6	12.1	66.3	1.2	1.8	3.0
benzene, 1,3-dimethoxy-	14.45	43.5	7.7	17.6	19.1	35.0	4.5	12.9	11.2	50.7	4.3	8.5	10.7
benzoic acid, ethyl ester	14.53	50.8	7.7	15.2	19.2	42.5	4.3	10.1	10.6	60.6	2.9	4.8	7.2
1-nonanol	14.83	63.3	10.0	15.8	24.8	61.8	5.4	8.8	13.5	78.1	1.0	1.3	2.6
1-dodecene	14.97	69.8	8.3	11.9	20.7	65.5	4.1	6.2	10.2	82.0	0.1	0.1	0.3
α-terpineol	14.98	45.8	8.0	17.4	19.8	37.5	6.5	17.3	16.1	65.9	0.6	0.9	1.5
methyl salicylate	15.06	47.9	7.8	16.2	19.3	39.5	4.2	10.6	10.4	57.2	3.4	5.9	8.4
decanal	15.26	50.7	6.6	13.0	16.4	44.6	4.2	9.3	10.3	69.3	0.7	0.9	1.6
β-citronellol	15.72	48.0	8.3	17.2	20.6	39.0	7.6	19.6	19.0	55.2	7.0	12.7	17.5
pulegone	16.01	51.3	7.7	15.0	19.1	43.1	5.0	11.5	12.3	66.1	1.4	2.2	3.6
(S)-(+)-carvone	16.09	48.4	7.8	16.1	19.3	39.5	5.5	13.9	13.7	61.4	1.1	1.8	2.7
citral	16.60	45.6	7.4	16.2	18.4	38.2	4.8	12.7	12.0	60.2	1.9	3.1	4.7
phenol, 4-ethyl-2-methoxy-	16.79	40.4	6.7	16.7	16.7	33.1	4.6	13.8	11.3	52.3	1.2	2.2	2.9
(-)-bornyl acetate	16.97	58.6	8.6	14.8	21.5	52.3	3.9	7.5	9.7	69.7	0.6	0.8	1.4
2-undecanone	17.05	60.8	8.5	14.0	21.2	53.9	3.7	6.8	9.1	71.7	1.2	1.6	2.9
eugenol	18.29	42.4	7.1	16.8	17.7	34.3	5.1	14.9	12.7	55.8	1.2	2.2	3.1
geranyl acetate	18.65	57.0	9.1	16.0	22.7	50.2	3.6	7.2	8.9	68.9	1.6	2.3	3.9
methyl eugenol	18.96	38.8	7.2	18.6	17.9	31.2	4.6	14.7	11.4	51.4	3.3	6.4	8.1
longifolene	19.09	64.5	9.0	14.0	22.4	59.7	4.6	7.7	11.5	75.0	0.8	1.1	2.0
α-cedrene	19.18	64.8	8.1	12.4	20.0	60.4	4.4	7.4	11.0	76.2	1.1	1.4	2.7
caryophyllene	19.26	62.6	7.7	12.4	19.2	56.9	3.6	6.4	9.0	76.6	0.5	0.7	1.3
β-cedrene	19.29	60.8	8.7	14.3	21.6	55.3	4.6	8.4	11.5	67.4	1.4	2.0	3.4
α-humulene	19.66	61.8	8.1	13.0	20.0	57.1	3.9	6.8	9.6	73.7	1.0	1.3	2.5
trans-β-Ionone	19.96	49.2	8.0	16.2	19.8	42.0	4.4	10.5	10.9	65.3	1.3	1.9	3.1
valencene	20.08	61.9	8.3	13.4	20.6	58.3	4.6	7.8	11.3	78.4	1.6	2.0	3.9
trans-nerolidol	20.66	56.6	9.1	16.1	22.6	51.1	4.3	8.5	10.7	74.4	0.8	1.1	2.1
caryophyllene oxide	20.93	55.2	8.6	15.6	21.3	49.3	4.3	8.7	10.7	70.0	1.5	2.2	3.8
methyl jasmonate	21.35	22.5	6.1	27.3	15.2	18.3	6.8	37.0	16.8	54.1	2.5	4.6	6.1
trans-farnesol	21.84	44.5	8.9	20.0	22.1	38.6	5.0	13.0	12.4	67.8	3.1	4.6	7.7

9.17 Table S11 Qualitative identification (A) of components from the competition tests conducted described under section 4.2.4, quantitative results (B) of the average concentration, standard deviation, relative standard deviation (RSD%) and confidence interval (CI) of the compounds detected during the competition test, using at least three external bracketing calibration points (linear regression, R2>0.99) for relative quantitation against nonane, and 1-bromodecane for internal standard correction

(A) Qualitative identification

m/z quant	Retention time (min)	CAS number	RI NIST17	RI calculated (HP5MS)	Component english common name as in NIST17	InChIKey	Comment
71	5.621	111-65-9	800	800	octane	TVMXDCGIABBOFY-UHFFFAOYSA-N	all
43	5.99	123-86-4	812+/-4	814.85	acetic acid, butyl ester	DKPFZGUDAPQIHT-UHFFFAOYSA-N	pear and less abundantly in blank
85	6.16	2213-23-2	821±1 (41)	821.69	heptane, 2,4-dimethyl-	AUKVIBNBLXQNIZ-UHFFFAOYSA-N	all
83	6.890	505-57-7	851	851.07	2-hexenal	MBDOYVRWFFCFHM-SNAWJCMRSA-N	pear and less abundantly in tomato
82	6.996	928-96-1	857±3 (169)	855.33	3-hexen-1-ol, (Z)-	UFLHIIWVXFIJGU-ARJAWSKDSA-N	tomato
85	7.200	2216-34-4	863±1 (36)	863.54	octane, 4-methyl-	DOGIHOCMZJUJNR-UHFFFAOYSA-N	all
57	7.275	928-95-0	862±6 (63)	866.56	2-hexen-1-ol, (E)-	ZCHHRLHTBGRGOT-SNAWJCMRSA-N	tomato
56	7.324	111-27-3	868±4 (223)	868.53	1-hexanol	ZSIAUFGUXNUGDI-UHFFFAOYSA-N	tomato and pear
71	8.106	111-84-2	900	900	nonane	BKIMMITUMNQMOS-UHFFFAOYSA-N	all
70	8.490	628-63-7	911±6 (40)	915.39	acetic acid, pentyl ester	PGMYKACGEOXYJE-UHFFFAOYSA-N	pear
93	8.957	80-56-8	937±3 (995)	934.11	α-pinene	GRWFGVWFFZKLTI-UHFFFAOYSA-N	all
71	8.961	2051-30-1	933±2 (14)	934.27	octane, 2,6-dimethyl-	ZALHPSXXQIPKTQ-UHFFFAOYSA-N	all
71	9.816	5881-17-4	965±1 (9)	968.54	octane, 3-ethyl-	OEYGTUAKNZFCDJ-UHFFFAOYSA-N	all
71	9.891	5911-04-6	971±1 (49)	971.54	nonane, 3-methyl-	PLZDDPSCZHRBOY-UHFFFAOYSA-N	all
71	10.601	124-18-5	1000	1000	decane	DIOQZVSQGTUSAI-UHFFFAOYSA-N	all
67	10.776	3681-82-1	1005±1 (19)	1007.45	3-hexen-1-ol, acetate, (E)-	NPFVOOAXDOBMCE-SNAWJCMRSA-N	all
61	10.926	142-92-7	1011±4 (112)	1013.84	acetic acid, hexyl ester	AOGQPLXWSUTHQB-UHFFFAOYSA-N	pear
85	10.948	17302-27-1	1021±6 (2)	1014.78	nonane, 2,5-dimethyl-	NQUMJENPNGXAIH-UHFFFAOYSA-N	all
82	10.994	2497-18-9	1016±3 (13)	1016.74	2-hexen-1-ol, acetate, (E)-	HRHOWZHRCRZVCU-AATRIKPKSA-N	pear
71	12.949	1120-21-4	1100	1100.00	undecane	RSJKGSCJYJTIGS-UHFFFAOYSA-N	all
71	15.134	112-40-3	1200	1200	dodecane	SNRUBQQJIBEYMU-UHFFFAOYSA-N	for RI calculation only
71	17.167	629-50-5	1300.00	1300.00	tridecane	IIYFAKIEWZDVMP-UHFFFAOYSA-N	for RI calculation only
135	18.125	112-29-8	1337±3 (3)	1356.06	**decane, 1-bromo- (INTERNAL STANDARD)**	MYMSJFSOOQERIO-UHFFFAOYSA-N	all
111	18.815	4493-42-9	1386±N/A (1)	1396.43	2,4-decadienoic acid, methyl ester, (E,Z)-	MBPMOZCKLKMNFP-UQGDGPGGSA-N	pear
71	**18.876**	**629-59-4**	**1400**	**1400**	tetradecane	BGHCVCJVXZWKCC-UHFFFAOYSA-N	for RI calculation only

(B) Quantitative results

relatively quantitated against nonane with 1-bromdecane internal standard correction applied (0 values for average concentration were <limit of quantification)													
sample and repetitions	blank (n=1)	pear (n=3)				tomato (n=3)				pear and tomato together (n=3)			
Component	concentration (µg/ml)	average concentration (µg/ml)	SD	RSD%	CI	average concentration (µg/ml)	SD	RSD%	CI	average concentration (µg/ml)	SD	RSD%	CI
octane	2.1	2.1	0.4	20.1	1.1	2.4	0.2	9.4	0.6	2.1	0.8	39.5	2.1
acetic acid, butyl ester	0.0	17.7	2.7	15.3	6.7	0.0	0.0	0.0	0.0	15.2	6.4	41.9	15.8
heptane, 2,4-dimethyl-	17.0	19.9	6.4	32.1	15.9	23.4	3.1	13.2	7.7	18.1	4.6	25.3	11.4
2-hexenal	0.0	2.4	0.2	9.2	0.5	0.3	0.0	18.6	0.1	2.1	1.1	51.1	2.6
3-hexen-1-ol, (Z)-	0.0	0.0	0.0	0.0	0.0	9.6	1.4	14.7	3.5	10.0	3.2	31.9	7.9
octane, 4-methyl-	4.8	6.3	2.4	37.9	6.0	8.0	1.3	16.4	3.3	5.8	1.2	19.9	2.9
2-hexen-1-ol, (E)-	0.0	0.3	0.0	17.6	0.1	13.1	1.8	13.9	4.5	13.9	4.4	31.8	11.0
1-hexanol	0.9	5.7	0.3	6.0	0.9	16.0	1.7	10.9	4.3	20.9	5.6	26.8	13.9
nonane	0.1	0.1	0.1	52.4	0.1	0.1	0.0	16.7	0.1	0.1	0.0	12.5	0.0
acetic acid, pentyl ester	0.0	0.5	0.1	16.7	0.2	0.0	0.0	20.2	0.0	0.5	0.0	7.5	0.1
α-pinene	0.1	0.3	0.4	150.5	0.9	0.1	0.0	30.4	0.1	0.4	0.2	51.5	0.5
octane, 2,6-dimethyl-	0.4	0.5	0.2	43.4	0.6	0.7	0.1	15.7	0.3	0.5	0.1	10.9	0.1
octane, 3-ethyl-	0.1	0.2	0.1	57.1	0.3	0.3	0.0	1.9	0.0	0.3	0.0	9.8	0.1
nonane, 3-methyl-	0.5	0.8	0.4	48.7	1.0	1.2	0.1	10.9	0.3	0.9	0.2	18.9	0.4
decane	9.4	14.9	6.0	40.4	14.9	19.3	1.7	9.0	4.3	15.2	1.8	12.1	4.6
3-hexen-1-ol, acetate, (E)-	0.0	0.1	0.0	22.4	0.0	0.0	0.0	3.8	0.0	0.2	0.0	14.4	0.1
acetic acid, hexyl ester	0.0	4.8	0.7	13.7	1.6	0.0	0.0	0.0	0.0	5.4	0.5	10.0	1.3
nonane, 2,5-dimethyl-	2.6	4.2	1.6	37.8	3.9	5.0	0.7	13.9	1.7	4.1	0.4	10.9	1.1
2-Hexen-1-ol, acetate, (E)-	0.0	0.4	0.1	17.6	0.2	0.0	0.0	0.0	0.0	0.5	0.1	24.8	0.3
undecane	1.6	3.6	4.7	129.9	11.6	1.1	0.1	13.2	0.3	4.8	3.5	73.4	8.7
dodecane	8.9	15.4	4.6	29.8	11.4	15.5	1.1	7.0	2.7	15.8	1.1	6.8	2.7
tridecane	0.2	0.5	0.5	103.1	1.3	0.2	0.0	5.8	0.0	0.7	0.4	65.4	1.1
2,4-decadienoic acid, methyl ester, (E,Z)-	0.1	0.8	0.1	6.6	0.1	0.2	0.0	12.8	0.1	1.0	0.1	9.6	0.2
tetradecane	2.6	4.8	0.8	16.8	2.0	4.5	0.3	7.2	0.8	5.2	0.2	3.2	0.4

9.18 **Table S12** Statistical evaluation (Stdev and t-test results) of the identified VOCs for 2018.

Table S12a. Statistical evaluation (Stdev and *t*-test results) of the identified VOC sfor 2018.			area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area
Treatment	**No. of samples**	**NOC. with *Bgt*. pathotype 51 only**	Octane	Heptane, 2,4-dimethyl-	**1,3-Octadiene**	ethylbenzene	Octane-4-methyl	m-xylene	**1,3-cis,5-cis-Octatriene**	3-heptanone	Styrene	o-xylene	Nonane	α-Pinene	Benzaldehyd	Benzene, 1-ethyl-3-methyl-	Benzene, 1,3,5-trimethy aka Mesytilene	**1-Heptanol**	**(5Z)-Octa-1,5-dien-3-ol**	β-Pinene	**1-Octen-3-ol**	**3-Octanone**	beta-Myrcene	Benzene, 1,2,4-trimethy aka psi.-Cumene	Decane	3-Carene
Control 7 DAI	1	18_1stEXP_CTR_7DAI_1	4893	8692	1	89623	11561	233536	1	3671	26251	109728	8222	155195	11322	222903	38298	1403	2661	23756	214	1172	4470	209305	14545	68830
	2	18_1stEXP_CTR_7DAI_2	6099	9415	2	87793	12271	242027	1	3966	26057	120776	8885	190633	6324	243757	44024	1135	3608	30350	174	722	3896	223286	16021	75436
	3	18_1stEXP_CTR_7DAI_3	548	9172	1	90353	11641	225220	2	4240	26041	107359	9040	150955	23372	223948	36655	1735	2686	24248	213	1484	5144	213586	17485	70594
	4	18_1stEXP_CTR_7DAI_4	8033	7488	1	90723	10773	233362	1	2808	26656	101048	6742	123996	4269	201003	34215	1338	1689	16670	254	1309	4371	191043	10128	60461
	5	18_2ndEXP_CTR_7DAI_1	1193	6715	1	9741	5047	41410	1	56	4067	5545	1487	14765	29	16479	3864	1321	1855	1103	404	810	886	17104	3012	3918
	6	18_2ndEXP_CTR_7DAI_2	917	2594	1	7768	1529	34204	3	236	3691	4226	188	12775	777	5800	1622	1282	1691	861	442	244	932	4826	445	3261
	7	18_2ndEXP_CTR_7DAI_3	1790	5550	1	21691	4358	71403	1	215	6825	28763	3291	99635	411	31761	6598	1132	3289	4714	866	287	3279	18980	3752	29550
	8	18_2ndEXP_CTR_7DAI_4	1884	5025	1	14837	3080	51238	1	179	5595	19005	1286	64847	925	23672	5657	2160	4219	3172	783	347	2576	14397	6916	21783
Control 14 DAI	1	18_1stEXP_CTR_14DAI_1	8408	3916	1	21717	2256	72881	1	103	6654	31007	2125	18732	321	34425	2817	1460	3860	1100	733	222	647	30347	2162	21779
	2	18_1stEXP_CTR_14DAI_2	3611	3894	2	21408	1747	61545	1	636	6075	23800	414	16081	693	26492	1934	734	2945	873	648	120	652	19109	750	17734
	3	18_1stEXP_CTR_14DAI_3	4365	5659	1	65510	3224	168287	2	137	12807	98257	2436	49305	3782	130680	13304	1302	3011	2561	1447	656	2854	106257	2877	73594
	4	18_1stEXP_CTR_14DAI_4	2323	3852	1	50876	2913	125775	1	865	8524	69184	1497	43296	1915	103905	10008	1242	3241	2262	668	351	1823	81486	1733	61454
	5	18_2ndEXP_CTR_14DAI_1	6846	3046	1	55695	2530	159699	1	85	10486	90422	1928	48704	7489	70881	10888	1337	2132	3042	425	184	1770	62835	380	28231
	6	18_2ndEXP_CTR_14DAI_2	1150	1801	1	13685	826	58422	17	102	3019	27988	2581	13927	161	15067	2255	1152	2887	1075	573	185	1013	11882	1371	7088
	7	18_2ndEXP_CTR_14DAI_3	2111	1995	2	13822	1207	47486	1	51	1250	22089	0	14623	560	13181	2090	649	1630	1151	1017	345	897	7900	552	6495
	8	18_2ndEXP_CTR_14DAI_4	6226	4250	1	27143	2328	107145	1	268	7231	33908	2944	8351	6448	64723	11039	202	2638	723	502	317	1712	61991	7091	6385
Inoculated 7 DAI	1	18_1stEXP_INOC_7DAI_1	2332	14109	605	22893	7803	95055	141	1093	11358	30286	3165	27772	1573	56812	11312	6846	13313	4306	4278	3525	1425	54888	10151	20381
	2	18_1stEXP_INOC_7DAI_2	1481	2801	642	11067	1917	46187	78	223	4386	9453	6937	24225	1052	19533	5098	6694	8859	4139	3778	2193	707	20321	8003	6896
	3	18_1stEXP_INOC_7DAI_3	2129	5672	626	27935	4994	95330	196	192	10406	37697	2099	31452	3329	56510	10023	8108	11453	4505	4279	2706	1845	50365	5108	22423
	4	18_1stEXP_INOC_7DAI_4	101	2633	490	8693	2357	44947	107	124	4822	7010	1586	19233	173	17663	3743	7671	10794	3332	4661	2630	726	19636	5349	5836
	5	18_2ndEXP_INOC_7DAI_1	0	6035	847	9296	5077	36821	359	76	3575	5374	5926	19644	931	17456	4708	5434	20390	1332	5780	6047	1385	17090	1993	4258
	6	18_2ndEXP_INOC_7DAI_2	1770	8939	716	11237	4526	41123	353	444	4387	8098	3114	26873	5124	23153	6215	6980	26112	1872	6441	7380	1564	22600	7109	5803
	7	18_2ndEXP_INOC_7DAI_3	4035	5013	1663	13942	2910	59727	260	349	6990	17733	1305	40341	4201	21422	5628	9038	25454	2322	7858	6783	1844	19669	3491	12175
	8	18_2ndEXP_INOC_7DAI_4	4326	10127	2565	15448	6640	55158	363	215	5664	17491	4136	43071	2873	31189	7697	8227	24599	2382	8188	7688	2148	30872	9703	11640
Inoculated 14 DAI	1	18_1stEXP_INOC_14DAI_1	248	4409	2987	45268	3008	116762	1265	165	5275	65244	725	28870	2496	80357	11205	15209	110541	1822	31424	15399	1883	53433	5267	52768
	2	18_1stEXP_INOC_14DAI_2	439	4779	2519	47352	2095	123071	1070	94	7798	65382	1641	30781	2086	78919	8869	11543	86081	1495	24820	12264	1500	52402	942	52885
	3	18_1stEXP_INOC_14DAI_3	3193	1914	2523	10316	1562	51630	1026	195	8052	5522	41	24172	381	10361	2515	13325	78996	1925	21769	11558	1040	12008	1483	6873
	4	18_1stEXP_INOC_14DAI_4	968	2755	2917	9182	3276	40296	1029	309	2546	6186	2916	22540	475	13438	2495	11820	78338	1746	21492	11227	1060	11080	4816	6412
	5	18_2ndEXP_INOC_14DAI_1	1719	2999	2108	13346	1542	60726	360	135	3806	19268	1855	22058	431	26057	5604	7804	38208	1908	12764	10624	1621	17429	2942	14811
	6	18_2ndEXP_INOC_14DAI_2	22090	11829	4415	45984	4000	129058	334	122	4882	43957	8083	7106	449	49322	10293	9205	53416	554	17925	19180	2311	39511	6530	8055
	7	18_2ndEXP_INOC_14DAI_3	3194	5592	4634	43295	4630	136072	361	557	11329	62659	6254	115084	4201	90137	16575	10925	66327	9582	21674	17960	2484	74771	12453	36155
	8	18_2ndEXP_INOC_14DAI_4	6229	6297	6049	79805	7982	217437	376	2772	24108	101800	5769	168455	1282	115839	21241	11811	65724	12546	20343	16507	2478	93609	7952	43139

Table S12a. Statistical evaluation (Stdev and *t*-test results) of the identified VOC sfor 2018.			area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area	area
Treatment	**No. of samples**	**INOC. with *Bgt*. pathotype 51 only**	p-cymene	(+)- Limonene	Indane *	Benzene, 1,2-diethyl-	Acetophenone	Benzene, 2-ethyl-1,3-dimethyl-	3-Octanol, 3,7-dimethyl	Undecane	Nonanal	Benzene, 1,2,3,4-tetramethyl-	Benzene, 1,2,3,5-tetramethyl-	Benzaldehyde, 3-ethyl-	Benzaldehyde, 4-ethyl-	Naphthalene	Dodecane	Decanal	Undecane, 2,6-dimethy	Ethanone, 1-(4-ethylphenyl)-	Tridecane	Tridecane, 3-methyl-	Tetradecane	LONGIFOLENE	B-caryophyllene	Pentadecane
Control 7 DAI	1	18_1stEXP_CTR_7DAI_1	55386	138576	31218	96412	68880	42421	2816	10835	5323	17145	20382	30128	11172	158002	12814	2981	7557	1005204	42044	5396	49689	1180	203	42574
	2	18_1stEXP_CTR_7DAI_2	59487	152729	32990	74474	73771	42977	608	14173	5965	19060	22171	26295	9722	159098	16205	3856	10803	869614	48803	11494	55751	1365	384	40642
	3	18_1stEXP_CTR_7DAI_3	58715	145986	31231	113280	70348	46885	4249	9556	3512	18637	21179	30730	11907	168519	10398	2883	7190	1049797	37646	2046	45678	1140	137	43377
	4	18_1stEXP_CTR_7DAI_4	47957	117012	29433	101483	62521	37402	3590	8776	6492	13740	17797	33358	11888	146390	11841	2205	4680	1096201	39683	2649	47638	1034	87	43703
	5	18_2ndEXP_CTR_7DAI_1	20151	5431	835	101638	49734	3252	170	5667	6193	1993	2059	32102	11527	32849	12718	1125	5671	1059890	31155	14516	36793	1620	58	52234
	6	18_2ndEXP_CTR_7DAI_2	1784	2562	610	11282	12394	753	96	3242	4008	1069	597	12508	5762	11362	7272	2236	2743	250510	23228	7106	26987	888	104	23316
	7	18_2ndEXP_CTR_7DAI_3	15211	11056	2838	29777	28726	5257	465	6405	3554	8420	2885	19582	7608	18847	7159	3010	3528	439326	29798	4674	32378	18464	551	27404
	8	18_2ndEXP_CTR_7DAI_4	4881	8445	2182	33754	23037	1277	145	3828	3954	6325	2673	17499	7124	15314	6692	2151	4283	464093	3439	12750	21465	13867	57	24198
Control 14 DAI	1	18_1stEXP_CTR_14DAI_1	20468	14425	5264	7559	22160	6426	310	2504	4286	6686	2694	10267	3848	18813	4960	2704	3273	118618	27286	5695	24671	1235	121	23549
	2	18_1stEXP_CTR_14DAI_2	4781	11187	4126	2352	8998	2748	119	2347	4131	4642	1809	9153	4100	15970	5750	2676	4223	111114	23710	1555	21674	1109	28	22596
	3	18_1stEXP_CTR_14DAI_3	27816	71879	19510	21055	37978	23802	205	4288	7460	17466	10241	14495	5997	52136	5701	3537	3355	231262	21587	2336	17498	5706	179	19063
	4	18_1stEXP_CTR_14DAI_4	23019	58672	14354	20111	17910	11752	315	5118	3612	14498	8823	7605	3040	45768	5667	232	3603	75234	18470	118	17299	4877	88	13839
	5	18_2ndEXP_CTR_14DAI_1	12028	19644	12017	10948	16050	13752	95	3775	4774	7396	6281	8406	3545	43263	6880	5260	3587	61421	13477	2378	20814	654	31	21817
	6	18_2ndEXP_CTR_14DAI_2	12209	3116	2338	1712	23440	2643	69	4029	4997	3000	983	9352	4173	6737	4709	4062	1339	55097	17000	1630	16468	118	13	27019
	7	18_2ndEXP_CTR_14DAI_3	1422	3418	1728	3551	12069	1963	263	2172	7353	2245	704	14896	6471	10280	5540	3619	3790	232624	3362	404	16743	179	64	29651
	8	18_2ndEXP_CTR_14DAI_4	10944	38344	10917	18875	11581	12891	318	14528	7438	8003	8886	78	49	4984	18395	6201	5477	1900	8707	850	51631	2347	316	67819
Inoculated 7 DAI	1	18_1stEXP_INOC_7DAI_1	31471	32569	7764	185999	68194	15126	967	17520	4521	7290	7614	40879	14853	54998	32260	9994	24839	1559591	79782	16982	134052	1077	84	108846
	2	18_1stEXP_INOC_7DAI_2	21573	11459	2558	22750	35582	3520	191	6241	6743	2912	2776	25771	11088	27814	9739	8004	2897	640877	34297	6346	65923	420	66	49215
	3	18_1stEXP_INOC_7DAI_3	14096	30664	8407	44262	39122	11703	1388	10056	8739	6902	5776	23826	8524	32353	17240	6357	22497	698836	51755	26389	89321	391	72	58562
	4	18_1stEXP_INOC_7DAI_4	16026	8562	1696	30236	37348	3118	877	4550	14070	2546	445	24659	10489	29014	9501	14944	3866	669000	58487	7606	97910	432	74	50589
	5	18_2ndEXP_INOC_7DAI_1	20043	7409	1394	81225	39224	3421	236	3582	4806	1476	2622	30930	12525	32825	8232	2829	2288	1034946	36214	2956	43340	1788	165	36972
	6	18_2ndEXP_INOC_7DAI_2	18879	7081	1661	129255	55588	5016	91	16467	4288	1723	3314	36378	14176	34528	9010	6647	5810	1333555	30577	11445	39960	3037	214	56971
	7	18_2ndEXP_INOC_7DAI_3	22699	7944	2292	44443	50814	5595	157	6123	10753	4210	3418	25257	9935	26856	9016	8596	9032	680292	30602	8390	46412	8302	451	35875
	8	18_2ndEXP_INOC_7DAI_4	27462	12948	2983	140962	69665	6649	302	6884	7037	4516	4721	39777	15649	42874	16199	8701	17248	1301632	36323	4784	64757	8047	455	55267
Inoculated 14 DAI	1	18_1stEXP_INOC_14DAI_1	13741	28433	10864	14795	14730	13452	561	11638	4247	10510	5942	11263	4717	22883	11386	3485	9947	70758	20542	1225	29642	2372	53	26883
	2	18_1stEXP_INOC_14DAI_2	14141	25494	10493	13463	15450	6533	190	1735	2151	10413	6158	6287	2945	21904	8444	2242	11537	49663	22185	783	23372	2133	59	22578
	3	18_1stEXP_INOC_14DAI_3	8561	6102	1267	3622	12126	1911	205	2042	5195	1054	270	10194	3960	15671	9387	2893	2487	128700	23690	1560	29639	652	46	23221
	4	18_1stEXP_INOC_14DAI_4	5324	5928	1124	23536	23523	1760	176	15348	3405	955	1355	21180	8303	22547	7971	2675	2824	580370	21992	2317	31227	963	45	33186
	5	18_2ndEXP_INOC_14DAI_1	4771	7255	2933	4809	8408	4449	309	3194	10061	4742	2326	8048	4168	15415	6211	3406	2970	92600	19282	887	18820	373	26	33426
	6	18_2ndEXP_INOC_14DAI_2	13206	23839	4759	9550	12787	8058	460	8286	8090	4874	4223	112	98	4946	22382	6188	6872	1088	66872	4460	69769	1278	185	147705
	7	18_2ndEXP_INOC_14DAI_3	11117	38101	12308	9115	22996	15114	46	10827	11809	9226	7307	12566	5764	87691	15177	12326	6671	57634	25759	1982	35942	1009	36	53494
	8	18_2ndEXP_INOC_14DAI_4	17859	41548	14364	17051	21261	15613	510	9828	11901	9360	8409	13093	5976	92359	13764	10527	5337	68263	34990	560	32589	1037	55	43812

	SUMMARY 2018		Octane	Heptane, 2,4-dimethyl-	**1,3-Octadiene**	ethylbenzene	Octane-4-methyl	m-xylene	**1,3-cis,5-cis-Octatriene**	3-heptanone	Styrene	o-xylene	Nonane	α-Pinene	Benzaldehyd	Benzene, 1-ethyl-3-methyl-	Benzene, 1,3,5-trimethy aka Mesytilene	**1-Heptanol**	**(5Z)-Octa-1,5-dien-3-ol**	β-Pinene	**1-Octen-3-ol**	**3-Octanone**	beta-Myrcene	Benzene, 1,2,4-trimethy aka psi.-Cumene	Decane	3-Carene
	AVG area 2018	**CTR_7DAI (n=8)**	3169.50	6831.20	1.13	51566.13	7532.38	141550.02	1.39	1921.42	15647.98	62056.02	4892.71	101600.16	5928.58	121165.26	21366.63	1438.31	2712.25	13109.18	418.69	796.84	3194.14	111565.85	9037.96	41729.17
		CTR_14DAI (n=8)	4380.13	3551.73	1.25	33731.95	2128.98	100155.06	3.14	280.88	7005.63	49581.88	1740.73	26627.30	2671.13	57419.19	6791.88	1009.64	2793.00	1598.20	751.51	297.59	1420.94	47725.78	2114.50	27845.00
		INOC_7DAI (n=8)	2021.45	6916.00	1019.23	15064.04	4527.99	59293.28	232.03	339.50	6448.16	16642.75	3533.50	29076.41	2407.00	30467.29	6803.00	7374.75	17621.78	3023.64	5657.81	4868.89	1455.43	29430.13	6363.38	11176.50
		INOC_14DAI (n=8)	4759.96	5071.73	3518.94	36818.51	3512.09	109381.54	727.65	543.63	8474.15	46252.16	3410.18	52383.04	1475.13	58053.66	9849.63	11455.25	72203.88	3947.21	21526.51	14339.90	1797.03	44280.29	5298.13	27637.25
	stdev area 2018	**CTR_7DAI (n=8)**	2793.25	2357.94	0.35	40896.45	4443.08	99006.03	0.78	1915.08	11376.46	51814.33	3721.58	66032.08	8045.34	109599.18	18361.22	347.30	943.66	12016.61	268.67	485.51	1610.04	104942.00	6483.19	30496.72
		CTR_14DAI (n=8)	2566.86	1254.20	0.46	20438.24	821.51	47272.50	5.65	303.09	3744.14	31393.64	1046.81	17289.61	2914.89	43092.17	4923.08	435.59	679.51	883.69	332.11	167.81	760.61	35835.55	2183.03	25936.52
		INOC_7DAI (n=8)	1585.62	3916.30	724.59	6895.68	2065.15	23322.59	118.03	326.34	2929.73	11806.55	2028.27	8818.42	1747.19	16737.10	2669.53	1120.17	7268.30	1210.94	1698.91	2328.99	519.83	14936.00	2895.79	6928.23
		INOC_14DAI (n=8)	7270.65	3107.32	1366.67	24416.59	2120.30	57932.02	402.53	912.82	6900.14	33972.85	2923.89	57420.42	1374.44	39035.51	6588.97	2284.43	21815.13	4485.19	5345.98	3335.75	590.53	30237.76	3762.00	20741.62
green background: p≤0.06	***t*-tests 2018**	**CTR7 VS INOC7**	0.334	0.959	0.005	0.040	0.114	0.052	0.001	0.053	0.058	0.043	0.384	0.017	0.262	0.052	0.060	0.000	0.001	0.049	0.000	0.001	0.019	0.063	0.313	0.025
		CTR14 VS INOC14	0.892	0.231	0.000	0.788	0.119	0.732	0.001	0.461	0.607	0.842	0.164	0.258	0.319	0.976	0.312	0.000	0.000	0.186	0.000	0.000	0.289	0.838	0.062	0.986
		CTR7 VSCTR14	0.382	0.005	0.554	0.295	0.011	0.311	0.413	0.046	0.073	0.572	0.050	0.015	0.310	0.160	0.062	0.048	0.847	0.030	0.046	0.023	0.018	0.139	0.020	0.344
		INOC7 VS INOC14	0.330	0.315	0.001	0.041	0.348	0.049	0.010	0.567	0.463	0.046	0.923	0.292	0.257	0.098	0.256	0.001	0.000	0.589	0.000	0.000	0.240	0.241	0.537	0.064
Cohen's *d* * (effect size)	**34**/48 ≥0.8	**CTR_7DAI VS INOC_7DAI**	0.505	-0.026	**-1.987**	**1.245**	**0.867**	**1.144**	**-2.763**	**1.152**	**1.107**	**1.209**	0.454	**1.540**	0.605	**1.157**	**1.110**	**-7.159**	**-2.877**	**1.181**	**-4.308**	**-2.421**	**1.453**	**1.096**	0.533	**1.382**
Power (α=0.05)					0.958				0.999									1.000	1.000		1.000	0.994				
False Discovery Rate (FDR, Benjamini-Hochbe			0.401	0.979	**0.034**	0.148	0.182	0.147	**0.016**	0.141	0.127	0.147	0.439	0.102	0.340	0.156	0.120	**0.000**	**0.012**	0.157	**0.000**	**0.001**	0.101	0.121	0.395	0.109
Cohen's *d* *	**13**/48 ≥0.8	**CTR_14DAI VS INOC_14DAI**	-0.070	-0.642	**-3.640**	-0.137	**-0.860**	-0.175	**-2.545**	-0.386	-0.265	0.102	**-0.760**	-0.607	0.525	-0.015	-0.526	**-6.352**	**-4.498**	-0.727	**-5.485**	**-5.946**	-0.552	0.104	**-1.035**	0.009
Power (α=0.05)					1.000				0.997									1.000	1.000		1.000	1.000				
FDR			0.931	0.652	**0.000**	0.901	0.519	0.950	**0.008**	0.763	0.883	0.919	0.606	0.619	0.638	0.997	0.651	**0.000**	**0.000**	0.638	**0.000**	**0.000**	0.661	0.935	0.425	0.986

	SUMMARY 2018		p-cymene	(+)- Limonene	Indane *	Benzene, 1,2-diethyl-	Acetophenone	Benzene, 2-ethyl-1,3-dimethyl-	3-Octanol, 3,7-dimethy	Undecane	Nonanal	Benzene, 1,2,3,4-tetramethyl-	Benzene, 1,2,3,5-tetramethyl-	Benzaldehyde, 3-ethyl-	Benzaldehyde, 4-ethyl-	Naphthalene	Dodecane	Decanal	Undecane, 2,6-dimethy	Ethanone, 1-(4-ethylphenyl)-	Tridecane	Tridecane, 3-methyl-	Tetradecane	LONGIFOLENE	B-caryophyllene	Pentadecane
	AVG area 2018	**CTR_7DAI (n=8)**	32946.40	72724.58	16417.20	70262.55	48676.38	22528.08	1517.33	7810.15	4875.06	10798.43	11217.92	25275.23	9588.54	88797.53	10637.36	2555.79	5806.77	#######	31974.44	7578.92	39547.24	4944.71	197.58	37180.85
		CTR_14DAI (n=8)	14085.94	27585.63	8781.75	10770.38	18773.15	9497.11	211.75	4845.01	5506.36	7991.89	5052.63	9281.41	3902.93	24743.80	7200.19	3536.25	3581.04	#######	16699.74	1870.75	23349.76	2028.13	105.00	28169.04
		INOC_7DAI (n=8)	21531.10	14829.50	3594.45	84891.31	49442.16	6768.44	526.13	8927.71	7619.53	3946.78	3835.75	30934.61	12155.06	35157.48	13899.48	8258.96	11059.68	#######	44754.75	10612.25	72709.43	2936.75	197.63	56537.14
		INOC_14DAI (n=8)	11089.84	22087.50	7263.96	11992.55	16410.13	8361.06	307.13	7862.35	7107.18	6391.70	4498.75	10342.89	4491.34	35426.96	11840.24	5467.80	6080.45	#######	29413.86	1721.75	33874.98	1227.13	63.13	48038.14
	stdev area 2018	**CTR_7DAI (n=8)**	24883.50	71165.58	15866.71	39572.46	24119.33	21461.04	1736.03	3720.79	1250.32	7333.89	9896.66	7766.08	2437.23	74472.80	3392.41	812.46	2622.14	#######	14002.07	4758.96	12024.89	7037.13	178.72	10723.47
		CTR_14DAI (n=8)	9052.58	26000.09	6397.63	8229.78	9277.20	7541.00	104.80	4050.05	1635.44	5389.38	3944.17	4597.93	1957.27	19166.13	4568.56	1801.09	1148.04	82875.64	7932.61	1753.43	11787.87	2143.91	101.48	16718.79
		INOC_7DAI (n=8)	5734.53	10570.28	2825.25	60336.93	13885.03	4370.95	482.94	5331.04	3430.99	2216.38	2183.17	7126.62	2556.11	9467.77	8194.88	3459.54	9149.41	#######	17399.50	7699.13	32535.53	3354.69	166.08	22806.08
		INOC_14DAI (n=8)	4570.16	14276.60	5317.34	6598.38	5564.61	5707.40	184.59	5019.08	3870.92	4018.56	2941.69	6061.46	2404.81	34223.46	5215.13	3894.41	3368.80	#######	15896.99	1260.43	15464.87	691.55	50.39	41622.24
green background: p≤0.06	***t*-tests 2018**	**CTR7 VS INOC7**	0.243	0.055	0.057	0.577	0.939	0.078	0.158	0.635	0.063	0.034	0.075	0.151	0.059	0.082	0.324	0.002	0.156	0.254	0.129	0.362	0.025	0.483	1.000	0.055
		CTR14 VS INOC14	0.422	0.611	0.614	0.748	0.549	0.739	0.230	0.208	0.308	0.513	0.755	0.699	0.600	0.457	0.080	0.232	0.080	0.784	0.070	0.848	0.150	0.343	0.320	0.241
		CTR7 VSCTR14	0.075	0.127	0.238	0.004	0.010	0.141	0.071	0.150	0.401	0.399	0.135	0.000	0.000	0.047	0.111	0.192	0.054	0.001	0.021	0.011	0.017	0.294	0.229	0.224
		INOC7 VS INOC14	0.001	0.269	0.114	0.011	0.000	0.542	0.261	0.687	0.784	0.160	0.617	0.000	0.000	0.983	0.560	0.152	0.183	0.000	0.087	0.014	0.012	0.198	0.059	0.623
Cohen's *d* * (effect	**34**/48 ≥0.8	**CTR_7DAI VS INOC_7DAI**	0.632	**1.138**	**1.125**	-0.287	-0.039	**1.018**	**0.778**	-0.243	**-1.063**	**1.265**	**1.030**	**-0.759**	**-1.028**	**1.010**	-0.520	**-2.270**	**-0.781**	-0.595	**-0.809**	-0.474	**-1.352**	0.364	0.000	**-1.086**
Power (α=0.05)																										
False Discovery Rate (FDR, Benjami			0.333	0.132	0.130	0.629	0.980	0.134	0.223	0.677	0.116	0.136	0.133	0.226	0.123	0.136	0.399	**0.016**	0.227	0.339	0.200	0.424	0.120	0.539	1.000	0.140
Cohen's *d* *	**13**/48 ≥0.8	**CTR_14DAI VS INOC_14DAI**	0.418	0.262	0.258	-0.164	0.309	0.170	-0.635	-0.662	-0.539	0.337	0.159	-0.197	-0.268	-0.385	**-0.946**	-0.637	**-0.993**	-0.141	**-1.012**	0.098	**-0.765**	0.503	0.523	-0.626
Power (α=0.05)																										
FDR			0.750	0.863	0.842	0.921	0.850	0.933	0.690	0.666	0.672	0.821	0.906	0.932	0.900	0.783	0.427	0.619	0.384	0.918	0.420	0.905	0.600	0.633	0.614	0.609

9.19 Table S13 Statistical evaluation (Stdev and t-test results) of the identified VOCs for 2019.

Table S12b. Statistical evaluation (Stdev and *t*-test results) of the identified VOCs for 2019.

Treatment	No. of samples	INOCULATED at 14 DAI only	area Octane	area Heptane, 2,4-dimethyl-	area **1,3-Octadiene**	area ethylbenzene	area Octane-4-methyl	area m-xylene	area **1,3-cis,5-cis-Octatriene**	area 3-heptanone	area Styrene	area o-xylene	area Nonane	area α-Pinene	area Benzaldehyd	area Benzene, 1-ethyl-3-methyl-	area Benzene, 1,3,5-trimethyl aka Mesytilene	area **1-Heptanol**	area **(5Z)-Octa-1,5-dien-3-ol**	area β-Pinene	area **1-Octen-3-ol**	area **3-Octanone**	area beta-Myrcene	area Benzene, 1,2,4-trimethyl aka psi.-Cumene	area Decane	area 3-Carene
Control	1	19_1stEXP_CTR_14DAI_1	4877.5	11386.1	1	4432.8	7174.9	21358.4	51.1	472	1491.4	7846.7	0	38343.7	1170	59170.1	18968	1086	413.1	2476.9	1811.4	352.4	2617.3	71173.1	1810	27939
	2	19_1stEXP_CTR_14DAI_2	3105.5	12546.5	2	3571.3	16505.2	18164.7	21.8	8888	1278.3	4072.2	3376.8	26025.8	761	22451.4	7649	968	988.6	2128.6	1480.5	304.9	4256.2	25421.2	563	11702
	3	19_1stEXP_CTR_14DAI_3	3079.3	10254.5	1	4203.3	5110.6	19825.7	76.9	16362	628.6	6421	4705.2	50020.7	6312	39001.3	19983	982	6248	2688.4	1066.7	429.3	3139.6	50145.8	2309	21701
	4	19_1stEXP_CTR_14DAI_4	4351	25274.8	2	3383.6	28949.9	19854	41.2	11358.6	743.2	4447.5	241.9	16579.5	887	18403.4	5661	1429	1655	1810.4	2823.5	341.1	4534.7	17564.1	571	9408
	5	19_2ndEXP_CTR_14DAI_1	3453.3	9573.1	1	7616.7	4551.8	29068.9	156.6	698	892.5	12407.2	1133.3	16434.5	497	16581.7	2808	1448.3	7771.5	2101.3	3833.6	645	2991	9609.8	3073	7685
	6	19_2ndEXP_CTR_14DAI_2	3348.9	4397.2	1	19158.2	2145.8	54032.6	140.7	476	2347.2	25210.1	4506.2	19179.8	2301	44829.2	7574	645	4244	3227.2	4959.4	415.7	3262.2	33926.6	1473	12330
	7	19_2ndEXP_CTR_14DAI_3	8332.6	5972.2	2	111888.2	7350	277789.7	249.3	5534	19587.1	117436.5	10674.9	142164.9	29212	273887.7	56676	1440	5345.2	16045.9	4002.1	963.6	6299.1	276790.4	7583	46620
	8	19_2ndEXP_CTR_14DAI_4	5424.7	10266.5	1	75566.5	9822.3	195722.6	91	349	16001	87462.7	6903.5	122570	22099	155945.8	34146	590	4983	14426.9	3378.1	755.5	4512	142651.1	8771	29896
Pathotype 51	1	19_1stEXP_51_14DAI_1	5767.3	13937.8	40501.7	24384.9	15257.3	80217.6	3830.1	6942.6	13016.9	33104.3	24705.1	540669.6	48840	396334.1	120067	21980	758304	36564	430386.7	167643.9	10178.1	529542.7	8727	16719
	2	19_1stEXP_51_14DAI_2	6074.4	7389.3	45105.4	3634.8	4564.4	17075.2	8071.7	15387.7	873.6	3847.6	3158.7	17216.7	2106	13897.2	3095	19581	1197764	2132.3	606352.2	172664.1	6917.2	9577.8	938	10317
	3	19_1stEXP_51_14DAI_3	3579	5658.8	73220.6	4268.5	4788.8	20685.3	12767.9	16392.2	1699.7	6364.8	3198.3	224256.6	1879	31030.1	9513	24433.3	1707467	8224.3	818210.9	272295.3	14058	30745.4	3303	36382
	4	19_1stEXP_51_14DAI_4	3186.8	9391.3	57632.6	4379.6	5179.2	17751.5	10642.8	19468.3	991.1	4737.4	6351.3	375750.2	56	19520.3	5266	28820	1723572	17825.6	798858.3	227199.3	17810.1	19321.1	1595	48399
	5	19_2ndEXP_51_14DAI_1	4972.2	10239.9	74393.6	81444.5	8806.9	206670.1	10730	1808	15036.9	93643.3	3253.7	137513.2	4324	149029.6	33202	19162	847285	16635.7	458740.7	161905.2	7287.5	131438.9	5668	31595
	6	19_2ndEXP_51_14DAI_2	2252.3	4743.2	31721.7	46523.2	4794.8	135931.8	5717.3	5830	7669.5	64345	4333.2	67908.8	3776	109137.5	23784	18341	404978	7752	209891	76747.1	7792.6	96291.9	1516	23309
	7	19_2ndEXP_51_14DAI_3	4438.9	3884.6	30638.1	48902.2	2867.7	138359.3	5617.6	479	6822.2	63158.4	1432.8	66962.8	4161	99948.6	21413	17159	360346	9925.9	206314.3	67569.6	7622.8	84538.5	1662	24329
	8	19_2ndEXP_51_14DAI_4	3446.5	23725.1	38171.2	41738.6	10822.9	125613.8	6519.8	2682	6043.5	58125.1	3442.2	62907.8	2203	90835.9	18796	19979	944043	11591.9	318958.9	91182.5	8007.3	69359.9	10506	24263
Pathotype 71	1	19_1stEXP_71_14DAI_1	3206.4	3972.5	41391.7	3419.2	4689.5	15082.9	7328.9	9935.9	1080.9	4223.7	4118.9	30059.9	1709	25984.8	9081	29797	1041130	4179	439576.8	137585.9	7646.5	76835.9	4009	23376
	2	19_1stEXP_71_14DAI_2	3817.3	10766.6	52883.8	3152.7	7591.7	14397.7	8400.9	8224.9	292.3	2815.4	870.5	7925.1	2108	7942.8	1020	18093	1037282	1274.9	477285.2	164871.5	6525.1	9014.9	7580	4089
	3	19_2ndEXP_71_14DAI_1	6150.4	11831	22522.4	103004.3	8843.1	266941.2	4660.6	4440	22303.5	116244.5	10941.7	200439.9	24492	230308.9	56175	20743	322042	23362.4	156390.1	49136.1	4194.7	224396	1663	44303
	4	19_2ndEXP_71_14DAI_2	18428.5	11332.3	13891.5	235885.4	16438.6	574628.9	1146.3	4218	73732.8	238740.7	32951.3	473683.5	6481	539503.3	144563	27903	176111	59125.8	96454	38724.2	6477.4	576263.4	4194	71737

Table S12b. Statistical evaluation (Stdev and *t*-test results) of the identified VOCs for 2019.

Treatment	No. of samples	INOCULATED at 14 DAI only	area p-cymene	area (+)- Limonene	area Indane *	area Benzene, 1,2-diethyl-	area Acetophenone	area Benzene, 2-ethyl-1,3-dimethyl-	area 3-Octanol, 3,7-dimethyl	area Undecane	area Nonanal	area Benzene, 1,2,3,4-tetramethyl-	area Benzene, 1,2,3,5-tetramethyl-	area Benzaldehyde, 3-ethyl-	area Benzaldehyde, 4-ethyl-	area Naphthalene	area Dodecane	area Decanal	area Undecane, 2,6-dimethy	area Ethanone, 1-(4-ethylphenyl)-	area Tridecane	area Tridecane, 3-methyl-	area Tetradecane	area LONGIFOLENE	area B-caryophyllene	area Pentadecane
Control	1	19_1stEXP_CTR_14DAI_1	59967	10182	8783.3	32731.5	22504.3	26943.3	210	6642.4	5383.1	17582.8	18083	31155.9	15356.2	15101.4	6158.3	5962.9	1495.6	565752.9	6426.9	7494	16187.1	268.7	397	45666.9
	2	19_1stEXP_CTR_14DAI_2	28139.6	16756	4035.5	29865.1	10493.3	10183.3	470	10591.3	9443.8	6245.3	6359	2576.5	813.7	9580.2	16951	7592.9	1668.1	45605.7	30677.1	10730	82840.4	963.7	14245	69164.5
	3	19_1stEXP_CTR_14DAI_3	36192.1	6086	7022.6	41936.1	17545.8	18897.7	350	5773.8	8390.7	15966.6	16109	3425.4	1319.1	8355.4	4123	5030.4	1807.6	40385.3	5987.7	10574	14707	209	5246	39873.2
	4	19_1stEXP_CTR_14DAI_4	29089	8902	3342.6	34778.8	5989.5	5938.4	421	13270.6	8039.4	4497.6	5194	3412.9	2095.7	4155.5	12590.7	5174.8	956.4	58235.5	5504.7	4144	52848.5	380.5	41457	103635.5
	5	19_2ndEXP_CTR_14DAI_1	25264.6	2959	1461.8	14949.9	5948.5	5104.6	243	4446.3	7600.3	3423	281	1854.5	1094.5	1559	3189.8	2409.2	466.9	44564.1	18343.6	7839	43822.5	175	391	4899084.4
	6	19_2ndEXP_CTR_14DAI_2	54379.7	8234	4714.3	23337.5	19085.7	8768.1	14579	6026.2	8226.6	5019.7	4154	2911.8	1974.5	6350.4	8558.4	11153.9	943.1	48777.9	22299.1	6806	51002.6	960	166	1331305.5
	7	19_2ndEXP_CTR_14DAI_3	72406.4	21261	29525.3	59886.6	36060.1	24541.7	142	14943	1601.9	16555.2	20220	3353.2	1290.6	78889	7487.3	1169.1	2285.6	53846.2	18516	8344	16731.7	233	847	112716.3
	8	19_2ndEXP_CTR_14DAI_4	62053.5	18409	16795	39041.4	20304.8	27680.4	19642	13650.5	7600.7	9465.7	10194	4090.7	1647.3	46470.1	12190.9	5448.5	747.2	58567.7	18483.1	8503	41044.1	715	430	65478.8
Pathotype 51	1	19_1stEXP_51_14DAI_1	107689.7	71294	53530.9	162294.3	140338.5	89805.8	383	56436.6	42818.2	80288.5	99451	41133.1	20792.1	277332.9	54153.6	52111.2	12015	643205.1	151435.8	8131	51288.1	888	300	62381.7
	2	19_1stEXP_51_14DAI_2	40289.8	14028	1851.8	32602.9	7823.7	4196.3	61	5301.1	14692.1	6632.8	3564	4136.1	3318.2	5149	6542.5	11027.4	0	77414.9	15294.9	2570	42826.3	876	54	95071.1
	3	19_1stEXP_51_14DAI_3	54652.9	26011	4258.5	38449.6	14171.9	12617	518	4929.6	16175.3	13256.1	10057	5242	2284.7	8746.3	6633.4	10021.2	463	65684.1	25207.2	8984	44913.2	93	496	43530.3
	4	19_1stEXP_51_14DAI_4	81810.1	23123	2786.8	36121.7	15998.9	7011.4	168	4624.8	14234.4	7105.2	6304	4673.8	1614.7	4865.1	7796.3	8668.5	1593.1	58790.7	13364.1	3438	24596.8	1369	121	31983.8
	5	19_2ndEXP_51_14DAI_1	48485.9	18040	17510.7	35428.4	18771.1	14839.7	17454	7604.2	6379.9	10313.6	10813	2672.1	1056.1	35766.4	8826.9	6851.5	1030	43276.5	14388.1	3823	32314.9	676	240	28691
	6	19_2ndEXP_51_14DAI_2	76402.9	7979	13309.9	30903.6	42590.8	21644.8	98	3716	4256.9	9998.6	9401	1931.7	1361.9	23589.1	4312.3	2423.1	204.5	37164.5	6858.2	3917	16398.3	298	91	33334.4
	7	19_2ndEXP_51_14DAI_3	65484.8	15315	11393.1	30900.8	26024.6	16880.8	28096	9149.4	7115.5	8247.8	7377	3032	989.4	18861.8	5834.9	7651.7	0	51377.4	13683.1	2171	22084.1	920	44	28336.7
	8	19_2ndEXP_51_14DAI_4	14901	25431	10993.7	28475.5	10369.3	14902.7	81282	12589.5	8119.1	7874.4	6389	2871.1	2211.3	19408	9948.6	8338.1	1426.6	57985.1	12713	5282	35784.9	467	50	165399.8
Pathotype 71	1	19_1stEXP_71_14DAI_1	40512.9	10768	3442.8	38341.1	14517.4	12396.2	251	3231	15149.9	8477.6	8595	4050	1935.8	3749	4575.8	5520	329.6	60739	6624.8	2058	11171.3	148	60	18834.5
	2	19_1stEXP_71_14DAI_2	83400.1	10728	1024.2	27408	12874.1	1289.6	95	12435.9	11313.4	671.9	784	3009.4	1551.2	3264.4	5326.3	6246.7	429	50468.7	14858.9	2265	27576.6	34	58	32155.7
	3	19_2ndEXP_71_14DAI_1	81156.2	30845	25748.2	52672.3	38603.5	37279	26672	19878.4	6643.1	14984.3	15336	5250.5	1678.2	77511.7	10660	9722.6	2614.5	71026.6	28459.3	5645	49822.8	960	70	118690.9
	4	19_2ndEXP_71_14DAI_2	99433.3	43346	56959.1	106985.9	70745.5	85038.5	113	74097.2	18039.2	27146.3	36916	11773.6	4839.9	239112.6	44476.4	6574.7	9275.2	156598.9	111864.6	11997	51371.4	438	56	98210

	SUMMARY 2019		Octane	Heptane, 2,4-dimethyl-	**1,3-Octadiene**	ethylbenzene	Octane-4-methyl	m-xylene	**1,3-cis,5-cis-Octatriene**	3-heptanone	Styrene	o-xylene	Nonane	α-Pinene	Benzaldehyd	Benzene, 1-ethyl-3-methyl-	Benzene, 1,3,5-trimethyl aka Mesytilene	**1-Heptanol**	**(5Z)-Octa-1,5-dien-3-ol**	β-Pinene	**1-Octen-3-ol**	**3-Octanone**	beta-Myrcene	Benzene, 1,2,4-trimethyl aka psi.-Cumene	Decane	3-Carene
	AVG area 2019	CTR_14DAI (n=8)	4496.60	11208.86	1.38	28727.58	10201.31	79477.08	103.58	5517.20	5371.16	33162.99	3942.73	53914.86	7904.88	78783.83	19183.13	1073.54	3956.05	5613.20	2919.41	525.94	3951.51	78410.26	3269.13	20910.13
		INOC_51_14DAI (n=8)	4214.68	9871.25	48923.11	31909.54	7135.25	92788.08	7987.15	8623.73	6519.18	40915.74	6234.41	186648.21	8419.00	113716.66	29392.00	23681.91	955469.88	13831.46	480964.13	154650.88	9959.20	121352.03	4239.38	45716.63
		INOC_71_14DAI (n=4)	7900.65	9475.60	33172.35	86365.40	9390.73	217762.68	5384.18	6704.70	24352.38	90506.08	12220.60	178027.10	8697.50	200934.95	52709.75	24134.00	644141.25	21985.53	292426.53	97579.43	6210.93	209127.55	4361.50	35876.25
		INOC_(51+71)_14DAI (n=12)	5443.33	9739.37	43672.86	50061.49	7887.08	134446.28	7119.49	7984.05	12463.58	57445.85	8229.81	183774.51	8511.83	142789.43	37164.58	23832.61	851693.67	16549.48	418118.26	135627.06	8709.78	150610.53	4280.08	42436.50
	STDEV area 2019	CTR_14DAI (n=8)	1776.52	6301.56	0.52	41599.53	8712.92	100199.45	75.24	6140.00	7746.00	44031.54	3634.00	50060.33	11275.31	90890.83	18318.96	346.04	2660.05	5970.68	1369.04	236.96	1200.91	90676.20	3157.72	13402.48
		INOC_51_14DAI (n=8)	1330.68	6490.37	17510.40	27853.28	4174.61	70411.56	3108.50	7391.42	5372.85	33927.93	7589.55	184143.47	16394.39	123939.86	38008.71	7594.89	537050.91	10461.66	241638.77	73026.20	3943.15	170092.89	3669.93	50299.20
		INOC_71_14DAI (n=4)	7132.29	3694.41	18056.85	110208.15	5010.34	265962.68	3233.46	2832.21	34462.89	112205.58	14443.68	215053.50	10749.26	247214.40	65889.62	5605.58	460057.95	26628.92	193853.10	63085.75	1448.65	263500.27	2435.36	29003.96
		INOC_(51+71)_14DAI (n=12)	4277.15	5528.75	18552.16	67268.79	4378.34	161965.96	3262.36	6151.98	20478.83	69009.80	10111.32	184957.97	14232.73	168187.64	47277.59	6732.48	514551.33	16707.99	236691.71	72585.34	3724.62	198027.49	3192.48	43161.41
green background: *t*-tests 2019 green background: p≤0.05		CTR_14DAI VS INOC_51_14DAI	0.725	0.682	0.000	0.860	0.390	0.764	0.000	0.376	0.736	0.700	0.459	0.085	0.943	0.532	0.509	0.000	0.002	0.080	0.001	0.001	0.003	0.542	0.580	0.215
		CTR14_1 VS INOC_71_14DAI	0.413	0.563	0.035	0.378	0.843	0.380	0.047	0.657	0.353	0.388	0.337	0.334	0.209	0.402	0.387	0.054	0.069	0.308	0.058	0.054	0.042	0.399	0.528	0.387
		CTR14_1 VS INOC_(51+71)_14DAI	0.504	0.600	0.000	0.549	0.504	0.361	0.000	0.393	0.893	0.350	0.199	0.038	0.917	0.287	0.252	0.000	0.000	0.056	0.000	0.000	0.001	0.286	0.495	0.129
		INOC_51_14DAI VS INOC_71_14D	0.379	0.896	0.201	0.398	0.472	0.420	0.232	0.533	0.378	0.446	0.482	0.948	0.973	0.544	0.548	0.910	0.331	0.591	0.185	0.204	0.039	0.575	0.947	0.678
Cohen's *d* * (effect size) 13/48 ≥0.8		CTR_14DAI VS INOC_51_14DAI	0.180	0.209	**-3.951**	-0.090	0.449	-0.154	**-3.586**	-0.457	-0.172	-0.197	-0.385	**-0.984**	-0.037	-0.321	-0.342	**-4.205**	**-2.506**	**-0.965**	**-2.798**	**-2.985**	**-2.061**	-0.315	-0.283	-0.674
Power (α=0.05)					1.000				1.000									1.000	0.996		0.999	1.000				
False Discovery rate (FDR, Benjamini-Hohcberg)			0.849	0.839	**0.000**	0.897	0.851	0.833	**0.000**	0.859	0.841	0.840	0.816	0.408	0.943	0.751	0.788	**0.000**	**0.016**	0.427	**0.010**	**0.010**	**0.021**	0.743	0.773	0.688

	SUMMARY 2019		p-cymene	(+)- Limonene	Indane *	Benzene, 1,2-diethyl-	Acetophenone	Benzene, 2-ethyl-1,3-dimethyl-	3-Octanol, 3,7-dimethyl	Undecane	Nonanal	Benzene, 1,2,3,4-tetramethyl-	Benzene, 1,2,3,5-tetramethyl-	Benzaldehyde, 3-ethyl-	Benzaldehyde, 4-ethyl-	Naphthalene	Dodecane	Decanal	Undecane, 2,6-dimethy	Ethanone, 1-(4-ethylphenyl)-	Tridecane	Tridecane, 3-methyl-	Tetradecane	LONGIFOLENE	B-caryophyllene	Pentadecane
	AVG area 2019	CTR_14DAI (n=8)	45936.49	11609.88	9460.13	34565.86	17241.63	15432.94	4507.13	9418.01	7048.31	9844.49	10074.25	6597.61	3198.95	21307.63	8906.18	5492.71	1296.31	########	15779.78	8054.25	39897.99	488.11	7897.38	########	
		INOC_51_14DAI (n=8)	61214.64	25152.63	14454.43	49397.10	34511.10	22737.31	16007.50	13043.90	14223.93	17964.63	19169.50	8211.49	4203.55	49214.83	13006.06	13386.59	2091.64	########	31618.05	4789.50	33775.83	698.38	174.50	61091.10	
		INOC_71_14DAI (n=4)	76125.63	23921.75	21793.58	56351.83	34185.13	34000.83	6782.75	27410.63	12786.40	12820.03	15407.75	6020.88	2501.28	80909.43	16259.63	7016.00	3162.08	84708.30	40451.90	5491.25	34985.53	395.00	61.00	66972.78	
		INOC_(51+71)_14DAI (n=12)	66184.97	24742.33	16900.81	51715.34	34402.44	26491.82	12932.58	17832.81	13744.75	16249.76	17915.58	7481.28	3636.13	59779.69	14090.58	11263.06	2448.45	########	34562.67	5023.42	34179.06	597.25	136.67	63051.66	
	TDEV area 201	CTR_14DAI (n=8)	18327.98	6471.98	9381.99	13373.00	9959.89	10435.27	7896.53	4172.45	2484.32	5959.34	7290.76	9945.40	4931.19	27256.71	4695.36	3051.92	615.03	########	9061.21	2104.50	23559.24	338.29	14399.48	########	
		INOC_51_14DAI (n=8)	28337.01	19639.68	16724.18	45733.49	44136.02	27648.10	28413.60	17774.68	12365.44	25272.79	32524.43	13348.31	6746.74	92760.48	16718.13	15856.63	4057.65	########	48676.82	2515.85	12199.13	404.82	160.48	47936.39	
		INOC_71_14DAI (n=4)	25098.06	16045.03	25951.05	35305.71	27062.66	37203.83	13259.68	31860.46	4935.85	11200.59	15522.86	3942.95	1567.27	########	19005.19	1857.44	4209.62	48656.36	48452.28	4638.40	19241.02	413.28	6.22	48921.88	
		INOC_(51+71)_14DAI (n=12)	27141.95	17777.38	19357.62	41020.32	37939.38	29911.40	24131.66	22976.76	10219.98	21144.39	27245.49	10899.04	5508.06	95314.13	16701.36	13068.37	3948.19	########	46551.05	3164.64	14000.93	416.15	139.73	46080.54	
green background: *t*-tests 2019 green background: p≤0.05		CTR_14DAI VS INOC_51_14DA	0.225	0.099	0.477	0.404	0.313	0.502	0.302	0.590	0.148	0.403	0.463	0.788	0.739	0.437	0.523	0.206	0.600	0.881	0.394	0.014	0.528	0.279	0.173	0.229
		CTR14_1 VS INOC_71_14DAI	0.089	0.224	0.418	0.309	0.303	0.395	0.767	0.341	0.098	0.646	0.553	0.889	0.723	0.364	0.498	0.312	0.442	0.676	0.385	0.358	0.710	0.712	0.168	0.286
		CTR14_1 VS INOC_(51+71)_14	0.062	0.034	0.268	0.200	0.159	0.258	0.280	0.239	0.049	0.339	0.360	0.854	0.855	0.209	0.327	0.166	0.341	1.000	0.198	0.019	0.550	0.528	0.171	0.235
		INOC_51_14DAI VS INOC_71_	0.385	0.911	0.632	0.779	0.988	0.616	0.461	0.449	0.781	0.636	0.792	0.678	0.516	0.643	0.782	0.297	0.689	0.579	0.776	0.792	0.914	0.273	0.086	0.850
Cohen's *d* * (e13/48 ≥0.8		CTR_14DAI VS INOC_51_14DA	-0.640	**-0.926**	-0.368	-0.440	-0.540	-0.350	-0.551	-0.281	**-0.805**	-0.442	-0.386	-0.137	-0.170	-0.408	-0.334	-0.691	-0.274	-0.076	-0.452	**1.408**	0.326	-0.564	**0.758**	0.648	
Power (α=0.05)																										
False Discovery rate (FDR, Benjamini-Hohcberg)			0.675	0.432	0.790	0.776	0.751	0.803	0.763	0.765	0.592	0.806	0.794	0.841	0.825	0.807	0.785	0.706	0.758	0.900	0.822	0.084	0.768	0.744	0.639	0.647

9.20 Table S14 Statistical evaluation (Stdev and t-test results) of targeted BVOCs for 2020.

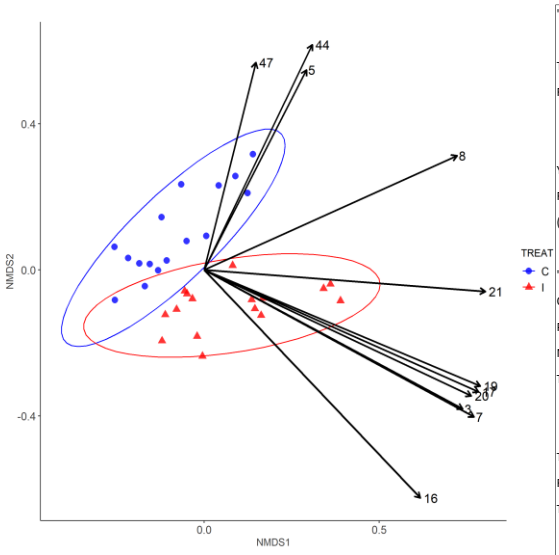
Table S12c. Statistical evaluation (Stdev and *t*-test results) of the identified VOCs for 2020.			area	area	area	area	area	area
Treatment	**No. of samples**		**1,3-Octadiene**	**1,3-cis,5-cis-Octatrien**	**1-Heptanol**	**(5Z)-Octa-1,5-dien-3-o**	**1-Octen-3-ol**	**3-Octanone**
Control 7 DAI	1	**20_CTR_7DAI_1**	**113**	**148**	**582**	**929**	**2089**	**19425**
	2	**20_CTR_7DAI_2**	**244**	**39**	**1587**	**1193**	**1698**	**6245**
	3	**20_CTR_7DAI_3**	**406**	**104**	**1515**	**746**	**1688**	**4435**
	4	**20_CTR_7DAI_4**	**239**	**25**	**1297**	**1364**	**1260**	**3155**
	5	**20_CTR_7DAI_5**	**488**	**26**	**1068**	**1396**	**944**	**2361**
	6	**20_CTR_7DAI_6**	**235**	**20**	**1362**	**1458**	**1187**	**2353**
	7	**20_CTR_7DAI_7**	**197**	**40**	**1422**	**2926**	**1694**	**4670**
	8	**20_CTR_7DAI_8**	**174**	**19**	**1397**	**4150**	**3420**	**5509**
Inoculated 7 DAI	1	**20_INOC_71_7DAI_1**	**17827**	**6003**	**16781**	**286140**	**187061**	**67504**
	2	**20_INOC_71_7DAI_2**	**10359**	**2563**	**5974**	**123970**	**80737**	**45825**
	1	**20_INOC_51_7DAI_1**	**10157**	**3261**	**12527**	**131884**	**71704**	**51001**
	2	**20_INOC_51_7DAI_2**	**5430**	**1372**	**9457**	**80368**	**50490**	**16095**
	3	**20_INOC_51_7DAI_3**	**2780**	**861**	**19330**	**70196**	**33988**	**38955**
	4	**20_INOC_51_7DAI_4**	**5674**	**1636**	**10932**	**73076**	**43925**	**32624**
	5	**20_INOC_51_7DAI_5**	**2211**	**558**	**14125**	**51747**	**32859**	**31380**
	6	**20_INOC_51_7DAI_6**	**6864**	**1974**	**27133**	**120010**	**60943**	**57774**
	7	**20_INOC_51_7DAI_7**	**2486**	**454**	**11893**	**61830**	**34740**	**29735**
	8	**20_INOC_51_7DAI_8**	**3499**	**1428**	**17260**	**79066**	**47055**	**39036**
Control 14 DAI	1	**20_CTR_14DAI_1**	**273**	**111**	**233**	**932**	**585**	**2651**
	2	**20_CTR_14DAI_2**	**223**	**91**	**1463**	**1393**	**739**	**3109**
	3	**20_CTR_14DAI_3**	**122**	**79**	**768**	**1650**	**544**	**2601**
	4	**20_CTR_14DAI_4**	**64**	**149**	**688**	**1660**	**563**	**2257**
	5	**20_CTR_14DAI_5**	**128**	**78**	**935**	**937**	**814**	**1947**
	6	**20_CTR_14DAI_6**	**212**	**61**	**978**	**2480**	**375**	**1764**
	7	**20_CTR_14DAI_7**	**192**	**50**	**956**	**2183**	**602**	**2416**
	8	**20_CTR_14DAI_8**	**201**	**150**	**727**	**1342**	**2364**	**4066**
Inoculated 14 DAI	1	**20_INOC_71_14DAI_1**	**2866**	**1462**	**2612**	**17944**	**11406**	**5489**
	2	**20_INOC_71_14DAI_2**	**3130**	**1239**	**3462**	**20538**	**13763**	**5843**
	1	**20_INOC_51_14DAI_1**	**13754**	**5312**	**6049**	**100555**	**63259**	**19576**
	2	**20_INOC_51_14DAI_2**	**9801**	**4396**	**6912**	**63540**	**42224**	**12095**
	3	**20_INOC_51_14DAI_3**	**17138**	**7607**	**9677**	**130759**	**74109**	**14951**
	4	**20_INOC_51_14DAI_4**	**4893**	**1011**	**6308**	**26616**	**17290**	**7774**
	5	**20_INOC_51_14DAI_5**	**10586**	**6518**	**8661**	**126867**	**68473**	**16510**
	6	**20_INOC_51_14DAI_6**	**19006**	**11157**	**10870**	**185403**	**108037**	**22149**
	7	**20_INOC_51_14DAI_7**	**8219**	**3106**	**5979**	**85766**	**47345**	**12275**
	8	**20_INOC_51_14DAI_8**	**12631**	**6382**	**7280**	**92992**	**56111**	**15610**

SUMMARY 2020

AVG area 2020	**CTR_7DAI (n=8)**	261.98	52.88	1278.86	1770.29	1747.28	6019.23
	INOC_51_7DAI (n=8)	4887.59	1442.82	15331.97	83522.13	46963.03	37075.09
	INOC_71_7DAI (n=2)	14092.86	4282.88	11377.79	205055.08	133899.19	56664.71
	INOC_(51+71)_7DAI (n=10)	6728.64	2010.83	14541.13	107828.72	64350.26	40993.02
	CTR_14DAI (n=8)	176.90	96.07	843.55	1572.11	823.29	2601.14
	INOC_51_14DAI (n=8)	12003.31	5685.93	7717.05	101562.05	59605.95	15117.50
	INOC_71_14DAI (n=2)	2997.97	1350.58	3036.77	19240.94	12584.70	5666.23
	INOC_(51+71)_14DAI (n=10)	10202.24	4818.86	6780.99	85097.83	50201.70	13227.25
STDEV area 2020	**CTR_7DAI (n=8)**	124.23	47.46	321.22	1164.58	767.38	5598.38
	INOC_51_7DAI (n=8)	2722.60	904.78	5781.55	27946.16	13866.18	12961.72
	INOC_71_7DAI (n=2)	5280.67	2432.82	7641.59	114671.86	75182.69	15329.39
	INOC_(51+71)_7DAI (n=10)	4891.63	1651.75	5938.52	68515.18	46056.69	15000.14
	CTR_14DAI (n=8)	67.01	37.55	346.03	548.90	636.17	725.73
	INOC_51_14DAI (n=8)	4638.38	3049.96	1824.39	47672.52	26466.03	4514.56
	INOC_71_14DAI (n=2)	186.47	157.19	601.16	1834.03	1666.68	250.07
	INOC_(51+71)_14DAI (n=10)	5581.62	3252.57	2554.04	54523.06	30629.56	5633.76

		1,3-Octadiene	**1,3-cis,5-cis-Octatriene**	**1-Heptanol**	**(5Z)-Octa-1,5-dien-3-ol**	**1-Octen-3-ol**	**3-Octanone**
***t*-tests 2020 (green background: p≤0.05)**	**CTR_7DAI VS INOC_51_7DAI**	0.002	0.003	0.000	0.000	0.000	0.000
	CTR_7DAI VS INOC_71_7DAI	0.168	0.246	0.313	0.242	0.243	0.125
	CTR_7DAI VS INOC_(51+71)_7DAI	0.002	0.005	0.000	0.001	0.002	0.000
	CTR_14DAI VS INOC_51_14DAI	0.000	0.001	0.000	0.001	0.000	0.000
	CTR_14DAI VS INOC_71_14DAI	0.025	0.053	0.100	0.042	0.056	0.000
	CTR_14DAI VS INOC_(51+71)_14DAI	0.000	0.001	0.000	0.001	0.001	0.000
	CTR_7DAI VS CTR_14DAI	0.117	0.064	0.021	0.673	0.021	0.129
	INOC_51_7DAI VS INOC_51_14DAI	0.003	0.005	0.007	0.375	0.258	0.002
	INOC_71_7DAI VS INOC_71_14DAI	0.206	0.337	0.365	0.262	0.263	0.133
	INOC_(51+71)_7DAI VS INOC_(51+71)_14I	0.156	0.030	0.002	0.423	0.431	0.000

9.21 Figure S5 Permanova results



"RESULTS OF ANOVA ON TREAT AND YEAR GROUPS" (TREAT: CTR-INF, YEAR: 2018-2019, only 14 DAI)

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
TREAT	1	16.531	16.531	64.51	5.77e-09 ***
Residuals	30	7.687	0.256		

	Df	Sum Sq	Mean Sq	F value	Pr(>F)
YEAR	1	0.781	0.7812	1	0.325
Residuals	30	23.438	0.7813		

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

"PERMUTATIONAL MULTIVARIATE ANALYSIS OF VARIANCE (PERMANOVA)"

Call: adonis(formula = sp. ~ TREAT, data = env)

Permutation: free

Number of permutations: 999

Terms added sequentially (first to last)

	Df	Sum Sq	MeanSqs	F.Model	R2	Pr(>F)
TREAT	1	0.9677	0.96767	6.964	0.1884	0.001 ***
Residuals	30	4.1686	0.13895		0.8116	
Total	31	5.1363			1.0000	

Call: adonis(formula = sp. ~ YEAR, data = env)

Permutation: free

Number of permutations: 999

Terms added sequentially (first to last)

	Df	Sum Sq	MeanSqs	F.Model	R2	Pr(>F)
YEAR	1	0.9954	0.99539	7.2114	0.1938	0.001 ***
Residuals	30	4.1409	0.13803		0.8062	
Total	31	5.1363			1.0000	

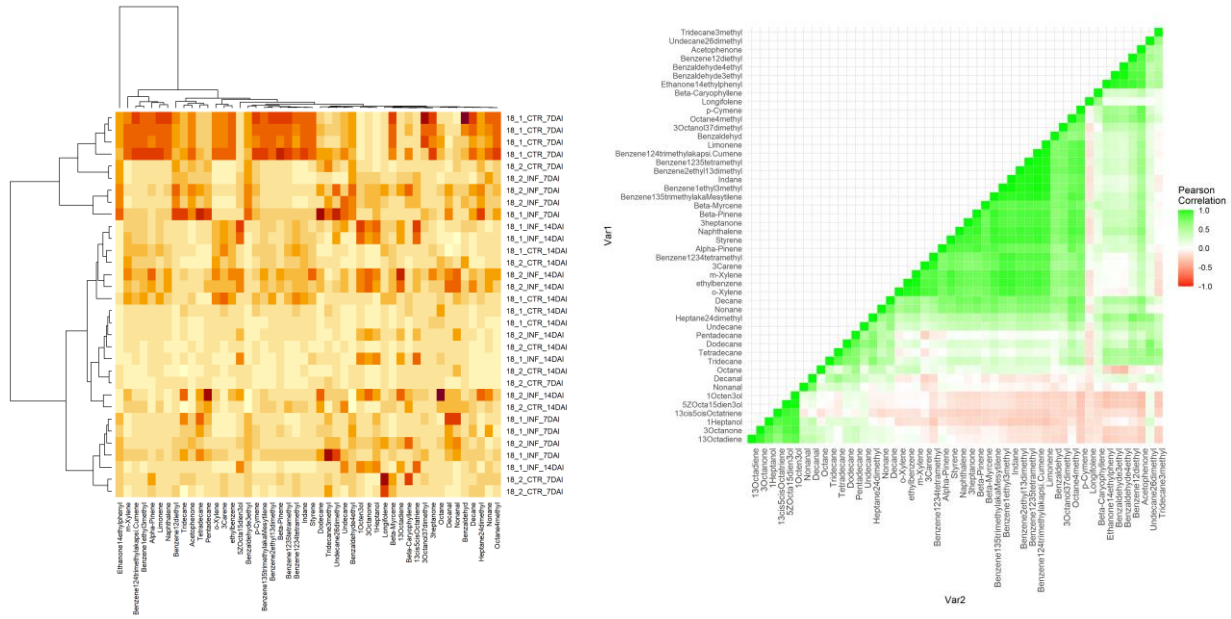
(Signif. codes: 0 '***' 0.001 '**' 0.01 '*' 0.05 '.' 0.1 ' ' 1)

"Extract p-values for each VOC" (VOCs in Table 1 in the ms)

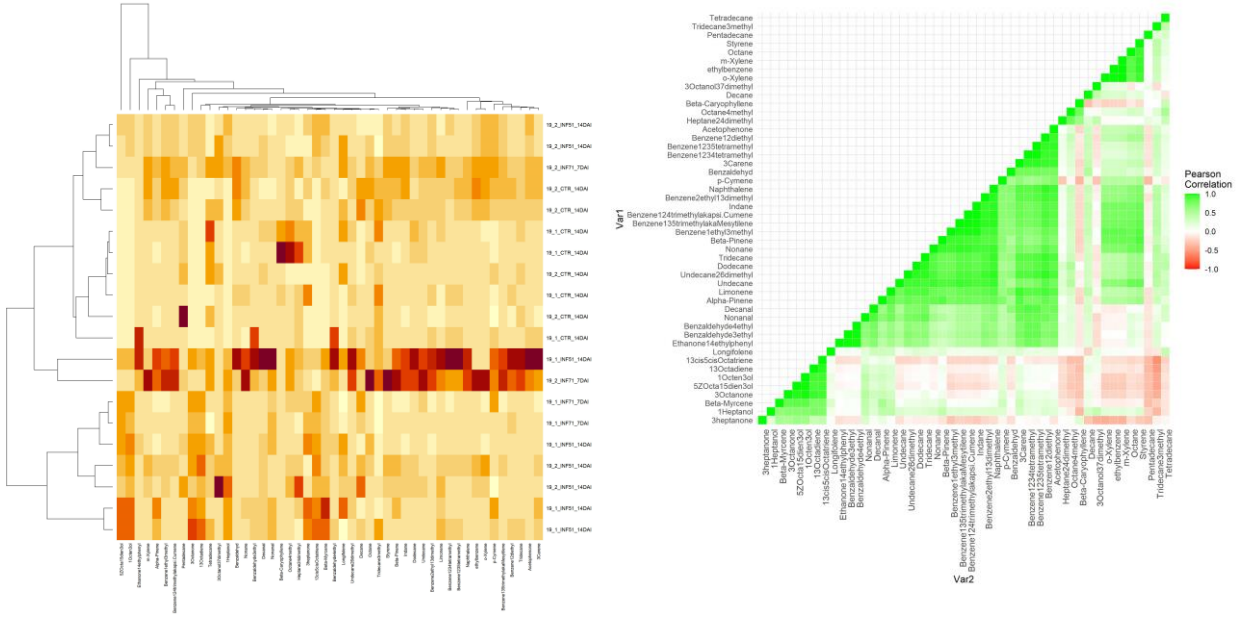
#	VOC	pvals
1	1	0.789
2	2	0.006
3	3	0.001
4	4	0.118
5	5	0.002
6	6	0.075
7	7	0.001
8	8	0.001
9	9	0.161
10	10	0.076
11	11	0.760
12	12	0.052
13	13	0.706
14	14	0.896
15	15	0.823
16	16	0.001
17	17	0.001
18	18	0.126
19	19	0.001
20	20	0.001
21	21	0.001
22	22	0.909
23	23	0.526
24	24	0.976
25	25	0.005
26	26	0.522
27	27	0.814
28	28	0.086
29	29	0.984
30	30	0.677
31	31	0.295

9.22 Figure S6 Heatmap and pearson correlation test results for year **2018 (A)** and year **2019 (B)**.

(A) year 2018



(B) year 2019



9.23 Table S15 List of highest scoring pairs (HSP) obtained by BLAST searches in B. graminis genome sequences and related references
Best hits for genes encoding dioxygenases

UniProt entry	Entry name	Protein name	Gene name	Organism	Length (aa)	Query (source)	E-value	Identity (%)	Expression	References
N1JEN6	N1JEN6_BLUG1	Fatty acid oxygenase PpoA	BGHDH14_bgh01772	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	1085	Q6RET3 (Aspergillus nidulans)	0.0	47.9	protein, RNA-sec	Bindschedler et al. 2011 and
A0A383UJI1	A0A383UJI1_BLUGH	Uncharacterized protein	BLGHR1_10719	Blumeria graminis f.sp. hordei (barley powdery mildew) (Oidium m	1085	Q6RET3 (Aspergillus nidulans)	0.0	47.9		Hacquard et al. 2013; Laur et al. 201
A0A381LGQ4	A0A381LGQ4_BLUGI	BgtA-20812 (Fragment)	BGT96224V2_LOCUS605	Blumeria graminis f.sp. tritici 96224	919	N1JEN6 (B. graminis f.sp. horde	0.0	95.9		
N1JA34	N1JA34_BLUG1	Putative fatty acid oxygenase Ppo/	BGHDH14_bgh01025	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	1058	A1CI17 (Aspergillus clavatus)	0.0	35.5	protein, RNA-sec	Bindschedler et al. 2011 and
A0A383UPD0	A0A383UPD0_BLUGI	Uncharacterized protein	BLGHR1_11968	Blumeria graminis f.sp. hordei (barley powdery mildew) (Oidium m	1058	A1CI17 (Aspergillus clavatus)	0.0	35.5		Hacquard et al. 2013; Laur et al. 201
A0A381LHG6	A0A381LHG6_BLUGI	Bgt-1516	BGT96224V2_LOCUS645	Blumeria graminis f.sp. tritici 96224	1058	N1JA34 (B. graminis f.sp. hordei	0.0	98.4		

Best hits for genes encoding monooxygenases

UniProt entry	Entry name	Protein name	Gene name	Organism	Length (aa)	Query (source)	Identity (%	Expression	References
N1JHB2	N1JHB2_BLUG1	Cytochrome P450	BGHDH14_bgh01926	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	565	UniProt database		RNA-seq	Hacquard et al. 2013; Laur et al. 201
N1J4S4	N1J4S4_BLUG1	Cytochrome P450 monooxygenase/CYP52A1	BGHDH14_bgh01897	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	516	UniProt database		RNA-seq	Hacquard et al. 2013; Laur et al. 201
A0A656KMF	A0A656KMF1_BLUGI	Uncharacterized protein	BGT96224_2253	Blumeria graminis f.sp. tritici 96224	521	N1J4S4	91.2		
N1JEI9	N1JEI9_BLUG1	Cytochrome P450 oxidoreductase	BGHDH14_bgh05568	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	518	UniProt database		RNA-seq	Hacquard et al. 2013; Laur et al. 201
N1J9N7	N1J9N7_BLUG1	Putative cytochrome P450 monooxygenase/cyp2	BGHDH14_bgh06327	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	534	UniProt database		RNA-seq	Hacquard et al. 2013; Laur et al. 201
A0A061HEP9	A0A061HEP9_BLUGR	Bgt-404	BGT96224_404	Blumeria graminis f.sp. tritici 96224	534	N1J9M7	95.7		
N1JQU4	N1JQU4_BLUG1	Putative cytochrome P450 monooxygenase	BGHDH14_bgh01041	Blumeria graminis f.sp. hordei (strain DH14) (barley powdery milde	511	UniProt database		RNA-seq	Hacquard et al. 2013; Laur et al. 201
A0A061HNG4	A0A061HNG4_BLUGI	Bgt-1532	BGT96224_1532	Blumeria graminis f.sp. tritici 96224	509	N1JQU4	89.6		

References

Bindschedler, L.V., McGuffin, L.J., Burgis, T.A., Spanu, P.D., Cramer, R., 2011. Proteogenomics and in silico structural and functional annotation of the barley powdery mildew Blumeria graminis f. sp. hordei. Methods 54, 432–441. Description: partial proteomes in sporulating hyphae and haustoria 7-10 days post inoculation

Hacquard, S., Kracher, B., Maekawa, T., Vernaldi, S., Schulze-Lefert, P., Ver Loren van Themaat, E., 2013. Mosaic genome structure of the barley powdery mildew pathogen and conservation of transcriptional programs in divergent hosts. Proc. Natl. Acad. Sci. USA 110, 2219–2228. Description: "RNA-seq during early pathogenesis (6-24 h post inoculation: conidiospore germination,haustorium formation)"

Laur, J., Ramakrishnan, G.B., Labbe, C., Lefebvre, F., Spanu, P.D., Belanger, R.R., 2018. Effectors involved in fungal–fungal interaction lead to a rare phenomenon of hyperbiotrophy in the tritrophic system biocontrol agent–powdery mildew–plant. New Phytol. 217, 713–725. Description: RNA-seq during early pathogenesis (4-5 days post infection with Blumeria graminis)

Zeng, F.-S., Menardo, F., Xue, M.-F., Zhang, X.-J., Gong, S.-J., Yang, L.-J., Shi, W.-Q., Yu, D.-Z., 2017. Transcriptome analyses shed new insights into primary metabolism and regulation of Blumeria graminis f. sp. tritici during conidiation. Front. Plant Sci. 8, 1146. Description: RNA-seq during early pathogenesis (3-5 days post inoculation)

9.24 Table S16 Estimated emissions of four quantitated marker VOCs

	1-Heptanol	(5Z)-Octa-1,5-dien-3-ol	1-Octen-3-ol	3-Octanone	50 pots/m^2 = ca. 700 pl./m^2	1-Heptanol	(5Z)-Octa-1,5-dien-3-ol	1-Octen-3-ol	3-Octanone	Total
	ng/pot/24 h	ng/pot/24 h	ng/pot/24 h	ng/pot/24 h		µg/m^2/24 h	µg/m^2/24 h	µg/m^2/24 h	µg/m^2/24 h	µg/m^2/24 h
AVERAGE OVERALL	**22.22**	**135.33**	**389.00**	**82.10**	**AVERAGE OVERALL**	**1.11**	**6.77**	**19.45**	**4.10**	**31.43**
AVERAGE 7 DAI ALL	19.46	44.34	130.14	34.07	AVERAGE 7 DAI ALL	0.97	2.22	6.51	1.70	
AVERAGE 14 DAI ALL	23.88	189.92	544.31	110.91	AVERAGE 14 DAI ALL	1.19	9.50	27.22	5.55	
MIN 7 DAI ALL	8.70	4.20	10.50	3.90	**1 ha average per day**	**mg/ha/24 h**	**mg/ha/24 h**	**mg/ha/24 h**	**mg/ha/24 h**	**mg/ha/24 h**
MAX 7 DAI ALL	47.52	188.21	586.63	89.20	**AVERAGE OVERALL**	**11**	**68**	**194**	**41**	**314**
MIN 14 DAI ALL	4.67	12.55	35.70	7.32	AVERAGE 7 DAI ALL	9.73	22.17	65.07	17.04	
MAX 14 DAI ALL	63.00	816.60	2295.30	492.30	AVERAGE 14 DAI ALL	11.94	94.96	272.15	55.46	
MIN 7 DAI 2018	8.70	4.20	10.50	3.90	**30 day contribution**	**g/ha/month**	**g/ha/month**	**g/ha/month**	**g/ha/month**	**g/ha/month**
MAX 7 DAI 2018	14.40	12.30	23.10	13.80	**AVERAGE OVERALL**	**0.33**	**2.03**	**5.83**	**1.23**	**9.42**
MIN 14 DAI 2018	12.30	4.20	10.50	3.90	AVERAGE 7 DAI ALL	0.29	0.67	1.95	0.51	
MAX 14 DAI 2018	24.00	52.50	88.20	34.80	AVERAGE 14 DAI ALL	0.36	2.85	8.16	1.66	
MIN 14 DAI 2019	27.00	83.40	270.60	69.90						
MAX 14 DAI 2019	63.00	816.60	2295.30	492.30						
MIN 7 DAI 2020	10.66	35.88	120.55	21.43						
MAX 7 DAI 2020	47.52	188.21	586.63	89.20						
MIN 14 DAI 2020	4.67	12.55	43.06	7.32	During three years of our survey there was cold 2018, medium 2019 and hot weather 2020 with					
MAX 14 DAI 2020	19.31	124.62	364.05	29.46	varying pathogen conditions from slightly to heavily infected samples.					

10. ACKNOWLEDGEMENTS

10.1 Acknowledgement of grants, funds supporting my research work and me in any way

- GINOP-2.3.2-15-2016-00051 E-nose research group - analysis of natural odor patterns and utilization in agricultural sciences
- Grant „RRF-2.3.1-21-2022-00007, Agrár-biotechnológia és precíziós nemesítés az élelmiszerbiztonságért”
- Industrial research and development projects in Hungarian–Vietnamese cooperation, grant number 2019-2.1.12-TÉT_VN-2020-00001.

10.2 Acknowledgements for research colleagues for their useful suggestions or support

I’d like to express my gratitude **to my thesis leader Dr. Katalin Posta** and to Hungarian University of Agriculture and Life Sciences and HUN-REN CAR.

My dear, supporting colleagues at Centre of Agricultural Research, Martonvásár and beyond: first and foremost to Dr. László Sági and to Dr. Mihály Dernovics as they deserve it before anyone. To Dr. Tibor Janda, Dr. Péter Lukács, Dr. Zsuzsanna Ambrózy, Dr. Gabriella Szalai, Dr. Magda Pál, Dr. Éva Darkó, Dr. Katalin Zboray, Dr. Gyula Vida, Dr. Ervin Balázs, Dr. Katalin Puskás, Dr. Mónika Cséplő, Dr. Imre Majláth, Dr. Csaba Éva, Dr. Gyöngyvér Gell, Larisza Szeidl, Tímea Taligás, Dr. Vilmos Soós, Dr. Zsolt Gulyás, Dr. Gábor Galiba, Dr. Béla Péter Molnár, Dr. Dalma Radványi, Dr. Veronika Bókony, Dr. Kinga Benczúr, Dr. József Bakonyi, Dr. Klára Mészáros, Dr. Mariann Rakszegi, Gábor Palotás, Ferenc Tóth and Dr. Tamás Weiszburg.

10.3 Acknowledgements for inspiring, supporting friends, students, muscians and family

I wanna take this opportunity to express how thankful I am to my family and its close friends: To my wonderful mom, Ingrid Hamow, sweet angel of a sister Zeire Hamow, also to my brother Ádam Hamow. To my cousin Mazloum Hamo and to my godmother Mária Muskovics and their families. To Dr. Mousa Mustafa and Dr. Hussein Daood and their families. And of course to my father, Ali Hassan Hamow (†), who taught me to be an honorable loving man, and that you should never be afraid of work, let the work be afraid of you! To my dear love, Rebeka Blanka Jordanov, who has supported me in the past months like no one before. **A special thanks are in order for my dear students** Réka Mátyus, Ráchel Bolford, Cintia Bese and Oszkár Jókai. **Addittional wonderous friends who supported me:** Niké Kicandasz, Dr. Gábor Glatz and his family, Gergely Huba Vígh, Ádám Bulyovszki, Gábor Alekszics and his family, Judit Bernadett Kőszegi, Dominik Hollender, Dr. Attila Gidófalvi and his family, Péter Pálfi and his family, Adrienn Mészáros, Alexandra Kulcsár, Zsolt Dolinka, Szabolcs Marton, Zsuzsanna Máró, Ágoston Stella, Andrea Pataky, Andrea Csimár, Anasztázia Pintye**. Musician friends who have helped and inspired me a lot through their art and music and/or friendship - From Hungary:** Balázs Biletzky (Psyletzky), Gergely Tóth (Toge), Alex Vargyasi (Metaverse), Bence Kiss-Leizer (Bimbiri), Balázs Rimóczi (Cabra), Dániel Zimányi-Faltisz (Körner), Dávid Gózon (Goeson), Fábián Zoltán (Snag the Sunshepherd), Florentína Agócs (Lissza) and Erika Csáky (Era). **From abroad:** Joske Vranken (Anoebis) and her wife (Pavane), Elias Gits (Agneton), Jannis Tzikas (Filteria), René Kaipel and Anja Pichler (KavanRay & ZavaConnex). Finally I wanna say thanks to “Dürer Kert” and all its staff members. **You all mentioned above, and many more fellow dear souls helped and motivated me immensely to** write my PhD and other scientific works. Also to become a fast yet precise young analytical chemist method developer in Hungary. Especially inspired me to be someone who is addicted to good music and the dancing how to keep on blastin joyfully as a CSK CSK CSK CSK, my thanks never have been more in order dear fellow inspiring loving souls, thanks dears! Keep on dancing, discovering and of course forever joyfully blastin’!