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List of VOCs released from relevant pests described in the literature

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Abstract

This document describes deliverable D1.6, i.e., a review of the available data on candidate VOCs for the detection of the five target pests published in peer-reviewed journals.

Public introduction[1]

The reduction by 50% of pesticide use and risk is among the proposals adopted by the European Commission, in line with the EU's Farm to Fork and Biodiversity strategies. To achieve this goal, it is important to control new pest invasions and already established pests. The PurPest project aims to develop, validate and demonstrate an innovative sensor system prototype (SSP) to detect pest-specific volatile organic compounds (VOCs) and thus identify five different target pests to reduce pesticide inputs and stop the establishment of the pest in the EU. The target pests are *Phytophthora ramorum*, *Spodoptera frugiperda*, *Helicoverpa armigera*, *Halyomorpha halys*, and *Bursaphelenchus xylophilus*.

The starting point for the project is an extensive literature review aiming at identifying a list of candidate VOCs for the detection of such pests. For some pests, such as *Phytophthora ramorum* and *Bursaphelenchus xylophilus*, literature data are too scarce for defining a list of candidate VOCs. In the case of the other target pests, a review of the available literature by experts in the field, allowed compiling preliminary lists of target VOCs which need to be complemented and refined with further experiments. The PurPest project will build on these lists and expand them with new candidate VOCs by studying pest and attacked plant emissions. Candidate VOC lists will be central for the development of the SSP.

[1] According to Deliverables list in Annex I, all restricted (RE) deliverables will contain an introduction that will be made public through the project WEBSITE

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1 INTRODUCTION ON THE USE OF VOC IN PLANT-PEST INTERACTIONS

Plants are engaged in constant interactions with a diverse array of organisms in their environment, including herbivores and pests. Plants naturally emit molecules, that can act as a cue for other plants or organisms. Volatile organic compounds (VOCs) are low-molecular-weight organic compounds that can be emitted as gases or aerosols from plants (Pichersky & Gershenzon, 2002). These compounds serve as chemical signals that facilitate communication between plants and pests and they play a crucial role in mediating plant-pest interactions, influencing both the behavior of pests and the defensive responses of plants (Heil et al., 2006). To defend themselves against attackers, plants have evolved various strategies, one of which involves the release of VOCs. When plants are subjected to herbivory or pest infestation, they change the released volatile profile, emitting specific blends of VOCs that are recognized by nearby organisms (herbivory-induced plant volatiles HIPVs), including pests and their natural enemies (D'Alessandro & Turlings, 2006). Pests, such as insects and pathogens, perceive these volatile signals and respond accordingly, leading to a series of cascading effects on plant-pest interactions. The effects of VOCs on pests can be diverse. Some VOCs can act as attractants, drawing pests to the infested plant, helping them locate suitable feeding sites. On the other hand, some VOCs act as repellents, deterring pests from attacking plants. These repellent VOCs can disrupt the host-seeking behavior of pests, reducing their feeding and oviposition rates. Moreover, VOCs can also influence the behavior of natural enemies of pests, such as predators and parasitoids. These beneficial organisms use VOCs emitted by infested plants as cues to locate their prey or hosts (Turlings & Erb, 2018).

Plants have a remarkable ability to respond to herbivore attack by altering their VOCemissions not only at the site of damage but also in neighboring plants. This phenomenon, known as "volatile priming," involves the modification of VOC profiles in undamaged parts of the same plant or in nearby plants, preparing them for potential future herbivore attack. The process of volatile priming is a key factor in enhancing the overall resistance of plant communities. When a plant is attacked by herbivores, it initiates a complex signaling cascade that triggers defense responses (Frost et al., 2008). Part of this response involves the release of specific VOCs, which serve as airborne signals to neighboring plants. These airborne signals can be perceived by intact, undamaged plants in the vicinity, priming them to activate their own defense mechanisms in anticipation of imminent herbivory. This priming process allows plants to mount a faster and stronger defense response when they encounter subsequent herbivore attacks (Heil & Karban, 2010).

Both the volatiles emitted by pests themselves and the pest-induced plant volatiles play significant roles in early pest detection. These volatile signals can be used as valuable cues for monitoring and identifying pest infestations, enabling timely interventions, reducing potential crop damage and optimizing pest management strategies (MacDougall et al., 2022).

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2 VOLATILE ORGANIC COMPOUNDS IN THE PHYTOPHTHORA-PLANT SYSTEM

2.1 *Phytopthora ramorum* and other important *Phytophthora* species: distribution, biology, diseases and management

The genus *Phytophthora* (Oomycota, Peronosporales, Peronosporaceae) currently includes six obligate biotrophic unculturable species and 208 hemibiotrophic or necrotrophic culturable species and is widely distributed on all continents except Antarctica. Approximately half of the known species have been spread from their native areas to other continents where they became invasive causing severe diseases on non-coevolved host plants in horticultural, forest and natural ecosystems (Erwin & Ribeiro, 1996; Yang et al., 2017; Jung et al., 2018a, 2022; Brasier et al., 2022; Chen et al., 2022). Since the 1960s, the global number of epidemic diseases of forests and natural ecosystems caused by invasive *Phytophthora* species has increased exponentially from 5 to currently 41 (Brasier et al., 2022).

Apart from a minority of sterile species most *Phytophthora* species are characterised by the production of sexually derived oospores inside female oogonia where they are fertilised by the germtube of the male antheridium. They have either a self-fertile, predominantly inbreeding ("homothallic") breeding system or are self-sterile and predominantly outcrossing, requiring pairing between two individuals of opposite mating or compatibility types (A1 and A2) ("heterothallic breeding system") (Erwin & Ribeiro, 1996; Chen et al., 2022; Jung et al., 2022). Oospores are the most enduring survival structures of Phytophthoras. In addition, many *Phytophthora* species form vegetative chlamydospores for short-term survival of unfavourable environmental conditions. All *Phytophthora* species produce sporangia which usually release biflagellate zoospores which are chemotactically attracted to and infect host tissues or germinate directly. Aerial *Phytophthora* species produce during periods of high humidity caducous sporangia at the surface of infected aerial host tissues which are passively spread via rain splash, fog and wind whereas soilborne Phytophthoras spread during rainy periods or floodings via zoospores in soil water and surface water (Erwin & Ribeiro, 1996; Chen et al., 2022).

Generally, the management of Phytophthora diseases includes a wide range of measures including the prevention of pathogen introduction by using non-infested nursery stock, substrates and irrigation water, disinfesting of tools, cleaning of vehicles and boots from adhering soil particles, and phytosanitary controls using both visual inspections and high-throughput molecular detection tests; best-practice maanagement in nurseries; avoiding of soil compaction and building of drainage systems to prevent waterloogging and flooding; application of potassium phosphite to stimulate defense reactions in the root system (horticulture and forestry); fungicide applications (horticulture and agriculture); eradication via host removal and destruction; use of nanoparticle technologies; resistance screening programmes and the use of resistant host genotypes or rootstocks (horticulture, agriculture and forestry); use of effectors and NLR resistance genes; and the development and use of general models to predict regions that might be most susceptible to epidemics by certain *Phytophthora* species (e.g. *P. cinnamomi*, *P. ramorum*) or regional models to predict periods with environmental conditions conducive to disease development (e.g. *P. infestans*) (Harris, 1991; Erwin & Ribeiro, 1996; Fernandez-Escobar et al., 1999; Colquoun & Hardy, 2000; Hardy, 2000; Meentemeyer et al., 2004; Rizzo et. al., 2005; Robin et al., 2006;

Anonymous, 2007; Henderson et al., 2007; Stukely et al., 2007; Frankel, 2008; Dunstan et al., 2009; Garbelotto et al., 2009; Brasier & Webber, 2010; Filipe et al., 2012; Pérez-Sierra & Jung, 2013; Crane & Shearer, 2014; Santos et al., 2014, 2017; Peterson et al., 2015; Jung et al., 2016, 2018a; O'Hanlon et al., 2016, 2018; Lu et al., 2019; Sniezko et al., 2019; Solla et al., 2021; Santos et al., 2022; Brandano et al., 2023; Martínez et al., 2023).

Phytophthora ramorum Werres, De Cock & Man in' t Veld from *Phytophthora* phylogenetic Clade 8c originates from the laurosilva forests of East Asia where 8 lineages and both mating types (heterothallic self-sterile breeding system) have recently been identified coexisting in an equilibrium with the native flora (Jung et al. 2020, 2021). *P. ramorum* is an airborne plant pathogen spreading during humid periods with caducous sporangia formed on infected leaves (Werres et al., 2001; Rizzo et al., 2002; Davidson et al., 2005; Harris & Webber, 2016; Jung et al., 2018a). It also produces thick-walled chlamydospores. Since the early 1990s, each two lineages have been introduced with infected plants and/or infested rhizosphere soil to Europe (EU1 and EU2; both A1 mating type) and the Pacific Northwest (NA1 and NA2; both A2 mating type) where they became highly invasive causing leaf and shoot blights and bark cankers on a particularly wide range of more than 100 host species, including *Rhododendron*, *Camelia* and *Viburnum* spp., and the devastating epidemics "Sudden Oak Death" (California and Oregon) and "Sudden Larch Death" (UK and Republic of Ireland) which killed millions of oak, tanoak and larch trees (Rizzo et al., 2002; Brasier & Webber, 2010; Grünwald et al., 2012; Van Poucke et al.; 2012; Jung et al., 2018a; Cobb et al., 2020). The EU1 lineage has later been spread from Europe to North America (Grünwald et al., 2012) and sexual recombination with North American A2 lineages has recently been confirmed (Hamelin et al., 2022). Disease management in forests comprises large-scale monitoring programmes; epidemiological modelling; sanitary fellings of host trees at disease foci and in a surrounding buffer zone (USA and UK) accompanied by burning of infected plant tissues and killing of oak and tanoak stumps with herbicides (USA); and phosphite applications (USA) (Meentemeyer et al., 2004; Rizzo et. al., 2005; Anonymous, 2007; Frankel, 2008; Garbelotto et al., 2009; Brasier & Webber, 2010; Filipe et al., 2012; Peterson et al., 2015; O'Hanlon et al., 2016, 2018). In the EU all *P. ramorum* lineages not yet introduced (= all lineages except of EU1) are listed as A1 quarantine pests. In nurseries infected plants and susceptible host plants in a surrounding buffer zone have to be destroyed.

The panglobal, heterothallic soilborne pathogen *Phytophthora cinnamomi* Rands from *Phytophthora* Clade 7c is the most notorious and invasive member of the genus infecting and causing root rot, bark cankers, dieback and mortality of more than 5000 woody plant species worldwide (Erwin & Ribeiro, 1996; Hardham & Blackman, 2018). A recent population genomic study showed that *P. cinnamomi* originates in Southeast Asia and that the global pandemic is driven by two clonal A2 mating type lineages (Shakya et al., 2021). Both mating types produce thin-walled chlamydospores for short-term survival. However, in contrast to the A1 mating type, many A2 isolates are partially self-fertile and produce oospores for the survival of harsh conditions (Brasier, 1978; Jayasekera et al., 2007; Jung et al., 2013). Besides being a major pathogen of many horticultural crops and ornamentals *P. cinnamomi* causes some of the most devastating epidemics of forest trees and natural ecosystems including decline and dieback of eucalypt forests, Banksia woodlands and heathlands across Australia; fynbos heathlands in South Africa; Valdivian rainforests in Chile; *Araucaria* forests in Chile and Brazil; oak forests in Southern Europe, the

USA and Mexico; and chestnut forests in Europe, the USA and Chile (Crandall, 1950; Von Broembsen & Kruger, 1985; Shearer & Tippett, 1989; Marks & Smith, 1991; Brasier et al., 1993; Erwin & Ribeiro, 1996; Tainter et al., 2000; Shearer et al., 2004; Vettraino et al., 2005; Dos Santos et al., 2011Correia, I., ; Jung et al., 2013, 2016, 2018a, b; McConnell & Balci, 2014; Sanfuentes et al., 2022). Recent studies demonstrated that climate change enables the frost-sensitive *P. cinnamomi* to survive winter conditions in forests and horticultural plantations in Central Europe with potentially devastating consequences in the future (Peters et al., 2019; Nechwatal & Jung, 2021). Disease management in natural ecosystems is mainly limited to the use of preventative measures like using non-infested nursery stock road building material and sanitary cleaning of vehicles, tools and boots, and curative measures like phosphite applications to enhance defence mechanisms in infected plants (Fernandez-Escobar et al., 1999; Colquoun & Hardy, 2000; Hardy, 2000; Crane & Shearer, 2014; González et al., 2020; Solla et al., 2021; Brandano et al., 2023), eradication of spot infestations (only in Australia; Dunstan et al., 2009) and resistance breeding in several tree species including *Castanea sativa*, *Castanea dentata*, *Eucalyptus marginata* and *Quercus suber* (Stukely et al., 2007; Santos et al., 2014, 2017; Martínez et al., 2023).

Phytophthora cactorum (Leb. and Cohn) Schroeter from *Phytophthora* Clade 1a was already described in 1886 and has reached a panglobal distribution. A recent population genetic study indicates that it is native to North America (Bourret et al., 2022). This homothallic *Phytophthora* species produces caducous sporangia and is known to cause both air- and soilborne diseases on a wide range of host plants including many ornamentals such as *Rhododendron* spp. (mainly leaf and shoot blight); forest trees like *Fagus sylvatica* (damping-off, root and collar rot, aerial bleeding cankers) and *Betula pendula* (root and collar rot); horticultural crops like strawberries (collar rot and leather rot of fruits); and fruit trees, in particular apple trees on which it is the major pathogen causing root, collar rot and fruit rot (Harris, 1991; Erwin & Ribeiro, 1996; Jung et al., 1996, 2016, 2018a, 2019; Hantula et al., 2000; Vettraino et al., 2008; Jung, 2009; Pánek et al., 2016; Corcobado et al., 2020). Several studies demonstrated the existence of various lineages with different host and tissue specifities (Oudemans & Coffey, 1991; Cooke et al., 1996; Hantula et al., 2000; Bourret et al., 2022). Disease management comprises primarily fungicide applications in nurseries and strawberry fields, and the use of resistant apple root stocks (Harris, 1991; Erwin & Ribeiro, 1996).

Phytophthora plurivora Jung & Burgess from *Phytophthora* Clade 2c is a homothallic soilborne plant pathogen with a wide distribution in the Northern Hemisphere and only few records from Chile, Argentina and New Zealand. It is an aggressive introduced pathogen in both Europe and North America causing root and collar rot, aerial bleeding bark cankers, and leaf and shoot blight on a wide range of woody host plants in natural ecosystems, nurseries and planting sites across (Jung, 2009; Jung & Burgess, 2009; Orlikowski et al., 2011; Reeser et al., 2011; Hansen et al., 2012; Jung et al., 2016, 2018a, 2019; Bienapfl & Balci, 2014; Brazee et al., 2016; Corcobado et al., 2020; Frankel et al., 2020). It is also one of the main drivers of current oak and beech declines across Europe (Jung, 2009; Jung & Burgess, 2009; Nechwatal et al., 2011, Milenković et al., 2012, Szabó et al., 2013, Jankowiak et al., 2014, Corcobado et al., 2020). Records from healthy, natural temperate forests in Nepal, Yunnan and Taiwan (Vettraino *et al.* 2011; Huai *et al.* 2013, Jung *et al.* 2017a) and an almost ubiquitous distribution of *P. plurivora* in native forests and streams across temperate regions of the Japanese archipelago without any

evident association with disease symptoms in the native vegetation (Jung et al., in preparation) suggest that *P. plurivora* is native to temperate regions of East Asia. Currently, disease management is restricted to fungicide applications in nurseries.

Phytophthora ×cambivora from *Phytophthora* Clade 7a has a heterothallic breeding system, a soilborne lifestyle and a cosmopolitan distribution which includes the Americas, Australia, Europe and East Asia (Erwin & Ribeiro, 1996; Jung et al., 2017b; Mullet et al., 2023). Recently, a populationgenomic study identified 11 lineages within *P. ×cambivora* of which several Japanese lineages were diploid and contained both mating types whereas the panglobal lineages were allopolyploid hybrids containing exclusively A1 or A2 isolates, respectively (Jung et al., 2017b; Van Poucke et al., 2021; Mullet et al., 2023), suggesting an East Asian origin of the species. *P. ×cambivora* causes root and collar rot and infrequently twig blight and aerial bleeding bark cankers on a wide range of woody host plants including many ornamentals, fruit trees and forest trees, and is one of the main drivers of Ink disease of sweet chestnut (*Castanea sativa*) in Europe and golden chinquapin (*Chrysolepis chrysophylla*) in Oregon, and the devastating oak and beech declines across Europe (Mircetich & Matheron, 1976; Erwin & Ribeiro, 1996; Jung et al., 1996, 2000, 2019; Vettraino et al., 2005; Saavedra et al., 2007; Jung, 2009; Jung & Burgess, 2009; Stępniewska & Dłuszyński, 2010; Nechwatal *et al.* 2011, Milenković *et al.* 2012, 2018, Telfer et al., 2015; Corcobado *et al.* 2020). Currently, disease management comprises fungicide applications in nurseries, phosphite injections in chestnut trees and resistance screening in *C. sativa* (Robin et al., 2006).

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2.2 Summary of literature on VOCs produced in relation to PHYTOPHTHORA species

In this summary we focus on studies with *Phytophthora*-infection related VOCs from different *Phytophthora*-inoculated substrates i.e., chemical analyses of VOCs directly from the pathogens or from the plants infected by *Phytophthora* species. A limited number of studies have identified and described VOCs emitted from substrates infected with *Phytophthora* species (and other oomycetes). For this work we included 10 studies, but only two studies are focused on or include VOCs from quarantine pathogen *P. ramorum*, the target pathogen in Purpest for developing an electronic nose (e-nose) system.

McCartney et al. (2018), used headspace sorptive extraction (HSSE), stir bar sorptive extraction (SBSE- and solid-phase microextraction (SPME) combined with gas chromatography-mass spectrometry (GC-MS) to find specific VOCs and VOC profiles from *P. ramorum*-infected *Rhododendron* hybrid 'Cunningham's White' plants. This is currently the only published study that investigates VOCs from *P. ramorum*-infected plants. For the HSSE method (*in situ* branch enclosure technique), 79 VOCs were detected. Three compounds were statistically different for *P. ramorum*-inoculated *Rhododendron* plants vs controls: linalool, (E)-3-hexen-1-ol and cis-3-Hexenyl pentanoate. For the SBSE liquid extraction method (leaf volatiles from a methanol

extract), 115 VOCs were detected, and 31 compounds were statistically different for the inoculated *Rhododendron* plants (see Table 1). One compound, cis-3-Hexenyl pentanoate, was expressed in higher abundances in healthy plants (control) for both HSSE and SBSE. The SPME method (water runoff technique from the soil of potted healthy and inoculated plants), four volatiles were only present in runoff water from soil infested with *P. ramorum*: (Z)-11-Hexadecenoic acid, (Z)-9-Hexadecenoic acid, Cyclic octaatomic sulfur, (Z)-9-Octadecenoic acid. These may be unique pathogen VOCs. Louier et al. (2020), utilized SPME/GC-MS to investigate VOCs from cultures (PDA) of *P. ramorum, P. plurivora, P. cinnamomi, P. cactorum* and a range of fungi. It was found that ethanol was shared between *P. ramorum* and *P. cinnamomi.* Acetone was shared between *P. plurivora* and *P. cactorum.* Other VOCs detected (but also present in various species of fungi) were 3-octanone and 1-octen-3-ol from *P. ramorum* and *P. cactorum*. *P. plurivora* emitted α-Pinene and Δ-D-3-Carene. *P. ramorum* also emitted 2-phenylethanol, a VOC that Li et al. (2019) detected from *P. infestans*-infected tomato leaves. Louier et al. (2020) further found that *P. ramorum* emitted higher amounts of compounds compared to the other *Phytophthora* species, and this was also confirmed in an analysis using an e-nose instrument developed in the same study. The e-nose could discriminate between VOCs emitted by *P. ramorum*, *Fusarium poae*, *Trichoderma asperellum* and *Rhizoctonia solani*. Furthermore, Louier et al. (2020) found that a major difference between the *Phytophthora* species and the fungi could be the amount of sesquiterpene produced, where the *Phytophthora* tested does not release these compounds/VOCs, but all tested fungal species did (except one).Borowik et al. (2021a) used headspace solid-phase microextraction and gas chromatography-mass spectrometry (HS-SPME/GC-MS) and found specific VOCs for *P. plurivora* and *Pythium intermedium* from *in vitro* infected germinated acorns of *Quercus robur*. In total, four VOCs were detected on the inoculated acorns, that were not found in the control acorns. Three of them, neophytadiene isomer 2, neophytadiene isomer 3 and isopentanol were significant and specific for acorns infected with *P. plurivora*, whereas Methylcarveol were specific for *Pythium intermedium*-infected acorns. Furthermore, Borowik et al. (2021b) also developed a low-cost electronic nose that applies six non-specific Figaro Inc. metal oxide sensors. A machine learning approach with this system was able to distinguish between *P. plurivora* and *Pythium intermedium* grown on Petri dishes with V8-Agar media (Borowik et al. 2021b) and using *in vitro* infected germinated acorns of *Q. robur* (Borowik et al. 2021a).

De Lacy Costello et al. (2001) used SPME/GC-MS and gas chromatography flame ionization detection (GC–FID) analysis for *P. infestans*- and *Fusarium coeruleum* inoculated potato tubers (*Solanum tuberosum* cv. Maris Piper). The four most abundant and significant VOCs were common for both pathogens, but not present in the control: benzothiazole, 2-ethyl-1-hexanol, 2-methylpropanoic acid-2,2- dimethyl-1-(2-hydroxy-1-methylethyl)-propyl ester and 2-methylpropanoic acid-3-hydroxy-2,4,4-trimethyl-pentyl ester. Four VOCs were specific (but at a low levels) for *P. infestans*-inoculated potato tubers: Butanal, 3-methylbutanal, undecane and verbenone.

Laothawornkitkul et al. (2010), also using SPME/GC-MS and GC–FID, detected three VOCs specific for *P. infestans*-infected potato leaves: 5-ethyl-2(5H)-furanone, (E)-2-hexenal, and benzene-ethanol. Even though both studies on potato used similar technology and methodology, the experimental conditions, potato growth stage and variety differed and could explain the difference in the VOCs emitted from *P infestans*-infected potato.

Li et al. (2019), developed a smartphone-based VOC fingerprinting platform that could detect *P. infestans* in tomato (*Solanum lycopersicum*) both *in vitro* and *in vivo*. In their work, SPME/GC-MS was used and they found four VOCs specific for *P. infestans*-infection: (Z)3-hexenal, (E)-2-hexenal, 2-phenylethanol and 1-hexanal. This confirmed Laothawornkitkul et al. (2010) that (E)-2-hexenal is a major diagnostic VOC marker for *P. infestans*-infection.

Qiu et al. (2014a & b) optimized and used a HS-SPME/GC-MS to find specific VOCs from *P. cinnamomi*. After inoculation of different substrates [V8A, PDA, lupin seedlings (*Lupinus angustifolius* 'Danja'), soil, and soil + lupin seedlings] with *P. cinnamomi*, this study identified 87 VOCs from infected and non-infected substrate. Five of these, 4-ethyl-2-methoxy phenol, 4-ethyl-phenol, 3-hydroxy-2-butanone, butyrolactone, and phenylethyl alcohol, were significant and specific for *P. cinnamomi*-infections. This study shows that it is possible to detect differences between inoculated and non-inoculated plants and substrates.

Jeleń et al. 2005 used HS-SPME/GC-MS and simultaneous distillation, and extraction (SDE) with gas chromatography–olfactometry (GC–O) to find specific VOCs for *P. cactorum*-infected strawberries (*Fragaria* × *ananassa*). Of 160 VOCs, 17 compounds were specific for inoculated strawberries and were absent in non-inoculated strawberries. Of these VOCs, two were found to be causing the characteristic off-odour from *P. cactorum*-infected strawberries: 4-ethyl phenol and 4-ethyl-2-metoxy phenol (4-ethyl guaiacol).Each of these studies found different VOCs and different VOC profiles obtained from the different *Phytophthora* species-infected substrates, indicating there are *Phytophthora* species-specific VOCs and VOC profiles. Hence, enabling the development of e-noses for aiding detection of these pathogens, especially those of quarantine status and high destructive potential. However, of the above referenced papers, only six species of oomycetes (*P. cactorum, P. cinnamomi, P. infestans, P. ramorum, P. plurivora* and *Pythium intermedium*) have been investigated so far and they have utilized several different infected substrates and various methods to collect VOCs from the pathogens themselves or the infected plants. The VOC information for *Phytophthora* is very scarce compared to other pests such as the fall armyworm (FAW) *Spodoptera frugiperda* (J. E. Smith), the brown marmorated stink bug *Halyomorpha halys* (Stål) or the Cotton Boll worm (CBW) *Helicoverpa armigera* Hübner. It is not yet possible for any *Phytophthora* species to find a VOC profile that is robustly produced in connection with the target organisms i.e., VOCs that are not only produced in one infected plant variety or under one certain temperature/light regime.

Table 2.1: List of VOCs released by *Phytophthora* sp. (A), and list of pest induced plant volatiles released by *Phytophthora* sp.-infested plants (B) described in the literature.

A. *Phytophthora* spp. Volatiles			
Pathogen	VOC name	CAS-Nr	Reference
P. plurivor;, P. cactorum	Acetone	67-64-1	Loulier et al., 2020
P. plurivora	α-Pinene	50-32-8	Loulier et al., 2020
P. plurivora	3-Carene	13466-78-9	Loulier et al., 2020
P. plurivora	4-Hydroxybutanoicacid	114959-05-6	Loulier et al., 2020
P. plurivora; P. cactorum	Hexanol	111-27-3	Loulier et al., 2020
P. plurivora	Acetoin	513-86-0	Loulier et al., 2020
P. cactorum	Dimethyl-disulphide	624-92-0	Loulier et al., 2020
P. cactorum	Dimethyl-sulphide	75-18-3	Loulier et al., 2020
P. cactorum; P. cinnamomi	Dimethyl-trisulphide	3658-80-8	Loulier et al., 2020; Qui et al., 2014
P. cactorum	S-Methyl Methanethiosulphonate	2949-92-0	Loulier et al., 2020

P. cactorum; P. ramorum	3-Octanone	106-68-3	Loulier et al., 2020
P. cactorum; P. ramorum; P. cinnamomi	1-Octen-3-ol	3391-86-4	Loulier et al., 2020
P. cactorum	Heptanol	111-70-6	Loulier et al., 2020
P. cactorum	2-Pentyl-furan	3777-69-3	Loulier et al., 2020
P. cactorum	2-Octen-1-ol	18409-17-1	Loulier et al., 2020
P. cactorum	1-Octanol	111-87-5	Loulier et al., 2020
P. ramorum; P. cinnamomi	Ethanol	64-17-5	Loulier et al., 2020
P. ramorum	3-Methyl-butanol	123-51-3	Loulier et al., 2020
P. ramorum	Phenylethyl alcohol	60-12-8	Loulier et al., 2020
P. ramorum	2-Methyl-butanol	137-32-6	Loulier et al., 2020
P. cinnamomi	2-Ethyl-hexanol	104-76-7	Loulier et al., 2020
P. cinnamomi	2,4,6-Trimethyl-heptane	2613-61-8	Qiu et al., 2014
P. cinnamomi	6-Methyl-5-hepten-2-ol	1569-60-4	Qiu et al., 2014
P. cinnamomi	6,10-Dimethyl-5,9-undecadien-2-ol	53837-34-6	Qiu et al., 2014
P. cinnamomi	2-Methoxy-4-vinylphenol	7786-61-0	Qiu et al., 2014
P. cinnamomi	Heptane	142-82-5	Qiu et al., 2014
P. cinnamomi	5-Methyl-3-heptanone	541-85-5	Qiu et al., 2014
B. Pest induced plant volatiles (PIPVs) after *Phytophthora* spp. infestation			
Plant species	VOC name	CAS-Nr	Reference
Quercus robur (seeds)	Neophytadiene isomer 2		Borowik et al., 2021
Quercus robur (seeds)	Neophytadiene isomer 3		Borowik et al., 2021; Qui et al., 2014
Quercus robur (seeds); Lupinus angustifolius (seedlings)	Isoamyl alcohol	123-51-3	Borowik et al., 2021
Quercus robur (seeds)	Methylcarveol	85710-64-1	Borowik et al., 2021
Potato (tubers)	Acetic acid	64-19-7	De Lacy Costello et al., 2001
Potato (tubers)	2-Butenal	4170-30-3	De Lacy Costello et al., 2001
Potato (tubers)	Acetamide	60-35-5	De Lacy Costello et al., 2001
Potato (tubers)	N,N-Dimethylformamide	68-12-2	De Lacy Costello et al., 2001
Potato (tubers)	Butyl acetate	123-86-4	De Lacy Costello et al., 2001

Potato (tubers)	2-Furancarboxaldehyde	98-01-1	De Lacy Costello et al., 2001
Potato (tubers)	N,N-Dimethylacetamide	127-19-5	De Lacy Costello et al., 2001
Potato (tubers)	Styrene	100-42-5	De Lacy Costello et al., 2001
Potato (tubers)	2-Ethyl-1-hexanol	104-76-7	De Lacy Costello et al., 2001
Potato (tubers)	Acetophenone	98-86-2	De Lacy Costello et al., 2001
Potato (tubers)	Methylbenzoate	93-58-3	De Lacy Costello et al., 2001
Potato (tubers)	Benzothiazole	95-16-9	De Lacy Costello et al., 2001
Potato (tubers)	Tridecane	629-50-5	De Lacy Costello et al., 2001
Potato (tubers)	2-Methylpropanoic acid2,2-dimethyl-1-(2-hydroxy1-methylethyl)-propyl ester	18491-15-1	De Lacy Costello et al., 2001
Potato (tubers)	2-Methylpropanoic acid-3hydroxy-2,4,4-trimethylpentyl ester	74367-34-3	De Lacy Costello et al., 2001
Potato (tubers)	iso-Menthol	23283-97-8	De Lacy Costello et al., 2001; Jeleń et al., 2005; Laothawornkitkul et al., 2010; Li et al., 2019; Qiu et al., 2014
Potato (tubers); strawberry (fruit); potato (leaves); tomato (leaves); *Lupinus angustifolius* (seeds)	Phenylethyl alcohol	60-12-8	De Lacy Costello et al., 2001
Potato (tubers)	Verbenone	80-57-9	De Lacy Costello et al., 2001
Potato (tubers)	Dodecane	112-40-3	Jeleń et al., 2005; McCartney et al., 2018
Strawberry (fruit); *Rhododendron* hybrid (branch)	Camphene	79-92-5	Jeleń et al., 2005
Strawberry (fruit)	1-Octene-3-ol	3391-86-4	Jeleń et al., 2005
Strawberry (fruit)	3-Octanone	106-68-3	Jeleń et al., 2005
Strawberry (fruit)	o-Cymene	527-84-4	Jeleń et al., 2005
Strawberry (fruit)	Phenyl methanol	67-56-1	Jeleń et al., 2005
Strawberry (fruit)	Phenyl acetaldehyde	122-78-1	Jeleń et al., 2005
Strawberry (fruit)	(*Z*)-Linalool oxide	1365-19-1	Jeleń et al., 2005
Strawberry (fruit)	Nonanal	124-19-6	Jeleń et al., 2005

Strawberry (fruit)	Pentyl benzene	538-68-1	Jeleń et al., 2005; Li et al., 2019
Strawberry (fruit); tomato (leaves)	4-Ethyl-phenol	123-07-9	Jeleń et al., 2005
Strawberry (fruit)	2,5-Dichloro-phenol	583-78-8	Jeleń et al., 2005
Strawberry (fruit)	2-Phenetyl acetate	103-45-7	Jeleń et al., 2005
Potato (tubers)	(*E*)-2-Hexenal	6728-26-3	Laothawornkitkul et al., 2010
Potato (tubers)	5-Ethyl-2(5H)-Furanone	2407-43-4	Laothawornkitkul et al., 2010
Tomato (leaves)	(*E*)-2-Hexenal	6728-26-3	Li et al., 2019
Tomato (leaves)	(Z)-3-Hexenal	6789-80-6	Li et al., 2019
Tomato (leaves)	1-Hexenal	66-25-1	Li et al., 2019
Tomato (leaves)	Benzaldehyde	100-52-7	Li et al., 2019
Lupinus angustifolius (seeds)	4-Ethyl-2-methoxyphenol	2785-89-9	Loulier et al., 2020
Rhododendron hybrid (branch)	Linalool	78-70-6	McCartney et al., 2018
Rhododendron hybrid (branch)	(*E*)-3-hexen-1-ol	928-91-6	McCartney et al., 2018
Rhododendron hybrid (branch)	(*Z*)-3-Hexenyl pentanoate	35852-46-1	McCartney et al., 2018
Rhododendron hybrid (branch)	1-Octen-3-ol	3391-86-4	McCartney et al., 2018
Rhododendron hybrid (leaves)	Pinocarvone	30460-92-5	McCartney et al., 2018
Rhododendron hybrid (leaves)	Cintronellol	106-22-9	McCartney et al., 2018
Rhododendron hybrid (leaves)	Caryophyllene	87-44-5	McCartney et al., 2018
Rhododendron hybrid (leaves)	4,4-Dimethyl-3-(3-methylbut-3-enylidene)-2-methylenebicyclo[4.1.0]heptane	79718-83-5	McCartney et al., 2018
Rhododendron hybrid (leaves)	8,9-Dehydroneoisolongifolene	67517-14-0	McCartney et al., 2018
Rhododendron hybrid (leaves)	β-Gurjurene	17334–55-3	McCartney et al., 2018

Rhododendron hybrid (leaves)	β-Vatirenene	NA	McCartney et al., 2018
Rhododendron hybrid (leaves)	Isogermacrene D	317819-80-0	McCartney et al., 2018
Rhododendron hybrid (leaves)	Alloaromadendrene	25246-27-9	McCartney et al., 2018
Rhododendron hybrid (leaves)	β-Chamigrene	18431-82-8	McCartney et al., 2018
Rhododendron hybrid (leaves)	γ-Muurolene	30021-74-0	McCartney et al., 2018
Rhododendron hybrid (leaves)	(+)-ß-Selinene	17066-67-0	McCartney et al., 2018
Rhododendron hybrid (leaves)	α-Selinene	473-13-2	McCartney et al., 2018
Rhododendron hybrid (leaves)	Ledene	21747-46-6	McCartney et al., 2018
Rhododendron hybrid (leaves)	4,5,9,10-Dehydroisolongifolene	156747-45-4	McCartney et al., 2018
Rhododendron hybrid (leaves)	Caryophyllene oxide I	1139-30-6	McCartney et al., 2018
Rhododendron hybrid (leaves)	(+)-Spathulenol II	6750-60-3	McCartney et al., 2018
Rhododendron hybrid (leaves)	Ledol	577-27-5	McCartney et al., 2018
Rhododendron hybrid (leaves)	Globulol	51371-47-2	McCartney et al., 2018
Rhododendron hybrid (leaves)	Ledene oxide		McCartney et al., 2018
Rhododendron hybrid (leaves)	(+)-Selin-7(11)-en-4α-ol	473-04-1	McCartney et al., 2018
Rhododendron hybrid (leaves)	Agarospirol	1460-73-7	McCartney et al., 2018
Rhododendron hybrid (leaves)	Sesquiterpene oxide I		McCartney et al., 2018
Rhododendron hybrid (leaves)	Aristolone	6831-17-0	McCartney et al., 2018
Rhododendron hybrid (leaves)	Diterpene I		McCartney et al., 2018
Rhododendron hybrid (leaves)	Diterpene II		McCartney et al., 2018
Rhododendron hybrid (leaves)	Labd-14-ene	1227-93-6	McCartney et al., 2018
Rhododendron hybrid (leaves)	Diterpene III		McCartney et al., 2018
Rhododendron hybrid (leaves)	(*Z*)-11-Hexadecenoic acid	2416-20-8	McCartney et al., 2018

Rhododendron hybrid (leaves)	(*Z*)-9-Hexadecenoic acid	373-49-9	McCartney et al., 2018
Rhododendron hybrid (leaves)	Cyclic octaatomic sulfur	10544-50-0	McCartney et al., 2018
Rhododendron hybrid (leaves)	(*Z*)-9-Octadecenoic acid	112-80-1	McCartney et al., 2018
Lupinus angustifolius (seeds)	4-Ethyl-phenol	513-86-0	Qiu et al., 2014
Lupinus angustifolius (seeds)	Butyrolactone	96-48-0	Qiu et al., 2014
Lupinus angustifolius (seeds)	3-hydroxy-2-butanone	51555-24-9	Qiu et al., 2014
Lupinus angustifolius (seedlings)	Ethyl-acetate	141-78-6	Qiu et al., 2014
Lupinus angustifolius (seedlings)	2-Methyl-propanoic acid	79-31-2	Qiu et al., 2014
Lupinus angustifolius (seedlings)	2-Methyl-butanoic acid	116-53-0	Qiu et al., 2014
Lupinus angustifolius (seedlings)	Benzyl alcohol	100-51-6	Qiu et al., 2014
Lupinus angustifolius (seedlings)	4-Ethyl-1,2-dimethoxybenzene	5888-51-7	Qiu et al., 2014

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2.3 Candidate VOCs for PHYTOPHTHORA RAMORUM detection

Since only two studies include VOCs from *P. ramorum*-infected plants (McCartney et al. 2018) or from the pathogen in culture (Louier et al. 2020), it is not possible to select any robust candidate VOCs for this pathogen. Therefore, all current VOCs that do not appear in the controls in these studies are listed as *P. ramorum* candidate VOCs in Table 2.1. More VOC profiling of *P. ramorum* and other *Phytophthora* species and *Phytophthora*-infected plants are desperately needed in order to find functioning candidate VOCs for these pathogens. Robust candidate VOCs are central for the development of the sensor system prototype (SSP) that PurPest aims to produce for detection of pest-specific VOCs.

3 VOLATILE ORGANIC COMPOUNDS IN THE FALL ARMY WORM-CROP SYSTEM

3.1 The fall army worm: distribution, biology and management

The fall armyworm (FAW) *Spodoptera frugiperda* (J. E. Smith) (Lepidoptera: Noctuidae) is native to the Americas (Todd and Poole 1980) and has been reported to attack a wide range of host plants and causes serious damage to many economical plants, in particular maize. The FAW lifecycle consists of four stages: egg, larva, pupa, and adult. After mating and a preoviposition period of about three days, female moths lay clusters of 100-200 eggs on leaves, stems, or other suitable surfaces. These eggs hatch within 2-4 days, and the emerging larvae go through six instars. Although the larvae are known to feed on many host plants, they exhibit a preference for grasses and cereal crops like maize, rice, sorghum, and wheat. The larval stage typically lasts for 14-30 days, depending on environmental conditions (Sparks 1979; Pitre and Hogg, 1983). The high invasiveness potential of FAW is attributed to the exceptional capacity of the adult moths to migrate, up to 400 km per night (Johnson, 1987; Westbrook et al., 2019).

FAW invaded all of sub-Saharan Africa after it was first observed in Nigeria in 2016 (Cock et al., 2017; Day et al., 2017) and also made its way from Africa to Asia (Sharanabasappa et al., 2018; Liu et al., 2020) and more recently to Australia (Day et al., 2017; Lamsal et al., 2020). It is now one of the biggest threats to food security on these continents, causing tremendous yield losses, especially in maize (Day et al., 2017; Baudron et al., 2019; Hruska & Gould, 1997; Rwomushana et al., 2018; Wan et al., 2021), threatening the livelihoods of millions of farmers and the food security of over 65 million people in Africa alone (Day et al., 2017; Rwomushana et al., 2018; Babendreier et al., 2020). As a consequence of the FAW invasion, the use of pesticides has dramatically increased (Tambo et al., 2020; Yang et al., 2021), causing health problems, harming the environment, and threatening biodiversity. The FAO considers FAW one of the most important threats to food security in these regions (http://www.fao.org/fall-armyworm/en/) (FAO,2020). It is expected that FAW will also invaded Europe in the coming years, and it has already been found on the Canary Islands and Cyprus (https://www.preventionweb.net/collections/fall-armyworm and https://efsa.maps.arcgis.com/apps/MapJournal/index.html?appid=75dcd4b98e96436a8375c5683a09db60).

Research on the chemical ecology of FAW has focussed on two aspects: the pheromone produced by the female moths to attract males, and the caterpillar-induced plant volatiles that attract natural enemies, in particular parasitoids, that attack the caterpillars. The sex pheromone of FAW is a blend of several volatile acetates, dominated by (Z)-9-tetradecenyl acetate (Z9-14:Ac). A combination of Z9-14:Ac with (Z)-7-dodecenyl acetate (Z7-12:Ac) is highly attractive to males in the field (Tumlinson et al., 1986), also to invasive populations in Japan (Wakamura et al., 2021). In a study in China a pheromone lure was optimized by still adding (Z)-11-hexadecen-1-yl acetate (Z11-16:Ac) to the blend. Indeed, the FAW pheromone blend has been shown to be different for different geographic regions (Batista-Pereira et al., 2006; Groot et al., 2008).

FAW was one of the first insects studied in the context of herbivore-induced plant volatiles (HIPVs). Maize plants in particular are very responsive to caterpillar attacks and have been found to emitted large amounts of mainly terpenoids, but also indole in response to such attacks (Turlings et al., 1990, 1993). The emissions of the truly inducible compounds is systemic and not just limited to the damaged site (Turlings and Tumlinson, 1992), enhancing their detectability. The fatty acid-amino acid conjugate volicitin (N-[17-hydroxylinolenoyl]-L glutamine) in caterpillar oral secretions was found to be the main elicitor that triggers this response (Alborn et al., 1997; Turlings et al., 2000). FAW also the emissions of such volatiles (Turlings et al., 1993), but to a lesser extent, possibly because it is able to somewhat suppress the emissions (De Lange et al.,

2020). There is tremendous variation among maize genotypes in the amounts of volatiles that they release upon caterpillar attack (Degen et al., 2004), the overall volatile profile shows clear consistencies in their caterpillar-induced emissions (Hoballah. et al., 2002; Gouinguené and Turlings, 2002; Gouinguené et al., 2003). Studying the FAW-maize model is therefore not only of great economic importance, but also an ideal model to demonstrate the potential of odor-based detection technologies (Turlings and Erb, 2018; Turlings and Degen, 2022).

3.1.1 References

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3.2 Summary of literature on FAW VOCs

The literature on volatiles directly emitted by FAW is limited to publications on the identification of the sex pheromone blend emitted by female moths. The first identification was done by extracting the pheromone directly from the female moth glands (Sekul and Sparks, 1967), which its composition is different from the pheromone released by the moths (Tumlinson et al., 1986). The moths were found to release (*Z*)-7-dodecen-1-ol acetate (Z7-12:Ac), dodecan-1-ol acetate (12:Ac), 11-dodecen-1-ol acetate (11-12:Ac), (*Z*)-9-tetradecen-1-ol acetate (*Z*9-14:Ac), and (*Z*)-11-hexadecen-1-ol acetate (*Z*11-16:Ac). To the best of our knowledge, this latter publication is the only one that used the dynamic headspace technique to collect and identify the sex pheromone of Spodopetras, including FAW. The composition of the sexual pheromone of two closely related species *S. exigua* and *S. frugiperda* (FAW) can be distinguished by the exclusive presence of the 12:Ac, Z7-12:Ac and 11-12:Ac in the FAW sex pheromone blend. Tests on the biological function of Z7-12:Ac have shown that it is the main compound responsible for the attraction of males (Tumlinson et al., 1986; Andrade et al., 2000; Cruz-Esteban et al., 2018). Their concentration is not very accurate, and composition and ratios of volatiles can vary depending on factors such as developmental stage, sex, feeding status, and environmental conditions. In subsequent studies it was shown that Z9-14:Ac and Z7-12:Ac are universal pheromone components of FAW, but other compounds, such as Z9-12:Ac, Z11-16:Ac and E7-12:Ac were also found to be released in different geographic populations (Tumlinson et al., 1986; Descoins et al., 1988; Fleischer et al., 2005; Batista-Pereira et al., 2006; Groot et al., 2008; Lima & McNeil, 2009; Jiang et al., 2021).

In addition to the pheromone work, considerable information is available on plant volatiles induced by the caterpillars of FAW and other *Spodoptera* species have been extensively studied (Turlings and Erb, 2018; Turlings and Degen, 2022). We have selected the most relevant papers on volatiles emitted by maize plants in responses to attacks by caterpillars, to simulated caterpillar damage (with oral secretion applications) and incubation of cut plants in solutions with caterpillar oral secretions. Another aspect to consider is that in the below-listed 14 publications different varieties of maize were used and we included works that were performed under greenhouses and field conditions. Therefore, we have an extensive overview of different scenarios of maize responses when attacked by FAW. Our purpose in selecting these publications was to show that different induction techniques and *Spodoptera* species induce similar volatile profiles. We did not see any specific volatiles that FAW induces on maize plants, but there are quantitative differences. Maize plants attacked by FAW and other *Spodoptera* species can release up to 25 different volatiles. These include a diverse array of green leaf volatiles (GLV's), monoterpenes, sesquiterpenes and aromatic compounds. Some of the most notable compounds include (Z)-3-hexen-1-yl acetate, linalool, indole, (3E)-4,8-dimethyl-1,3,7-nonatriene (DMNT), (3E, 7E)-4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT) and E-β-farnesene. The release of the GLVs is induced within seconds, whereas the others are released after 4 to 6 hours after FAW attack

(terpenoids and indole) small maize plants typically release these compounds at rates of 50-200 ng per hour.

Table 3.1: List of VOCs released f by FAW (A), and list of HIPVs released by FAW-infested plants (B) described in the literature.

A. Insect volatiles			
Related pest developmental stage	VOC name	CAS-Nr	Reference
FAW, adult female	Dodecan-l-olacetate	112-53-8	Tumlinson et al., 1985
FAW, adult female	7-Dodecen-l-olacetate	16677-06-8	Tumlinson et al., 1985
FAW, adult female	11-Dodecen-l-olacetate	35153-10-7	Tumlinson et al., 1985
FAW, adult female; *Spodoptera exigua*, adult female	(*Z*)-9-Tetradecen-1-ol	53939-27-8	Tumlinson et al., 1985; Tumlinson et al., 1990
FAW, adult female; *Spodoptera exigua*, adult female	(*Z*)-9-Tetradecen-1-olacetate	16725-53-4	Tumlinson et al., 1985; Tumlinson et al., 1990
FAW, adult female	(*Z*)-1l-Hexadecenal	53939-28-9	Tumlinson et al., 1985
FAW, adult female; *Spodoptera exigua*, adult female	(*Z*)-11-Hexadecen-1-olacetate	34010-21-4	Tumlinson et al., 1985; Tumlinson et al., 1990
Spodoptera exigua, adult female	(*Z*,*E*)-9,12-Tetradecadienylacetate	31654-77-0	Tumlinson et al., 1990
B. Herbivore induced plant volatiles (HIPVs) after FAW infestation			
Plant species	VOC name	CAS-Nr	Reference
Maize	(*Z*)-3-Hexen-1-ol	928-96-1	Turlings et al., 1998; Turlings et al., 1998a; Hoballah et al., 2002; Carroll et al., 2006; Pinto-Zevallos et al., 2016; de Lange et al., 2020
Maize	Indole	120-72-9	Turlings et al., 1993; Turlings et al., 1998; Turlings et al., 1998a; Turlings et al., 2000; Hoballah et al., 2002; Peñaflor et al., 2011a; Carroll et al., 2006; Robert et al.,

			2013; de Lange et al., 2016; Pinto-Zevallos et al., 2016
Maize	(+) Cycloisosativene	22469-52-9	Pinto-Zevallos et al., 2016
Maize	(3*E*)-4,8-Dimethyl-1,3,7-nonatriene	19945-61-0	Turlings et al., 1993; Turlings et al., 1998; Turlings et al., 1998a; Turlings et al., 2000; Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011a; Peñaflor et al., 2011a; Robert et al., 2013; de Lange et al., 2016; Pinto-Zevallos et al., 2016; de Lange et al., 2020; Yactayo-Chang et al., 2021
Maize	(3*E*, 7*E*)-4,8,12-Trimethyl-1,3,7,11-tridecatetraene	62235-06-7	Turlings et al., 1993; Hoballah et al., 2002; Carroll et al., 2006; de Lange et al., 2016; Pinto-Zevallos et al., 2016; de Lange et al., 2020
Maize	(*E*)-2-Hexen-1-ol	928-95-0	Hoballah et al., 2002
Maize	(*E*)-2-Hexenal	6728-26-3	Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011a; Robert et al., 2013; Pinto-Zevallos et al., 2016; de Lange et al., 2020
Maize	(*E*)-2-Hexenyl acetate	2497-18-9	de Lange et al., 2020
Maize	(*E*)-3-hexen-1-ol	928-97-2	Peñaflor et al., 2011a; Robert et al., 2013
Maize	(*E*)-α-bergamotene	13474-59-4	Turlings et al., 1993; Turlings et al., 1998a; Turlings et al., 2000; Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011; Peñaflor et al., 2011a; Robert et al., 2013; de Lange et al., 2016; Pinto-Zevallos et al., 2016; de Lange et al., 2020; Yactayo-Chang et al., 2021
Maize	(*E*)-α-Farnesene	502-61-4	Turlings et al., 1998a
Maize	(*E*)-β-caryophyllene	87-44-5	Turlings et al., 1998; Turlings et al., 1998a; Hoballah et al., 2002; Peñaflor et al., 2011; Peñaflor et al., 2011a; Pinto-Zevallos et al., 2016; de Lange et al., 2016; de Lange et al., 2020
Maize	(*E*)-β-Farnesene	18794-84-8	Turlings et al., 1993; Turlings et al., 1998; Turlings et al., 1998a; Turlings et al., 2000; Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011; Peñaflor et al., 2011a; Robert et al., 2013; Pinto-

			Zevallos et al., 2016; de Lange et al., 2016; de Lange et al., 2020
Maize	(*E*)-β-Ocimene	3779-61-1	Hoballah et al., 2002; Carroll et al., 2006; Robert et al., 2013; Pinto-Zevallos et al., 2016; de Lange et al., 2016
Maize	(*Z*)-3-Hexenal	6789-80-6	Turlings et al., 1998a; Hoballah et al., 2002; Peñaflor et al., 2011a; Robert et al., 2013; de Lange et al., 2020
Maize	(*Z*)-3-Hexenyl acetate	3681-71-8	Turlings et al., 1993; Turlings et al., 1998a; Turlings et al., 2000; Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011a; Robert et al., 2013; de Lange et al., 2016; Pinto-Zevallos et al., 2016; de Lange et al., 2020
Maize	(*Z*)-β-Ocimene	3338-55-4	de Lange et al., 2020
Maize	Anthranilic acid	118-92-3	Pinto-Zevallos et al., 2016
Maize	Benzyl acetate	140-11-4	Peñaflor et al., 2011a; de Lange et al., 2020
Maize	Decanal	112-31-2	Pinto-Zevallos et al., 2016
Maize	Geranyl acetate	105-87-3	Hoballah et al., 2002; Peñaflor et al., 2011; Peñaflor et al., 2011a; Pinto-Zevallos et al., 2016; de Lange et al., 2020; Yactayo-Chang et al., 2021
Maize	Linalool	78-70-6	Turlings et al., 1993; Turlings et al., 1998a; Turlings et al., 2000; Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011; Peñaflor et al., 2011a; Robert et al., 2013; de Lange et al., 2016; Pinto-Zevallos et al., 2016; de Lange et al., 2020
Maize	Methyl-anthranilate	85-91-6	de Lange et al., 2020
Maize	Nerolidol	7212-44-4	Turlings et al., 1993; Hoballah et al., 2002; Carroll et al., 2006; Pinto-Zevallos et al., 2016; de Lange et al., 2020
Maize	Nonanal	124-19-6	Pinto-Zevallos et al., 2016
Maize	Phenethyl acetate	103-45-7	Hoballah et al., 2002; Peñaflor et al., 2011; Peñaflor et al., 2011a; de Lange et al., 2016; de Lange et al., 2020
Maize	Ylangene	14912-44-8	Pinto-Zevallos et al., 2016

Maize	α-Humulene	6753-98-6	Carroll et al., 2006; Pinto-Zevallos et al., 2016
Maize	α-Muurolene	10208-80-7	Pinto-Zevallos et al., 2016
Maize	α-Zingiberene	495-60-3	Pinto-Zevallos et al., 2016
Maize	β -bisabolene	495-61-4	Hoballah et al., 2002; Pinto-Zevallos et al., 2016
Maize	β-Sesquiphellandrene	20307-83-9	Hoballah et al., 2002; Pinto-Zevallos et al., 2016; de Lange et al., 2020;
Maize	β-Myrcene	123-35-3	Hoballah et al., 2002; Carroll et al., 2006; Peñaflor et al., 2011a; Robert et al., 2013; Pinto-Zevallos et al., 2016; de Lange et al., 2020

3.2.1 References

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3.3 Candidate VOCs for FAW detection

There are 3 compounds that adult females of FAW emit (dodecan-l-ol acetate; (*Z*)-7-dodecen-l-ol acetate and (*Z*)-11-dodecen-l-ol acetate) and are found only in this species compared to other species of *Spodoptera*. They have biological relevance for male attraction in the field. As mentioned in the previous section there are no unique compounds emitted by maize plants under FAW attack in comparison to attacks by other *Spodoptera* species, but ratios differences can be used to determine which species is attacking a plant. The most relevant compounds that are consistently emitted and have an ecological relevance are (Z)-3-hexen-1-yl acetate, linalool, indole, (3E)-4,8-dimethyl-1,3,7-nonatriene (DMNT), (3E, 7E)-4,8,12-trimethyl-1,3,7,11-tridecatetraene (TMTT) and E-β-farnesene.

Table 3.2: List of candidate VOCs for FAW detection.

VOC name	CAS-Nr	Biological relevance
Dodecan-l-olacetate	112-53-8	Sexual pheromone
7-Dodecen-l-olacetate	16677-06-8	Sexual pheromone
11-Dodecen-l-olacetate	35153-10-7	Sexual pheromone
(*Z*)-3-Hexenyl acetate	3681-71-8	Relevant HIPV
Indole	120-72-9	Relevant HIPV
Linalool	78-70-6	Relevant HIPV
(*E*)-β-Farnesene	18794-84-8	Relevant HIPV
(3*E*)-4,8-Dimethyl-1,3,7-nonatriene	19945-61-0	Relevant HIPV
(3*E*, 7*E*)-4,8,12-Trimethyl-1,3,7,11-tridecatetraene	62235-06-7	Relevant HIPV

4 VOLATILE ORGANIC COMPOUNDS IN THE BROWN MARMORATED STINK BUG-PLANT SYSTEM

4.1 The Brown marmorated stink bug: distribution, biology and management

Halyomorpha halys (Stål) (Hemiptera: Pentatomidae), known as the Brown marmorated stink bug (BMSB), is an insect native to eastern Asia, and is now considered one of the most harmful invasive pests in North America and Europe (Zobel et al., 2016).

Halyomorpha halys has successfully invaded and established itself in 43 US states, Canada, and five European nations (Italy, France, Switzerland, Portugal and Slovakia) (EPPO Global Database, 2023), with recent incursions reported in Russia, Georgia, and Bulgaria (Nixon et al., 2018). Starting with its geographic range in Asia, where it originated, *H. halys* can be found in all of the temperate and subtropical areas of eastern China and Japan (Haye & Weber, 2017). Finally, the presence of the pest has been documented throughout South Korea and on some of the Honshu, Shikoku, and Kyushu islands (Bae et al., 2009). In 1993, when a specimen was discovered in a cargo coming from Asia, *H. halys* was first identified outside of its native continent in Canada's Province of British Columbia (Fogain et al., 2011). Even though there were other interceptions across the nation after this initial arrival, the pest's establishment was not thought to have occurred until 2010 (Fogain et al., 2011). *H. halys* was occasionally discovered in shipments entering ports in the United States prior to its introduction in Europe. Hoebeke et al. (2003) noted two reports of specimens in shipping containers, aircraft, and other vehicles from 1973 to 1987 and eight reports from 1989 to 1998. Later, the insect proceeded to spread gradually to other east coast states. In central, southern, and western states such Mississippi, Ohio, Oregon, and California, limited finds or populations started to be reported and the pest now spread across 43 states (Nixon et al., 2018). The first confirmed population of *H. halys* in Europe was found in 2004 in Liechtenstein followed by Switzerland in 2007 (Hess et al., 2022). Swiss reports of *H. halys* increased dramatically between 2007 and 2010. Likely spreading from this location, two years later *H. halys* was also present in France and Germany. Since the pest was initially only present in at low numbers in these two countries, there was no cause for alarm. But the insect colonisation continued to increase until today (Wermelinger et al., 2008; Mueller et al., 2011; Heckmann, 2012). In Italy, the first *H. halys* detection was in the Emilia Romagna region (Maistrello et al., 2016) and the pest is now successfully established. The most southern record of *H. halys* in Europe is now Turkey (Güncan & Gümüs, 2019). *Halyomorpha halys* consumes plant juices for nutrition. Nymphs primarily eat the green parts of the plant, such as leaves, stems, and fruit, whereas adults typically prefer fruits. The most significant crop damage comes from eating seeds from legume pods like beans and soybeans as well as pome and stone fruits. Small lesions with a diameter of 3 mm are indicative of leaf feeding; these lesions may later turn necrotic. Fruits that have been attacked may have small necrotic blotches or spots, grooves, or brownish discolorations. It goes without saying that these flaws could render the fruits unmarketable. The fruits are severely deformed in cases of severe infestations, and there may be significant financial losses (Zobel et al., 2016).

Due to its extreme polyphagy, *Halyomorpha halys* has roughly 40 hosts among domesticated plants and much more (around 300) wild hosts. Among the plants species of economic importance, some major hosts, where the pest is able to cause even more severe damages, are cherry (*Prunus avium*), plum (*Prunus domestica*), peach (*Prunus persica*), apple (*Malus domestica*), pear (*Pyrus communis*), grapevine (*Vitis vinifera*) and corn (*Zea mays*) (EPPO Global Database, 2023). After fruit set, bugs typically begin to feed and continue doing so throughout the entire growth season. The outcomes vary: for example, apple damage is usually insignificant until mid-June, whereas feeding on peaches resultes in immediate economic damage as the surface becomes distorted, dented, discoloured, and the flesh beneath turned brown due to the insertion of the stylet from the

animal's feeding apparatus. Nymphs and adults freely travel between host plants based on which species is now most suitable in the area. Adults are excellent dispersers and can colonise new hosts quickly (Wiman et al., 2014). Some plants, such as peaches, allow the insect to complete their entire life cycle. *H. halys* has one or two generations per year in the USA, but there have been reports of 5–6 generations per year in the species' native range. In its adult stage, the stink bug spends the winter in natural shelters or anthropogenic structures. On the underside of the leaves, in clusters of 20–30 eggs, females lay 50–150 eggs, but they can also lay up to 400 eggs per female. There are five nymphal stages before reaching the adult stage (Lee et al., 2013).The effectiveness of several insecticides was assessed in an effort to stop the *H. halys* invasion. Initially discovered to be effective against *H. halys* are carbamates, organophosphates, pyrethroids, and neonicotinoids, such as bifenthrin, dinotefuran, acetamiprid, malathion, and methomyl. Despite having been demonstrated to be effective against *H. halys*, not all of these active ingredients are registered or accessible for use on all crops. Moreover, in recent years, regulatory action have been taken against the relatively few organophosphates, carbamates, or neonicotinoids that were still registered on food crops (Kuhar & Kamminga, 2017). Additional research has also shown that many compounds tested at field application rates had insufficient efficacy due to low initial knock-down effects and/or the recovery of bugs from a dormant state (Kuhar & Kamminga, 2017). Leskey et al. (2014) point at the following effects as reasons that could contribute to this lack of efficacy: presence, persistence, spread, and presence of residues. Since *H. halys* is widely dispersed throughout a variety of wild and cultivated crops throughout the season, it is unlikely that the vast majority of the pest populations will be directly exposed to insecticides. Moreover, there is a different susceptibility among *H. halys* generations: overwintered *H. halys* populations are more vulnerable to insecticide applications than the first and second generation which are present in the field during the mid- to late-season.

Nonetheless, the use of excessive chemicals has disturbed low-impact Integrated Pest Management (IPM) practises (usually employed for other pests) or caused secondary pest outbreaks due to a lack of efficient monitoring methods. IPM emerged in the 1980s as a result of increasing awareness of environmental impact in society and in agriculture. With the protection of the environment as its primary goal, efforts are being made to reduce the use of chemicals, implement damage thresholds, and employ natural antagonists. This final characteristic, which is also known as biological control, is increasingly important for the sustainability of agriculture today. Depending on the ecological relationship between the species and their antagonists—predators, parasitoids, or pathogens—it can be done in a variety of ways (Kuhar & Kamminga, 2017). It has been shown that alien pests initially experience less parasitism, but over time, they tend to attract more native parasitoids (Cornell & Hawkings, 1993). Furthermore, their antagonists may also show up after the pest initial appearance. Various Asian and European species currently parasitize *H. halys* in Europe. In 2014, egg masses of the Asian egg parasitoid *Trissolcus spp*. (Hymenoptera: Scelionidae), in particular *T. japonicus*, were discovered in wooded habitats in Maryland, USA (Talamas et al., 2015). This egg parasitoid was previously thought to be a viable classical biological control agent in the USA before the adventive population arrived. It represents the primary limiting factor of *H. halys* in its native range of northeast Asia (Yang et al., 2009). Indicating its oligophagous ability, it has also been collected from several other Pentatomidae species (Zhang et al., 2017). *Trissolcus basalis* Wollaston (Hymenoptera: Scelionidae), *Trissolcus japonicus* Ashmead (Hymenoptera: Scelionidae), and *Trissolcus mitsukurii* Ashmead (Hymenoptera: Scelionidae) are the three main species identified for classical biological control. On the other hand, native egg-parasitoids like *Anastatus bifascatus* Geoffroy (Hymenoptera: Eupelmidae) and *Ooencyrtus telenomicida* Vassiliev (Hymenoptera: Encyrtidae) may be used to supplement biological control. There are some debates surrounding the use of *Trissolcus* species against *H. halys*, despite the fact that this has currently been proven to be the most successful

tactic. Since they are not specialised, their use in traditional biological control has been questioned (Haye et al., 2015). For instance, Roversi et al. (2016) claim that the use of generalists carries a well-recognized risk of effects on the non-target species. Other IPM options for the control of *H. halys* are staking, trap crops, perimeter reshaping in orchards, push-pull, exclusion nets, and behavioural manipulation. These had the potential to drastically minimise fruit loss (Falagiarda et al., 2023).

The use of semiochemicals plays an important role in the management of *H. halys*. Before the actual pheromone was identified, it was known that *H. halys* is attracted to methyl-(2*E*,4*E*,6*Z*)-2,4,6-decatrienoate, the aggregation pheromone of brown-winged green stink bug *Plautia stali* Scott (Lee et al., 2002). The discovery of the pest aggregation pheromone (Khrimian et al., 2014) opened for further pest control strategies. The pheromone is as a 3.5:1 mixture of two stereoisomers, (3*S*,6*S*,7*R*,10*S*)-10,11-epoxy-1-bisabolen-3-ol and (3*R*,6*S*,7*R*,10*S*)-10,11-epoxy-1-bisabolen-3-ol and it is solely produced by adult males. They usually begin to release the pheromone at the average age of 13 days, and it is mostly emitted during the day. It attracts both adult males, adult females, and nymphs (Weber et al., 2017). For this reason, the pheromone lures are employed in traps for monitoring, early detection (Vandervoet et al., 2019) and for pest management decision making. However, the aggregation pheromone functions as an attractant with only a portion of individuals entering the trap. This is because the pheromone trap is meant to be a monitoring tool rather than a mass-trapping instrument. Although it could lengthen retention period within a trap crop, the short range of the aggregation zone does not significantly reduce the number of *H. halys*. Besides semiochemicals, a new term, semiophysicals, has been recently coined (Nieri et al., 2021) to indicate the use of physical stimuli (e.g., lights, sounds, and vibrations) to interfere with pest behaviors. The development of traps with combined pheromonal and visual stimuli with UV-A and blue or green wavelengths led to significant increase of the trapped individuals (Rondoni et al., 2022). Similarly, integrating substrate-borne vibrations in pheromone traps allowed to improve the traps efficacy, with higher numbers of males and females captures (Zapponi et al., 2023). These techniques may prove effective in the development of mass trapping strategies.

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4.2 Summary of literature on BMSB VOCs

Numerous studies have identified and characterized the volatile compounds emitted by *H. halys*. These volatiles primarily consist of a diverse array of aldehydes, alcohols, esters, terpenes, and sulfur-containing compounds. Some of the most notable compounds include the aldehydes (*E*)-2-decenal, (*E*)-2-octenal, (*E*)-2-hexenal, sesquiterpenes and alkanes. The composition and ratios of these volatiles can vary depending on factors such as developmental stage, sex, feeding status, and environmental conditions.

Stink bugs, including *H. halys*, possess specialized scent glands located on their thorax and abdomen that release volatiles when disturbed or threatened. The emission of volatiles is primarily a passive process, relying on the release of pressure built up within the scent gland reservoir. These defense compounds are shared among many species and (*E*)-2-decenal, (*E*)-2-octenal, (*E*)-2-hexenal, (*E*)-2-decenyl acetate are reported in not only *H. halys* (Zhong et al., 2017, Nixon et al., 2018), but also in a cosmopolitan species, the green stink bug *Nezara viridula* L. (Aldrich et al., 1987).

Khrimian et al. (2014a) characterized the male-produced aggregation pheromone of *H. halys* as a 3.5:1 mixture of two stereoisomers, (3S,6S,7R,10S)-10,11-epoxy-1-bisabolen-3-ol and (3R,6S,7R,10S)-10,11-epoxy-1-bisabolen-3-ol. According to Harris et al. (2015), mature males started producing pheromone at a mean age of 13 days. Males who were housed alone produced a mean of 843 ng of pheromone each day, in daily volatile collections in levels that ranged fivefold. Males in groups emitted <10% pheromone per bug per day than lone males due to a strong negative reaction to male density. The pheromone is mainly emitted during the day. The pheromone is effective to both adult sexes and nymphs.

An array of linear hydrocarbons has been detected in *H. halys*: undecane, dodecane, tridecane and pentadecane (Kitamura et al., 1984, Baldwin et al., 2014, Harris et a., 2015, Fraga et al., 2017, Zhong et al., 2017). Among them, tridecane was the most frequently found. Linear hydrocarbons are also reported among the emissions of *N. viridula*: dodecane, tridecane and nonadecane (Borges et al., 1987). It is unclear whether these volatiles might be relevant to biology. Authors going back to Calam and Youdeowei (1968) proposed that such hydrocarbons serve as solvents or carriers, rather than as inherently bioactive substances, to mediate the effective evaporation of aldehydes and other active compounds on the structurally specialized thoracic scent efferent system shared by many pentatomoids (Kment and Vilimova 2010), explaining the reason for the comparatively large amounts found in stink bug glands.

Table 4.1: List of VOCs released by BMSB (A), and list of HIPVs released by BMSB-infested plants (B) described in the literature.

A. Insect volatiles			
Related pest developmental stage	VOC name	CAS-Nr	Reference
BMSB, adult male	(3*S*,6*S*,7*R*,10*S*)-10,11-Epoxy-1-bisabolen-3-ol		Khrimian et al. 2014a; Harris et al. 2015; Weber et al.2017
BMSB, adult male	(3*R*,6*S*,7*R*,10*S*)-10,11-Epoxy-1-bisabolen-3-ol		Khrimian et al. 2014a; Harris et al. 2015; Weber et al.2017
BMSB, adult, nymph, male genital capsule; *Nezara viridula*, adult	Tridecane	629-50-5	Aldrich et al., 1987; Tognon et al., 2016; Harris et al. 2015; Zhong et al., 2017; Nixon et al. 2018
BMSB, adult, eggs; *Nezara viridula*, adult	(*E*)-2-Decenal	3913-81-3	Aldrich et al., 1987; Sturaro et al., 1994; Harris et al. 2015; Tognon et al., 2016; Zhong et al., 2017; Nixon et al. 2018
BMSB, adult	(*E*)-2-Decen-1-ol	22104-80-9	Kitamura et al. 1984
BMSB, adult; *Nezara viridula*, adult	(*E*)-2-Decenyl acetate	19487-61-7	Aldrich et al., 1987; Zhong et al., 2017
BMSB, adult; *Nezara viridula*, adult	(*E*)-2-Hexenal	6728-26-3	Aldrich et al., 1987; Solomon et al. 2013; Zhong et al., 2017
BMSB, adult	(*E*)-2-Octenal	2548-87-0	Zhong et al., 2017
BMSB, adult	(*E*,*E*)-2,4-Hexadienal	142-83-6	Solomon et al. 2013
BMSB, adult	(*Z*)-Cyclodecene	935-31-9	Solomon et al. 2013
BMSB, adult	1-Ethyl-1,5-cycloctadiene		Solomon et al. 2013
BMSB, adult	3-Hepten-2-one	1119-44-4	Solomon et al. 2013
BMSB, adult, eggs	2,4-Decadienal	25152-84-5	Kitamura et al. 1984; Tognon et al., 2016
BMSB, adult	4-Oxo-(*E*)-2-hexenal	2492-43-5	Zhong et al., 2017; Nixon et al. 2018
BMSB, adult	5-Ethyl-2(5H)-furanone	2407-43-4	Solomon et al. 2013
BMSB, adult; *Nezara viridula*, adult	Dodecane	112-40-2	Kitamura et al. 1984; Aldrich et al., 1987; Borges et al., 1987; Zhong et al., 2017, Nixon et al. 2018
BMSB, adult	Pentadecane	629-62-9	Kitamura et al. 1984
BMSB, adult	Tetradecane	629-59-4	Kitamura et al. 1984

BMSB, adult	Undecane	1120-21-4	Kitamura et al. 1984
BMSB, eggs	Hexadecanal	629-80-1	Tognon et al., 2016
BMSB, eggs	Octadecanal	638-66-4	Tognon et al., 2016
BMSB, eggs	Eicosanal	2400-66-0	Tognon et al., 2016
BMSB, eggs	Nonanal	124-19-6	Tognon et al., 2016
BMSB, eggs	2-Undecenal	53448-07-0	Tognon et al., 2016
Nezara viridula, adult	Nonadecane	629-92-5	Aldrich et al., 1987; Borges et al., 1987
Nezara viridula, adult	(*Z*)-α-Bisabolene	29837-07-8	Aldrich et al., 1987
Nezara viridula, adult	(*E*)-Nerolidol	40716-66-3	Aldrich et al., 1987
Nezara viridula, adult	(E,*Z*)-α-Bisabolene epoxide		Aldrich et al., 1987
Nezara viridula, adult	(Z,*Z*)-α-Bisabolene epoxide		Aldrich et al., 1987
B. Herbivore induced plant volatiles (HIPVs) after BMSB infestation			
Plant species	VOC name	CAS-Nr	Reference
Peach	4'-Ethylacetophenone	937-30-4	Peterson et al., 2022
Peach	(*E*)-β-Caryophyllene	87-44-5	Peterson et al., 2022
Peach	(*Z*)-3-Hexenyl acetate	3681-71-8	Peterson et al., 2022
Peach	4-Hexen-1-ol, acetate	72237-36-6	Peterson et al., 2022
Peach	Benzaldehyde	100-52-7	Peterson et al., 2022
Tree of heaven	2,4-Di-tert-butylphenol	96-76-4	Peterson et al., 2022
Tree of heaven	(*E*)-β-Ocimene	3779-61-1	Peterson et al., 2022
Tree of heaven	Methyl palmitate	112-39-0	Peterson et al., 2022
Tree of heaven	(*E*)-Nerolidol	40716-66-3	Peterson et al., 2022
Tree of heaven	Sesquirosefuran	39007-93-7	Peterson et al., 2022
Tree of heaven	(3*E*)-4,8-Dimethyl-1,3,7-nonatriene	19945-61-0	Peterson et al., 2022
Tree of heaven	Alloocimene	3016-19-1	Peterson et al., 2022
Tree of heaven	Cinerone		Peterson et al., 2022
Tree of heaven	*E*-Farnesene epoxide		Peterson et al., 2022

Tree of heaven	Linalool	78-70-6	Peterson et al., 2022
Tree of heaven	Nonanal	124-19-6	Peterson et al., 2022
Tree of heaven	p-Mentha-1,3,8-triene	18368-95-1	Peterson et al., 2022
Bean	Tridecane	629-50-5	Fraga et al., 2017

4.3 Candidate VOCs for BMSB detection

So far, the most unique compounds are two stereoisomers identified as the main component of the aggregation pheromone released by adult males. All the other VOCs (Table 4.1) are generic of stink bugs or other organisms. It is however worth considering (*E*)-2-Decenal, (*E*)-2-octenal, (*E*)-2-hexenal and (*E*)-2-decenyl acetate, the unpleasant odors released by stink bugs when disturbed (alarm/defense pheromones). These VOCs, even if very generic, can at least indicate presence of stink bugs.

Table 4.2: List of candidate VOCs for BSMB detection.

VOC name	CAS-Nr	Biological relevance
(3*S*,6*S*,7*R*,10*S*)-10,11-Epoxy-1-bisabolen-3-ol		Aggregation pheromone
(3*R*,6*S*,7*R*,10*S*)-10,11-Epoxy-1-bisabolen-3-ol		Aggregation pheromone
(*E*)-2-Decenal	3913-81-3	Defense/alarm pheromone
(*E*)-2-Decenyl acetate	19487-61-7	Defense/alarm pheromone
(*E*)-2-Hexenal	6728-26-3	Defense/alarm pheromone
(*E*)-2-Octenal	2548-87-0	Defense/alarm pheromone

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5 VOLATILE ORGANIC COMPOUNDS IN THE COTTON BOLL WORM-PLANT SYSTEM

5.1 The Cotton Boll worm: distribution, biology and management

The Cotton Boll worm (CBW) *Helicoverpa armigera* Hübner (Lepidoptera: Noctuidae) is considered as one of the major pests in tropical and warm-temperate regions worldwide (Jones et al. 2019). Global economic losses caused by this species are estimated at over 3 billion $ per year (Haile et al. 2021; Riaz et al. 2021). CBW is widely distributed throughout Asia, Oceania, Africa, and southern Europe, and has recently invaded South America (Tay et al. 2013, Jones et al. 2019).

H. armigera is a highly polyphagous pest infesting more than 200 host plant species of diverse plant families. Many crops of high economic importance are included in the host range of CBW, such as cotton, maize, tomato, sunflower, soybean, and several legumes (Cunningham et al. 1999; Cunningham & Zalucki 2014). The adults of CBW are excellent flyers and can migrate over long distances up to 2000 km (Behere et al. 2013; Jones et al. 2015). The species has a high fecundity and rapid reproduction rates, resulting in average in 4-6 generations per year and up to 10-11 generations per year in tropical regions (Riaz et al. 2021). The larvae are highly destructive plant feeders and very polypagh, not only regarding plant species but also concerning plant parts. The species has the ability to adapt its diapause depending on environmental conditions, in order to optimize survival. All these characteristics in their biology – its polyphagy, high mobility and reproduction rates and its facultative diapause - makes the CBW to that serious pest, quickly invading new areas.

A blind trust of synthetic pesticides as main control measure for CBW has led to resistance development to all major classes of synthetic insecticides across many regions of the world (Downes et al. 2016; Jones et al. 2019; Riaz et al. 2021). As an alternative pest control measure have genetically modified crops, such as Bt cotton, shown a good control effect of CBW over a period. But, as for synthetic pesticides, resistant populations have developed also for Bt crops, making well deliberated resistance management strategies necessary (Jin et al. 2015; Downes et al. 2016; Tabashnik & Carriere 2017). Today, IPM strategies based on forecast, monitoring and decision support systems combined with biological, chemical, and physical control measures have to be developed and used for successful control of CBW (Downes et al. 2016; Jones et al. 2019; Riaz et al. 2021).

5.1.1 References

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5.2 Summary of literature on CBW VOCs

In this review we focus on studies on CBW related VOCs, which have shown that the pest itself or plants infested by CBW can release herbivore-specific signals by chemical analyses and behavioral and/or electrophysiological bioassays. The huge number of studies regarding other issues of the chemical ecology of CBW are not included here.

Research on VOCs related to CBW has started in the 1970s with identification of sex pheromones (Piccardi et al. 1977; Nesbitt et al. 1980; Zhang et al. 2012). We want to highlight here for our purpose most important pheromones, so called oviposition marking pheromones (OMPs) or oviposition deterring pheromones (ODPs). ODPs have been identified for *H. armigera* around the turn of the millennium (Guoqing et al. 2001; Xu et al. 2006; Liu et al. 2008). ODPs are deposited by many parasitic and phytophagous insects associated with egg-laying, aiming for modification of the oviposition behaviour of conspecifics such that subsequent eggs are not deposited into an already utilized resource. After behavioural observations on CBW have indicating the existence of oviposition-deterrent compounds, the three compounds 4-methyl-4-hydroxyl-pentanone-2, hexadecanoic acid (palmitic acid) and (*Z*)-9-octadecenoic acid (oleic acid) have been identified from the tarsi of female CBW as oviposition-deterrent compounds (Guoqing et al. 2001). In further studies on ODPs in larval frass of CBW, a blend of fatty acid and corresponding methyl esters was found in the larval frass. Some compounds were found independent of the diet of the larvae, while others seem to be dependent on the food source. All compounds elicited responses on CBW moths antennae using Electroantennography (EAG) analyses (Xu et al. 2006). Further, it was found that laid eggs resulted in similar EAG responses. Compounds identified from the laid eggs were the 4 oviposition deterring fatty acids myristic, palmitic, stearic, and oleic acid and their corresponding methyl esters (Liu et al 2008).

Another for our purpose important type of VOCs are herbivore induced plant volatiles (HIPVs). As a plant defense mechanism release plants attacked by herbivores these plant volatiles to the environment as a signal for higher trophic levels or other plants (Paré & Tumlinson 1999; Gebreziher 2018; Turling & Erb 2018; War et al. 2011). It has been shown by chemical analyses and behavioural bioassays that plants can release herbivore-specific signals which are detectable by natural enemies of the pest species (De Moraes et al. 1998). In this study, a parasitoid was able to use HIPVs to distinguish plants infested by its host *Heliothis virescens* Fabricius (Lepidoptera: Noctuidae) from those infested by *Helicoverpa zea* Boddie (Lepidoptera: Noctuidae), a close related non-host herbivore species. It has been shown that in tobacco, cotton and maize, each plant produces herbivore-specific volatile blends in response to the particular herbivore species feeding on the leaves. These differences are observable by GC/MS and detectable by the parasitoids (De

Moraes et al. 1998). Thereafter were also in other plant-pest-systems shown that qualitative and quantitative different HIPV-blends were emitted from plants depending on pest species feeding on them (Silva et al. 2017; Paré & Tumlinson 1999; Gebreziher 2018; Turling & Erb 2018).

For CBW, the HIPVs emission of tobacco plants induced by larvae feeding of the sibling species *H. armigera* and *H. assulata* were studied, and the corresponding behavioural response (wind tunnel bioassay) of a main parasitoid of both species, *Campoletis chlorideae* Uchida (Hymenoptera: Ichneumonidae), towards the different HIPV blends were recorded. GC/MS analyses showed that β-pinene was specifically produced after feeding of *H. armigera* larvae, whereas (*Z*)-3-hexenal was particularly induced by infestation of both species, and hexyl acetate by mechanical damage (Yan, Yan & Wang 2005). In another study, the HIPVs emission of maize plants induced by feeding of larvae of *H. armigera* and *Pseudaletia separata* Walker (Lepidoptera: Noctuidae) and the behavioural response of *C. chlorideae* in a wind tunnel were investigated. Infestation of *H. armigera* induced particularly the 4 terpenoids β-pinene, β-myrcene, D-limonene, and (*E*)-nerolidol. All these compounds were not induced after attack of *P. separata* or mechanical damage (Yan & Wang 2006). It has also been investigated the transcriptome changes and volatile characteristics of cotton plants after larvae infestation of *H. armigera*. GC/MS analyses showed that CBW infestation induced cotton plants to release several green leaf volatiles and terpenoids, whereas other compounds were found in both, infested and non-infested plants (Huang et al. 2015). Further studies compared by chemical analyses the HIPV emission of tomato, French bean, and maize plants after infestation of *H. armigera* larvae, and by Y-tube olfactormeter bioassays the behavioural response of the predator *Orius strigicollis* Poppius (Heteroptera: Anthocoridae). In all three plant species, *H. armigera* infested plants released a higher number and larger amounts of VOCs than undamaged or mechanically damaged plants (Gebreziher & Nakamuta 2016). In some of these studies the odour profile of CBW infested plants have been compared with mechanical damaged plants, as both types of damage, biotic and abiotic, are stress for the plants and induce specific VOC emission. However, we did not find studies comparing volatile profiles from CBW-infested plants with those of plants stressed by other abiotic factors such as water logging, drought, darkness, or extreme temperatures, or even volatile profiles of plants stressed by both, CBW infestation and abiotic factors, at the same time.

Table 5.1: List of ODPs released by CBW (A), and list of HIPVs released by CBW-infested plants (B) described in the literature.

A. Oviposition deterrent pheromones (ODPs)			
Related pest developmental stage	VOC name	CAS-Nr	Reference
Adult, egg, larval frass	Oleic acid	112-80-1	Guoqing et al. 2001; Liu et al. 2008; Xu et al. 2006
Adult, egg, larval frass	Palmitic acid	57-11-3	Guoqing et al. 2001; Liu et al. 2008; Xu et al. 2006
Adult	4-Methyl-4-hydroxyl-pentanone-2	112-42-2	Guoqing et al. 2001
Egg	Myristic acid	544-63-8	Liu et al. 2008
Egg, larval frass	Stearic acid	57-11-4	Liu et al. 2008; Xu et al. 2006
Larval frass	Pentadecanoic acid	1002-84-2	Xu et al. 2006
Larval frass	Methyl palmitate	112-39-0	Xu et al. 2006

Larval frass	Methyl oleate	112-62-9	Xu et al. 2006
Larval frass	Methyl linoleate	112-63-0	Xu et al. 2006
Larval frass	Methyl stearate	112-63-8	Xu et al. 2006
Larval frass	Linoleic acid	463-40-1	Xu et al. 2006
B. Herbivore induced plant volatiles (HIPVs) after CBW larval infestation			
Plant species	VOC name	CAS-Nr	Reference
Cotton	3-Hexenyl isovalerate	10032-11-8	Huang et al. 2015
Cotton	Limonene	138-86-3	Huang et al. 2015
Cotton	β- Elemene	33880-83-0	Huang et al. 2015
Cotton	α-Guaiene	3691-12-1	Huang et al. 2015
Cotton	β-Ocimene	3779-61-1	Huang et al. 2015
Cotton	δ-Cadinene	483-76-1	Huang et al. 2015
Cotton	Hexenyl valerate	56922-74-8	Huang et al. 2015
Cotton	TMTT	62235-06-7	Huang et al. 2015
Cotton	1-Decyne	764-93-2	Huang et al. 2015
Cotton, french bean, maize, tabacco, tomato	(*Z*)-3-Hexen-1-ol	928-96-1	Huang et al. 2015; Gebreziher & Nakamuta 2016; Yan & Wang 2006; Yan, Yan & Wang 2005
Cotton, maize	β-Myrcene	123-35-3	Huang et al. 2015; Yan & Wang 2006
Cotton, maize	Hexyl acetate	142-92-7	Huang et al. 2015; Yan & Wang 2006
Cotton, maize	DMNT	19945-61-0	Huang et al. 2015; Yan & Wang 2006
Cotton, maize, tabacco	(*E*)-2-Hexen-1-ol	928-95-0	Huang et al. 2015; Yan & Wang 2006; Yan, Yan & Wang 2005
Cotton, maize, tobacco	(E)-2-Hexenyl acetate	2497-18-9	Huang et al. 2015; Yan & Wang 2006; Yan, Yan & Wang 2005
Cotton, maize, tobacco, tomato	β-Pinene	18172-67-3	Huang et al. 2015; Yan & Wang 2006; Yan, Yan & Wang 2005; Gebreziher & Nakamuta 2016
Cotton, maize, tobacco, tomato	(*Z*)-3-Hexenyl acetate	3681-71-8	Huang et al. 2015; Yan & Wang 2006; Yan, Yan & Wang 2005; Gebreziher & Nakamuta 2016
Cotton, maize, tobacco, tomato	(*E*)-2-Hexenal	6728-26-3	Huang et al. 2015; Yan & Wang 2006; Yan, Yan & Wang 2005; Gebreziher & Nakamuta 2016

Cotton, maize, tomato	Linalool	126-91-0	Huang et al. 2015; Yan & Wang 2006; Gebreziher & Nakamuta 2016
Cotton, tomato	α-Caryophyllene	6753-98-6	Huang et al. 2015; Gebreziher & Nakamuta 2016
Cotton, tomato	α-Pinene	7785-70-8	Huang et al. 2015; Gebreziher & Nakamuta 2016
Cotton, tomato	β-Caryophyllene	87-44-5	Huang et al. 2015; Gebreziher & Nakamuta 2016
French bean	Thujopsene	470-40-6	Gebreziher & Nakamuta 2016
French bean	1-Propanone	71-23-8	Gebreziher & Nakamuta 2016
French bean	Ethanal	75-07-0	Gebreziher & Nakamuta 2016
French bean	2-Buten-1-ol	764-01-2	Gebreziher & Nakamuta 2016
French bean, maize	(*E*)-2-Eicosene	121909-29-3	Gebreziher & Nakamuta 2016
French bean, maize	2-Butyl-1-octanol	3913-02-8	Gebreziher & Nakamuta 2016
French bean, maize	3-Methyl-2-buten-1-ol	556-82-1	Gebreziher & Nakamuta 2016
French bean, maize	2-Ethyl-2-hexenal	645-62-5	Gebreziher & Nakamuta 2016
French bean, maize	(*Z*)-2-Hexen-1-ol	928-94-9	Gebreziher & Nakamuta 2016
French bean, maize, tomato	2-Ethyl-1-hexanol	104-76-7	Gebreziher & Nakamuta 2016
French bean, maize, tomato	D-Limonene	5989-27-5	Gebreziher & Nakamuta 2016; Yan & Wang 2006
French bean, tomato	o-Cymene	527-84-4	Gebreziher & Nakamuta 2016
French bean, tomato	α-Terpinene	99-86-5	Gebreziher & Nakamuta 2016
Maize	Phenylethyl acetate	103-45-7	Yan & Wang 2006
Maize	Geranyl acetate	105-87-3	Yan & Wang 2006
Maize	1-Octene	111-66-0	Gebreziher & Nakamuta 2016
Maize	Indole	120-72-9	Yan & Wang 2006
Maize	(*E*)-α-Bergamotene	13474-59-4	Yan & Wang 2006
Maize	(*E*)-β-Farnesene	18794-84-8	Yan & Wang 2006
Maize	β-Sesquiphellandrene	20307-83-9	Yan & Wang 2006
Maize	5-Methyl-2-(1-methyl ethyl)-1-hexanol	2051-33-4	Gebreziher & Nakamuta 2016
Maize	2-Ethyl-1-decanal	21078-65-9	Gebreziher & Nakamuta 2016
Maize	(*E*)-Nerolidol	40716-66-3	Yan & Wang 2006

Maize	α-Farnesene	502-61-4	Gebreziher & Nakamuta 2016
Maize	Pentadecane	629-62-9	Yan & Wang 2006
Maize	2-Ethylhexyl, 2-ethylhexanoate	7425-14-1	Gebreziher & Nakamuta 2016
Maize, tobacco	γ-Terpinene	99-85-4	Yan & Wang 2006; Yan, Yan & Wang 2005
Tobacco	1,4-Dichlorobenzene	106-46-7	Yan, Yan & Wang 2005
Tobacco	1-Hexanol	111-27-3	Yan, Yan & Wang 2005
Tobacco	Methyl salicylate	119-36-8	Yan, Yan & Wang 2005
Tobacco	n-Nonanal	124-19-6	Yan, Yan & Wang 2005
Tobacco	(*Z*)-3-Hexenyl butyrate	16491-36-4	Yan, Yan & Wang 2005
Tobacco	Nicotine	54-11-5	Yan, Yan & Wang 2005
Tobacco	(*Z*)-3-Hexenal	69112-21-6	Yan, Yan & Wang 2005
Tomato	3-Carene	13466-78-9	Gebreziher & Nakamuta 2016
Tomato	(*E*)-3-Hexenyl-acetate	3681-82-1	Gebreziher & Nakamuta 2016
Tomato	(+)-4-Carene	5208-49-1	Gebreziher & Nakamuta 2016
Tomato	β-Phellandrene	555-10-2	Gebreziher & Nakamuta 2016
Tomato	Tridecane	629-50-5	Gebreziher & Nakamuta 2016
Tomato	Tetradecane	629-59-4	Gebreziher & Nakamuta 2016
Tomato	α-Phellandrene	99-83-2	Gebreziher & Nakamuta 2016
Tomato	p-Cymene	99-87-6	Gebreziher & Nakamuta 2016
Tomato	(*E*)-2-Eicosene		Gebreziher & Nakamuta 2016

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5.3 Candidate VOCs for CBW detection

As ODPs are species-specific VOCs, detectable also in absence of the adult pest insect and identified for CBW, these compounds might be potential candidates for detection of CBW. In all three studies we found the specific fatty acids myristic, palmitic, stearic, and oleic acid and their corresponding methyl esters have been identified as ODPs of CBW (Guoqing et al. 2001; Xu et al. 2006; Liu et al. 2008). Particularly, palmitic and oleic acid have been extracted from female moths (tarsi), larval frass and laid eggs of CBW, which might render them as robust and reliable candidates for detection purpose.

With a view to detecting a herbivore-specific volatile blend emitted from plants in response to CBW larvae feeding, we compared the volatile profiles from CWB infested plants with those from non-infested plants of different plant species found in literature. Compounds reported to be released after CBW larval infestation of different plant species, but not or in very small amounts only from non-infested, mechanically damaged or plants infested of another pest species, might be possible candidates for detection of CBW. The terpenoids β-pinene, β-myrcene, D-limonene, and (*E*)-nerolidol were found to be species-specific for CBW larval infestation of maize plants (Yan & Wang 2006). The compound β-myrcene were found in maize and cotton particularly after CBW larval infestation (Yan & Wang 2006; Huang et al. 2015). D-limonene was species-specific emitted after CBW larval infestation on maize, french bean and tomato (Gebreziher & Nakamuta 2016; Yan & Wang 2006). A compound noticed in four different studies as species-specific volatile emitted from a plant in response to CBW larvae feeding on maize, cotton, tobacco, and tomato is β-pinene (Huang et al. 2015; Yan & Wang 2006; Yan, Yan & Wang 2005; Gebreziher & Nakamuta 2016).

All these VOCs related to CBW described in the literature and relevant for our purpose are listed in Table 5.1, split after biological function in ODPs released from CBW, laid eggs or larval frass (Table 5.1, A), and HIPVs released from CBW-infested plants (Table 5.1, B). Candidate VOCs for CBW detection are marked in bold italic in the Table 5.1.

We are aware of that different approaches and conditions for insect and plant rearing, as well as different methods for volatile collection, chemical analyses and compound ID have been used, and thus a selection of candidate compounds for detection of CBW based on these data is very vague and a preliminary approach for our own studies only.

Table 5.2: List of candidate VOCs for CBW detection.

VOC name	CAS-Nr	Biological relevance
Oleic acid	112-80-1	Oviposition deterrent pheromone
Palmitic acid	57-11-3	Oviposition deterrent pheromone
β-Myrcene	123-35-3	Herbivore induced plant volatile
β-Pinene	18172-67-3	Herbivore induced plant volatile
D-Limonene	5989-27-5	Herbivore induced plant volatile
(*E*)-Nerolidol	40716-66-3	Herbivore induced plant volatile

6 VOLATILE ORGANIC COMPOUNDS IN THE PINEWOOD NEMATODE-PINE SYSTEM

6.1 The Pinewood nematode: distribution, biology and management

The pinewood nematode (PWN), *Bursaphelenchus xylophilus* (Steiner & Buhrer 1934), is a migratory plant parasitic nematode that causes pine wilt disease (PWD), a serious forest disease responsible for the devastation of vast pine stands in Asian and European countries, causing massive ecological, economic and cultural impacts (Vicente et al., 2012). The PWN is believed to be originally from North America, where the incidence of PWD is very low, probably because of a co-evolution between the PWN and the native pine species (Sutherland, 2008). However, in the beginning of the 20th century, symptomatic trees began to appear in Japan, and soon afterwards the PWN was identified as the cause (Futai, 2008). Despite the control measures set up for containing PWD, in the following years, the PWN spread to neighbouring Taiwan, China (in 1982) and Korea (in 1988) and, in 1999, it was detected for the first time in the European Union, in Portugal (Mota et al., 1999). While the PWN was initially contained in the Setúbal area, where it was first detected, 20 km south of Lisbon, new foci of infection soon appeared in Leiria, where maritime pine (*Pinus pinaster*) stands are extensive (Mota and Vieira, 2008). By 2008, Portugal mainland was considered a quarantine zone and wood export restrictions were then extended to the whole country (Rodrigues et al., 2008). Since then, this phytoparasite has been found in Madeira Island, in 2010 (Fonseca et al., 2012), and in Spain, in 2011 (Abelleira et al., 2011). Given its extreme pathogenicity and the abundance of susceptible pines in European countries (namely *Pinus pinaster*, *P. sylvestris* and *P. nigra*), the European Plant Protection Organization (EPPO) has considered the PWN as an A2 type quarantine pest in the EU, even though its presence in Europe is currently limited to Portugal and Spain (Cabi & EPPO, 2023). However, it is believed that future environmental conditions in northern European countries, as a result of climate change, may create a highly susceptible environment for PWN which threatens the extensive northern pine forests (Hirata et al., 2017; de la Fuente et al., 2018).

The complex infection mechanism of PWD involves the host pine tree, an insect vector, the parasitic PWN and associated microbiota. The PWN can display two different feeding habits, phytophagous and mycophagous, which is characteristic of this species (Moens and Perry, 2009; Zhao et al., 2014). In its mycophagous phase, the PWN feeds on fungi growing on dead or decaying pine wood, rapidly multiplying and completing its life cycle (Mamiya, 1983; Wang et al., 2008). The decaying pine wood can also be used as a nursery site for beetles of the *Monochamus* genus, whose callow adults can become colonized with the PWN and then disperse it across long distances (Futai, 2013; Zhao et al., 2014). During the beetle's maturation feeding, the PWN can enter healthy pines through wounds made by the beetle on young tree branches. The exit of juvenile nematodes from the host beetle, and subsequent infection of young pine shoots, is regulated by both its nutritional status and specific chemical cues emitted by the beetle host and/or the susceptible pine tree. In fact, low levels of neutral lipids in the juvenile PWNs were found to be determinant for its attraction to *β*-myrcene, a pine volatile monoterpene, while higher levels increased its attraction to toluene, a beetle cuticular hydrocarbon (Stamps and Linit, 2001). In the new host tree, PWNs begin invading the resin canals, attacking epithelial cells, and causing great damage while moving through the canal system and rapidly reproducing. Pine wilting can be observed as soon as 3 weeks after infection, as a result of reduced oleoresin accumulation and damage to xylem tracheids, promoting embolism throughout the xylem column (Kuroda, 2008). The tree may collapse within 40 to 60 days after infection and, at that point, can contain millions of nematodes throughout the trunk and branches. The decaying pine becomes attractive to the adult *Monochamus* beetles and, consequently, a source for new infections (Futai, 2013; Jones et al., 2008).

Several pest management techniques are currently used against PWD, however no single pest management strategy can be considered effective in controlling PWN spread. There has been considerable investment in the exploitation of resistant pine species, either for reforestation or in crossbreeding programs that create resistant hybrids with economic value. Also, breeding resistance in species with naturally variable susceptibility is being successfully performed (Carrasquinho et al., 2018; Menéndez-Gutiérrez et al., 2018; Nose and Shiraishi, 2008). The most common control strategies focus on eradicating infested trees and wood, treating wood before its use for exportation or industrial purposes and controlling the insect vector population. Several control strategies are used for PWN pest management in each affected country, that are mainly concerned with eliminating the PWN and/or its insect vector. In areas where PWD is identified, quarantine measures are put into effect and several practices are implemented, namely, the establishment of pine free buffer zones, that reduce the spread of vector insects, a tight control of wood movements and the elimination of forest debris capable of harbouring insect vector eggs or larva. Infected wood can also be treated by chemical means, by spraying or fumigating wood pieces with pesticides, or by thermal treatment to eliminate both the insect and the nematode (Kamata, 2008; Rodrigues, 2008; Xu, 2008).

Insecticidal pesticides can also be used to prevent beetle spread to new infection sites. Aerial and ground spraying of (hemi)synthetic chemicals is a tactic with relatively good efficiency. Although the use of chemical pesticides is highly effective, some reports of increased mortality in birds and plant species as well as accumulation in food products above regulated concentrations have created distrust in their use (Bi et al. 2015; Kamata 2008). Alternative measures for controlling the spread of vector beetle populations involve the use of traps with pheromones, namely monochamol, or attractive tree volatiles, such as α-pinene and ethanol, and even biological control using the beetle's natural parasites or predatory birds (Kim et al., 2016; Nakamura, 2008; Shimazu, 2008).

Chemical control, through trunk injection of powerful nematicides, remains one of the most effective and reliable containment strategies within integrated management and is amply used in the most affected countries, although in restricted areas. Directly killing the PWN at its site of action is performed by applying lethal concentrations of commercial pesticides (Kamata, 2008). Unfortunately, commonly used insecticides and nematicides can show toxicity to beneficial microorganisms, to humans and animals, and can accumulate in the ecosystem above the regulated levels.

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6.2 Summary of literature on PWN VOCs

Literature on the volatiles emitted by PWN-infected plant material is very scarce and only 6 volatile compounds could be identified as being induced by PWN infection, in field and greenhouse grown infected *Pinus* trees (Table 6.1). The compounds found were not novel identifications since they were also identified in control experiments, however, they were produced in the affected trees in greater proportions. In a study on 30-year-old *Pinus thunbergii* trees, sativene, carvacrol methyl ether and camphor proportions were seen to increase, however the number of samples was very low and this reaction was detected on a single tree alone (Takeuchi et al., 2006). In a different study using 2-year-old *P. thunbergii* seedlings, slightly higher proportions of borneol were signaled as a result of PWN inoculation in a susceptible variety (Wang et al. 2022). For *P. densiflora* and *P. koraiensis* 5-year-old trees, the emission of the monoterpene hydrocarbon 3-carene was 9.7 and 54.7 times higher than in control trees, when analyzed by HS-SPME/GC-MS (Hwang et al., 2021). For *P. pinaster*, limonene emission was seen to increase in PWN-infected trees, however, this was only detected for two out of four tested trees (Gaspar et al. 2020).

Table 6.1: List of VOCs released by PWN described in the literature.

B. Pest induced plant volatiles after PWN infestation

Plant species	VOC name	CAS-Nr	Reference
Pinus thunbergii	Sativene	6813-05-4	Takeuchi et al., 2006
Pinus thunbergii	Carvacrol methyl ether	6379-73-3	Takeuchi et al., 2006
Pinus thunbergii	Camphor	76-22-2	Takeuchi et al., 2006
Pinus pinaster	Limonene	138-86-3	Gaspar et al., 2020
Pinus densiflora and P. koraiensis	3-Carene	13466-78-9	Hwang et al., 2021
Pinus thunbergii	Borneol	507-70-0	Wang et al., 2022

6.2.1 References

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Candidate VOCs for PWN detection

The available literature lacks an acceptable sample size or repeatability in results to suggest suitable VOC candidates for this pest.

7 CONCLUSION

The PurPest project aims to develop, validate and demonstrate an innovative sensor system prototype (SSP) to detect pest-specific volatile organic compounds (VOCs) and thus identify five different target pests to reduce pesticide inputs and stop the establishment of these five pests in the EU. The target pests are *Phytophthora ramorum*, *Spodoptera frugiperda*, *Helicoverpa armigera*, *Halyomorpha halys*, and *Bursaphelenchus xylophilus*.

The starting point for the project was an extensive literature review aiming at identifying a list of candidate VOCs for the detection of such pests. For *Phytophthora ramorum* and *Bursaphelenchus xylophilus*, literature data was summarized in this document, but the data was too scarce for establishing a list of candidate VOCs. In the case of *Spodoptera frugiperda*, *Helicoverpa armigera*, *Halyomorpha halys*, a review of the available literature summarized in this document, allowed experts in the field to compile preliminary lists of candidate VOCs, reported in this document (sections 3.3, 4.3, 5.3). The Purpest project will build on these lists and expand them with new candidate VOCs by studying emissions from the target pests and host plants attacked by these pests. Candidate VOC lists will be central for the development of the SSP. Validation in the field of the SSP and thus of the candidate VOCs will be then carried out in the prosecution of Purpest.

8 REFERENCES

The references are reported separately for each target pest in the corresponding sections.