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Exploiting volatile organic compounds in crop protection: A systematic review of 1-octen-3-ol and 3-octanone

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Abstract

The 21st century has brought new challenges to the agri-food industry due to population growth, global warming, and greater public awareness of environmental issues. Ensuring global food security for future generations is crucial. However, pests, weeds, and diseases still significantly contribute to crop losses, and the availability of effective conventional synthetic pesticides is decreasing. To address this, new and diverse pest management tools are needed. One pest management tool showing potential for invertebrate pest management is the exploitation of volatile organic compounds (VOCs)—in particular, the compounds 1-octen-3-ol and 3-octanone. This review aims to explore the extent to which 1-octen-3-ol and 3-octanone show potential in the future management of invertebrate crop and animal pests. A significant increase in the rate of publication of literature on the use of 1-octen-3-ol and 3-octanone in crop protection since 2018 is identified by this review, therefore, showing the potential importance of these compounds for use in future pest management. This review also identifies key interactions between naturally occurring biosynthesised 1-octen-3-ol and 3-octanone, and a range of invertebrate targets. Many of these interactions with key crop pests are sourced from the taxonomic families Lamiaceae, Fabaceae, and Trichomaceae. However, analysis of the practical application of these sources in an integrated pest management programme identifies clear limitations with the use of naturally occurring biosynthesised 1-octen-3-ol and 3-octanone. Rather, future focus should be placed on the development and exploitation of synthesised nature identical 1-octen-3-ol and 3-octanone for use as a biopesticide product. Overall, 1-octen-3-ol and 3-octanone show potential for exploitation in future crop protection, being abundant in source and diversity of invertebrate interactions. However, their use as a naturally occurring biosynthesised chemical is likely not practical for direct implementation in crop protection. Rather, focus should be placed on the development and exploitation of synthesised nature identical variants of these compounds for use as a biopesticide.

KEYWORDS

biopesticide, bioprotectant, chemical interactions, integrated pest management, invertebrate pests, synthesised VOCs

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1 | INTRODUCTION

Volatile organic compounds (VOCs) have long been studied due to their diversity, abundance, and wide-ranging impacts on living organisms (Stotzky et al., 1976). From intraspecies chemical messages between organisms of the same species (pheromones) to interspecific messages between differing species (allelochemicals; Nordlund & Lewis, 1976), these volatiles intrinsically link the world and its ecosystems. Historically, much research has focussed on exploring the source and effect of VOCs within living systems (Akimov, 1986; Isidorov et al., 1985; Namkung & Rittmann, 1987). However, focus has slowly shifted in recent years due to a need to develop new plant protection products that replace an ever-diminishing portfolio of conventional synthetic pesticides to sustainably control crop pests, which cause 25% of all crop losses globally, within an integrated pest management framework (Savary et al., 2019). Increased understanding of VOC-mediated interactions has led to more recent research focusing on manipulating VOCs to benefit humans (Duan et al., 2021; Kim et al., 2020; Kraakman et al., 2021) and the environment (Liang et al., 2020; Zhao et al., 2020). Efforts have been made to exploit VOCs to improve food flavourings and aromas (Wu et al., 2022), drive medical advances (Wang et al., 2023) and engineering (Simasatitkul et al., 2017) as well as develop novel tools for crop and livestock protection (Bourdon et al., 2022; Hummadi et al., 2021; Khoja et al., 2019; Oyarzún et al., 2009). Two VOCs showing great potential are 1-octen-3-ol and 3-octanone, otherwise more commonly known as 'the mushroom alcohols' (Morath et al., 2012).

1-Octen-3-ol ($C_8H_{16}O$) is an alkenyl alcohol known as 'mushroom alcohol' that is produced by plants and fungi, but found in especially high concentrations within Japanese Matsutake mushrooms and used as a flavour and fragrance ingredient (Tsuji et al., 1976; Mosandl et al., 1986; Zawirska-Wojtasiak, 2004). Commercial use of 1-octen-3-ol is largely used to manage human health pests, such as mosquitoes, as it is commonly found in human sweat and breath (Takken & Kline, 1989; Watentena et al., 2019). This, when combined with carbon dioxide, makes 1-octen-3-ol an effective attractant that can be combined with electronically charged dispatch units to reduce pest populations in urban environments. 3-octanone ($C_8H_{16}O$) is a dialkyl ketone produced by plants and fungi that is also widely used as a flavour and fragrance ingredient. This VOC has also been found to be synthesised by oyster mushrooms in response to nematode infestation and is a potent paralytic that acts as an effective toxin and defence chemical (Lee et al., 2023). While commercial products based on these chemicals are predominantly targeted at the human pest market, their potential for managing a broader range of invertebrate pests is increasingly recognised. Both compounds have been shown to have properties as an attractant (Khoja et al., 2021; Unelius et al., 2014), antifeedant (Khoja et al., 2019) or repellent (Hummadi et al., 2021), for invertebrates. Such properties indicate that 1-octen-3-ol and 3-octanone have significant potential to provide novel crop protection tools, particularly when considering the shift toward greater use of biopesticides to manage invertebrate pests (Olson, 2015). However, much of this research in the context of crop

protection remains experimental and diverse in its application. This makes it difficult to quantify the commercial value of 1-octen-3-ol and 3-octanone for use in integrated pest management. This problem is particularly prevalent when considering the potential application of naturally occurring biosynthesised compounds compared to those synthetically manufactured.

Decades of published research across the biological sciences has made it difficult to assess our current understanding of how 1-octen-3-ol and 3-octanone may fit into crop protection. This review therefore offers a comprehensive overview of the literature on 1-octen-3-ol and 3-octanone, which has not previously been quantified for crop protection. This study is not a meta-analysis or conceptual framework and does not quantify effect strength (i.e. the intensity of the impact of 1-octen-3-ol and 3-octanone on target/effector species) but instead categorises, through a field synopsis and systematic review, what has been studied in relation to these VOCs and crop protection (Lowry et al., 2013; Schenkel et al., 2015). It characterises interactions between taxonomic families within the functional groups invertebrates, plants, fungi and bacteria, and how such interactions may be utilised in crop protection and influence research direction.

2 | MATERIALS AND METHODS

A three-stage approach was taken for this review: (1) a scoping literature search, (2) field synopsis and (3) systematic review. These stages were completed sequentially in the order described, with the refined search string identified by the scoping literature search used to complete both the field synopsis and systematic review.

2.1 | Scoping literature search

A scoping literature search was undertaken on 13 April 2021 using Web of Science (WoS) to determine which combination of search terms were most appropriate for this study. The scoping literature search included two stages of refinement, within which the capabilities of the search string were assessed.

The first search string was formed using the depositor-supplied synonyms published by PubChem[®] (National Library of Medicine, 2022) for 1-octen-3-ol and 3-octanone to account for variance in compound names recorded in published literature. A high-sensitivity and low-specificity approach was used to ensure that most, if not all, relevant records were included but also to improve reproducibility and reduce bias. Using this search string, a total of 2024 records were returned with the oldest dating from 1970 until the most recent in April 2021. All records returned by this first search string were then assessed for relevance using the record titles. Of these records, 68 were not relevant to this study and were subsequently removed. A critical appraisal was then conducted for the first search string to further determine its success in retrieving relevant literature. The records returned by the first search string were scanned to confirm that the search had successfully returned ten pre-selected, highly relevant records.

A secondary assessment was conducted for the first search string, aiming to curate a final, refined search string. One at a time, search terms were removed from the first search string to assess their influence on the search. All search terms that did not return additional records were removed from the first search string. A total of seven search terms were considered superfluous by this assessment. The refined search string consisted of all remaining search terms and was then used to complete the field synopsis and systematic review.

2.2 | Systematic search

The search string identified and refined by the final scoping literature search was used in the systematic search for the field synopsis and systematic review. The systematic search was conducted using WoS, with a secondary search using the same search string (adapted to the requirements of the database) in Centre for Agriculture and Bioscience (CAB) Direct. The secondary search using CAB Direct was undertaken to ensure completeness of records, with all records additional to WoS being added to the search database formed by this study. The systematic search was last updated on 27 July 2021, for both WoS and CAB Direct, with a total of 3266 records (WoS 2006; CAB Direct = 1260 excluding duplicate records) being returned across both WoS and CAB Direct. Records returned by the systematic search were further refined at the point of field synopsis (see Section 2.3) and systematic review (see Section 2.4).

2.3 | Field synopsis

A field synopsis was undertaken with the aim of categorising records returned by the systematic search to assess external validity, thereby ensuring only records generalisable to crop protection are included (Stuart et al., 2018). External validity assessment was undertaken in two stages: (1) assessment against a-priori inclusion criteria and (2) categorisation of records. All assessment stages within the field synopsis were conducted using the record title and abstract (where available) only to reduce bias.

2.3.1 | A priori inclusion criteria

All records returned by the systematic search had to clearly state the publication type and status (all types of publication were considered at this stage to reduce problems associated with publication bias), including the overestimation of effect size (Leimu & Koricheva, 2005); state the date of initial publication; clearly identify the area of biological science within which the research was intended to directly benefit; state the origin and/or intended target of the compounds 1-octen-3-ol and 3-octanone, or declare synthesis/other unnatural origin. Records which did not meet all aspects of the a-priori inclusion criteria were removed.

2.3.2 | Categorisation of records

All records meeting a-priori inclusion criteria were then broadly categorised based on research focus and associated area of biological science (Table 1). Once placed into a category, records with findings not of relevance to a crop protection setting (external validity) were removed. Removed records included those in categories with a focus of medicinal application, chemistry and food science. All records passing assessment within the field synopsis were then taken forwards for secondary assessment and inclusion in the systematic review.

2.4 | Systematic review

A Population, Intervention, Comparator, Outcome (PICO) question framework was used for this review to allow for the identification of key and concise concepts as recognised by this research (Eriksen & Frandsen, 2018). The systematic review aimed to explore the primary question 'to what extent does 1-octen-3-ol and 3-octanone show potential in the future management of invertebrate crop and animal health pests' (Table 2); records identified as relevant through

TABLE 1 Description of six broad categories of biosciences found within the literature search.

Crop protection	Relating to the management of a pest, weed or disease-causing pathogen within a traditional cropped environment
Animal protection	Relating to the management of a pest (largely disease vectoring) for the protection of animals (excluding humans). Often referring to the protection of farmed livestock
Chemical ecology	Relating to all chemically-mediated interactions between living organisms for the purpose of recording. Does not have a rationale or statement of intent to apply research to another context
Food science	Relating to all human food sciences
Chemistry	Relating to composition, properties, and reactions of chemical compounds for the purpose of recording. Does not have a rationale or statement of intent to apply research to another context
Medicinal application	Relating to all human medical sciences

TABLE 2 Population, intervention, comparator, outcome (PICO) elements used for systematic review.

Population	Invertebrate crop and animal health pests
Intervention	1-Octen-3-ol and 3-octanone from a naturally occurring biosynthesised source
Comparator	Alternative invertebrate crop and animal health pest management strategies
Outcome	Any outcomes relating to behavioural modification, lethal effects, and mortality of invertebrate pests

assessment in the field synopsis process were subjected to secondary assessment for inclusion in the systematic review. Approved records were then assessed at full-text level to determine whether all elements stated in the PICO were extractable from the record. All records not providing full PICO information were removed. Information collected during the field synopsis was also used, and all records within which the origin was synthesised or unknown, were removed from the search. Internal validity (risk of bias) was also assessed for each record. Upon completing the final assessment, a total of 134 papers met the final inclusion criteria and were used in the systematic review (Figure 1).

The systematic review provided a more detailed analysis of the papers meeting the final inclusion criteria and assessment. The source of the naturally occurring biosynthesised compounds 1-octen-3-ol and 3-octanone and identified target(s) were recorded for each study. Both sources and targets of the compounds were identified to both family and species level where applicable. Interactions between a specified source and target were summed. For this study, an interaction was considered as any recorded reaction (described as an explicable response to a stimulus) by an identified target organism in response to the emission of 1-octen-3-ol or 3-octanone by a recognised source. Interactions were recorded independently of paper count, and therefore multiple interactions may have been recorded for a single published paper. Finally, interactions between functional groups (plant, fungi, invertebrate, bacteria, human consumption, promotor and other) and taxonomic

families were explored in relation to their potential influence on future crop protection research.

2.5 | Analysis

Heatmaps showing the interactions between functional groups of source and target were produced (Haddaway et al., 2019) for all papers included in the systematic review (Crop Protection, Animal Protection and Chemical Ecology). A Sankey diagram was also produced to explore the interactions between source, compound and target on a taxonomic family level. All analyses were conducted using R Version 4.1.0 using the NetworkD3 package to produce Sankey diagrams (Allaire et al., 2022) and EviAtlas for the heatmaps (Haddaway et al., 2019).

3 | RESULTS

3.1 | Publication rates across the biological sciences

For the field synopsis, a total of 2412 records were identified as meeting the initial search criteria. This search contained all papers relating to research of the compounds 1-octen-3-ol and 3-octanone within the context of biological science. Publication of these records dated from January 1970 to July 2021. Overall, the mean number of publications per decade is increasing but at a decelerating rate (Figure 2). The greatest increase in average publications per year was seen between the decades 1980 and 1990, with yearly publications up an average of 390% across the 1990s when compared to those in the 1980s. Subsequent decades saw an average increase on the previous decade of 56.3% (2000s vs. 1990s), and 37.3% (2010s vs. 2000s).

All records were then categorised by their area of biological science research focus, conducted using the criteria as previously described (Table 1). The total number of publications between January 1970 and July 2021 were then calculated for comparison (Figure 3). A large proportion of the categorised records (549) focussed on the study of 1-octen-3-ol and 3-octanone in relation to food science. Due to the nature of this area of study, no food science research had an intended target/effector outside of humans. Another biological science category containing many records (434) was chemistry. The entirety of research within this category focussed on the characterisation of compounds and associated matter. No research within this category explored the potential uses of these compounds, nor applied context outside of chemical profiling. The smallest category (110) determined by this study was research associated with medicinal applications in human health. Whilst not every study within this category stated a target of the compounds, those which did had an obvious focus on human and related mammalian species. Due to the nature of these areas of biological science and their intended target/ effectors, the biological science research categories of food science,

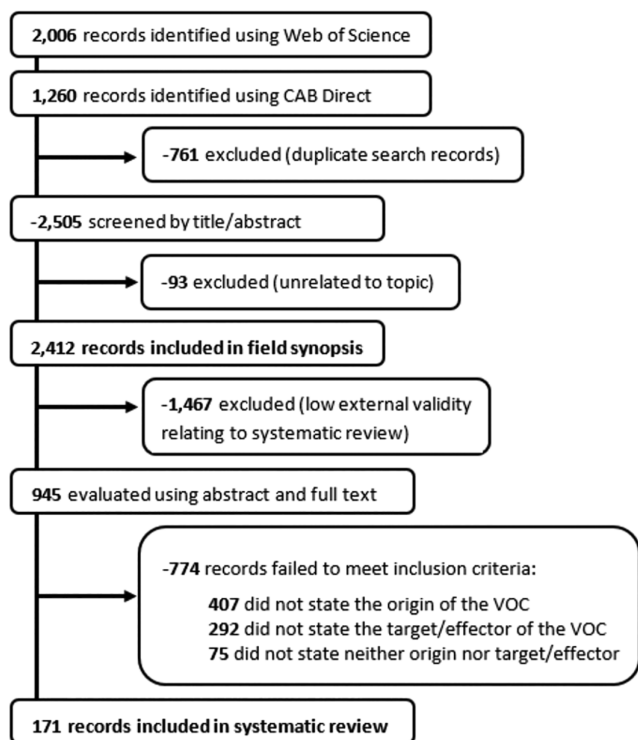


FIGURE 1 Exclusion chart detailing the process of exclusion of records from the study.

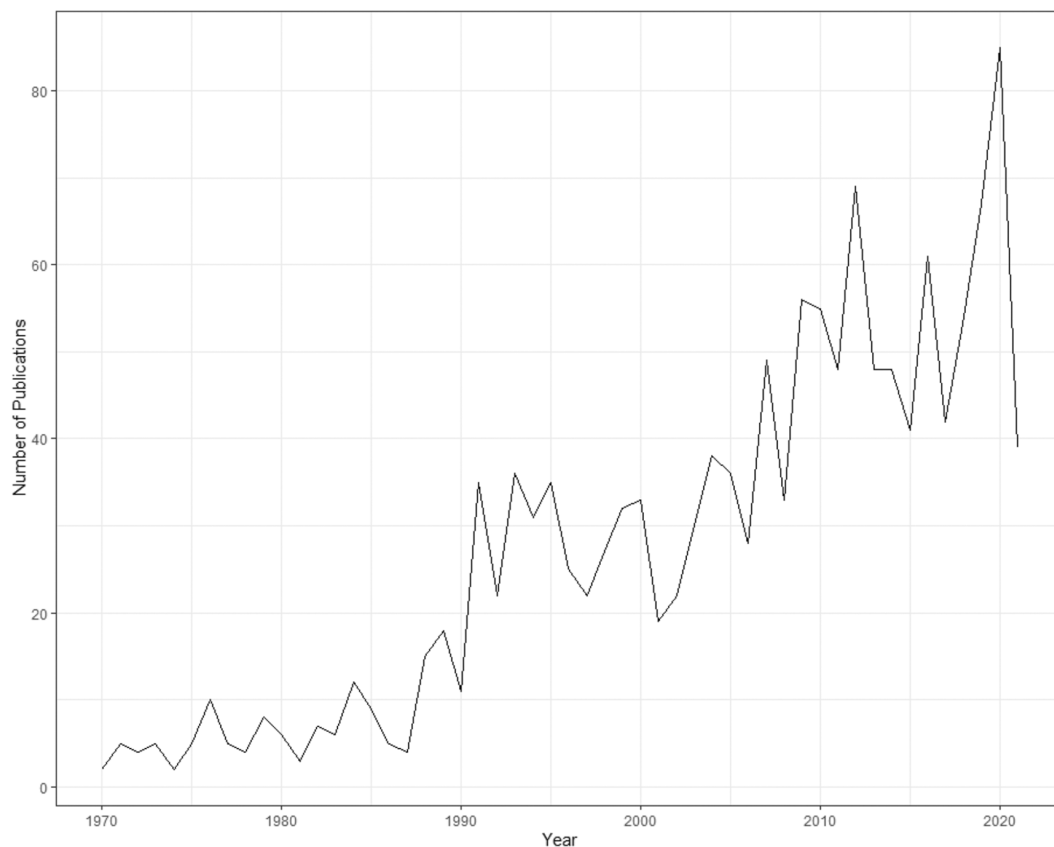


FIGURE 2 Number of studies published per year included in the field synopsis. The most recent year (2021) has been included for reference, however only included records indexed on Web of Science and Centre for Agriculture and Biosciences Direct as of July 2021.

chemistry and medicinal application were not passed forward for secondary assessment for inclusion in the systematic review due to low external validity.

3.2 | Publication of research into chemically mediated interactions

Three categories were selected to progress onto secondary assessment for inclusion in the systematic review due to their relevance and high external validity. Once categorised, it was possible to identify differences in publication rates of each area of biological science research addressed within this study (Figure 4). Records relating to chemical ecology formed much of the early research on 1-octen-3-ol and 3-octanone, with the first record in this category published in 1972. By contrast, the first records published relating to animal protection and crop protection were 1984 and 1989 respectively. Records on the topic of crop protection have continued to increase with time. When comparing records for the start of the current decade (January 2020–July 2021), no difference in the number of publications is observed between research in chemical ecology, animal protection and crop protection for the first time in over 30 years. It is possible to see a recent, rapid increase in publication rate of papers in the context of crop protection, with the mean number of papers published rising.

3.3 | Systematic review of 1-octen-3-ol and 3-octanone

The systematic review only considered records that passed the secondary assessment and inclusion criteria. Interactions between 1-octen-3-ol and/or 3-octanone and a specified target/effector were recorded. It is important to note that multiple interactions may have been recorded within a single record and, therefore, for the systematic review these were counted as individual entities. A large proportion of interactions researched (36.05%; Figure 5) fell within the functional groups of plant (origin of 1-octen-3-ol and 3-octanone) and invertebrate (intended target/effector of the interaction) when considering all studies across all three categories of biological science (chemical ecology, animal protection and crop protection). Secondary to this was the interaction between fungi and invertebrates (14.53%), followed by interactions between invertebrates (11.05%).

3.4 | Interactions between functional groups

When analysed independently, it was possible to identify which category of research most influenced the interactions between different types of functional groups. Within chemical ecology, 30.95% of interactions occurred between invertebrates, and only

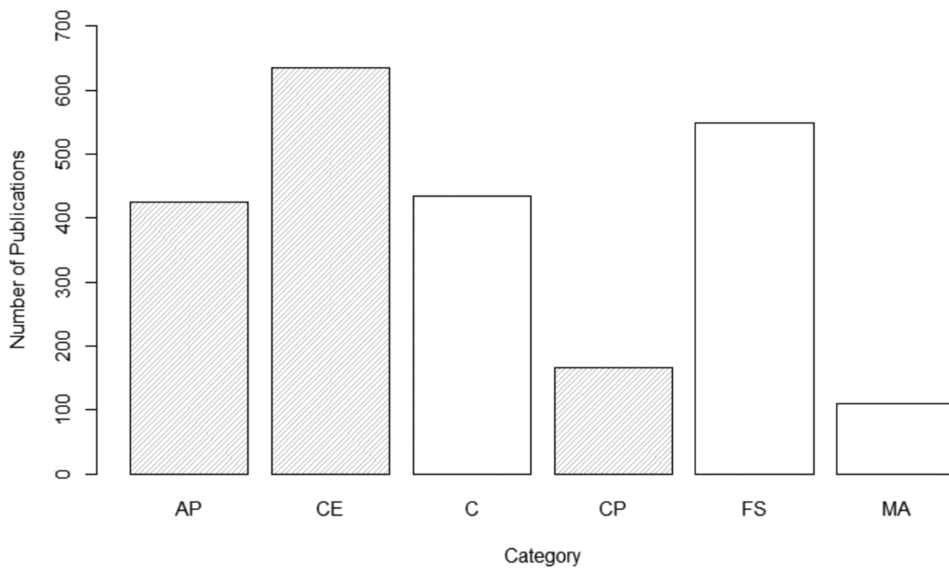


FIGURE 3 Number of studies published per biological science research category (AP, animal protection; CE, chemical ecology; C, chemistry; CP, crop protection; FS, food science; MA, medical applications) as determined by the field synopsis. Records include those published between 1970 and 2021 as indexed on Web of Science and Centre for Agriculture and Biosciences Direct as of July 2021.

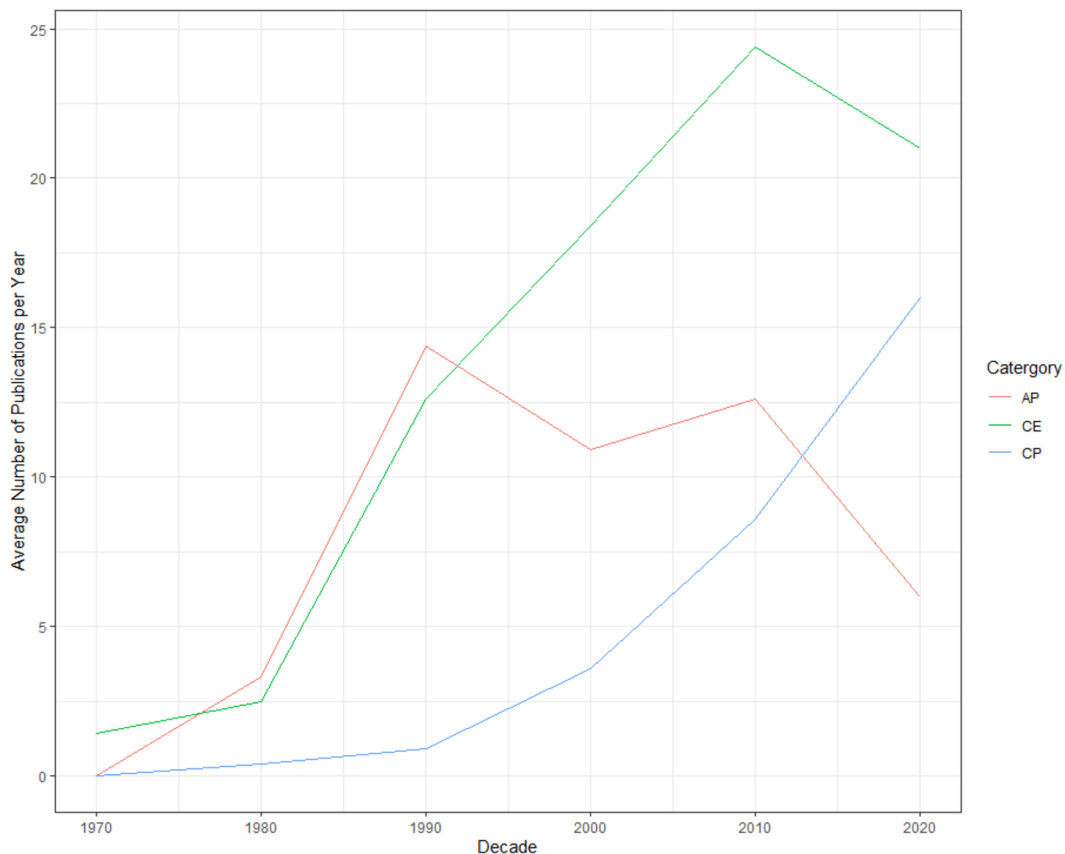


FIGURE 4 Number of studies published within the biological science research categories chemical ecology (CE), animal protection (AP) and crop protection (CP) per decade (70 = 1970–1978; 80 = 1980–1988; 90 = 1990–1999; 00 = 2000–2009; 10 = 2010–2019; 20 = 2020 to July 2021) as determined by the field synopsis. Records include those published between 1970 and 2021 as indexed on Web of Science and Centre for Biosciences Direct as of July 2021.

11.90% exploring the interactions between plants and invertebrates. Contrastingly, within animal protection (60.00%) and crop protection (41.67%) research, most interactions explored were between plants and invertebrates. In the context of animal

protection, research focussed on the use of plant sources to attract invertebrate pests away from animal hosts. Only 5.00% and 4.63% of animal and crop protection, respectively, looked at interactions between invertebrates. All categories also contained

FIGURE 5 Number of interactions between functional groups of 1-octen-3-ol and/or 3-octanone sources/origins and their intended target/effector. Interactions were recorded independently of record number as individual entities regardless of occurrence within a single record. Records include those published between 1970 and 2021 as indexed on Web of Science and Centre for Agriculture and Biosciences Direct as of July 2021.

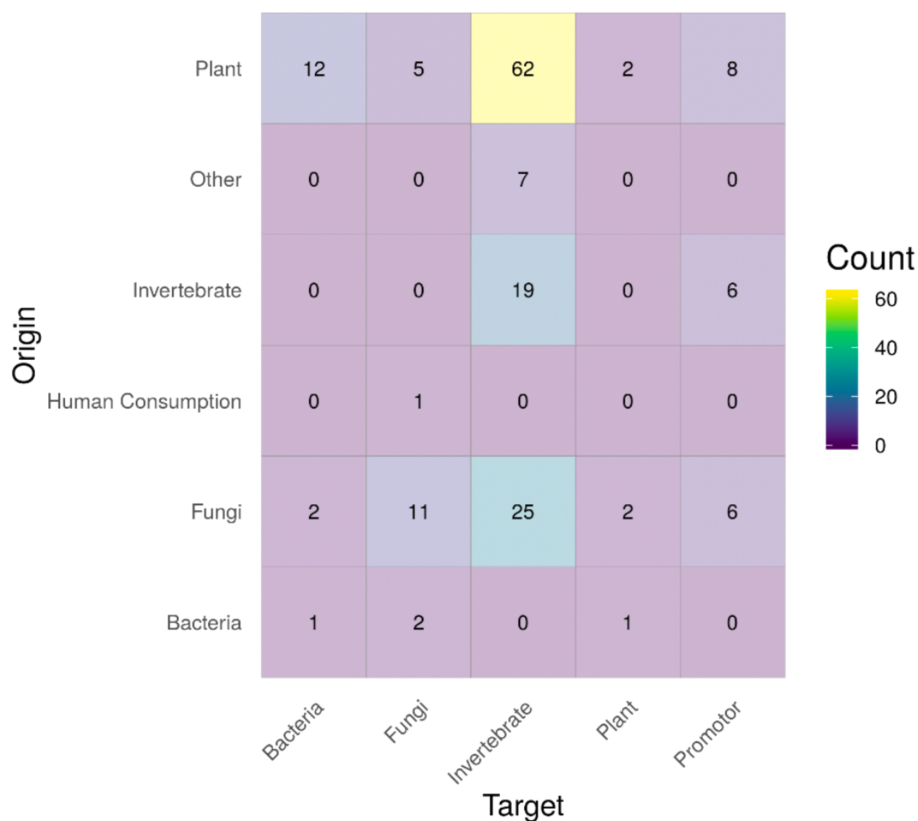
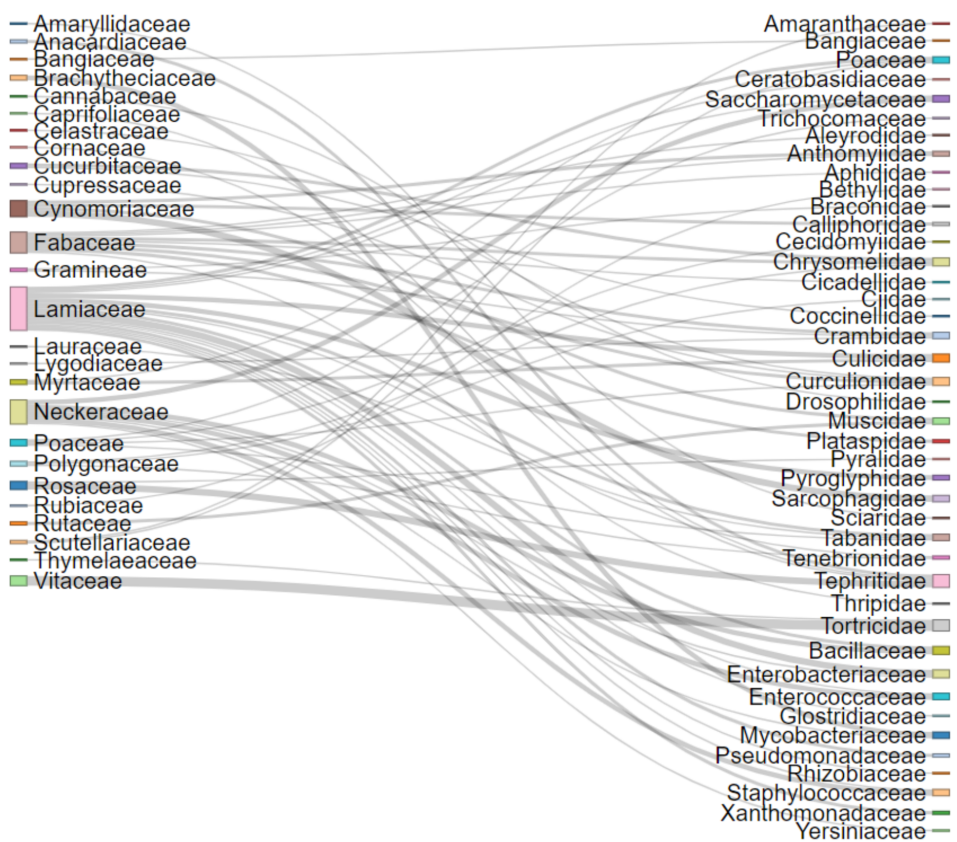


FIGURE 6 1-Octen-3-ol and 3-octanol mediated interactions between plant sources and targets (recorded to taxonomic family) as identified within the literature of this review.



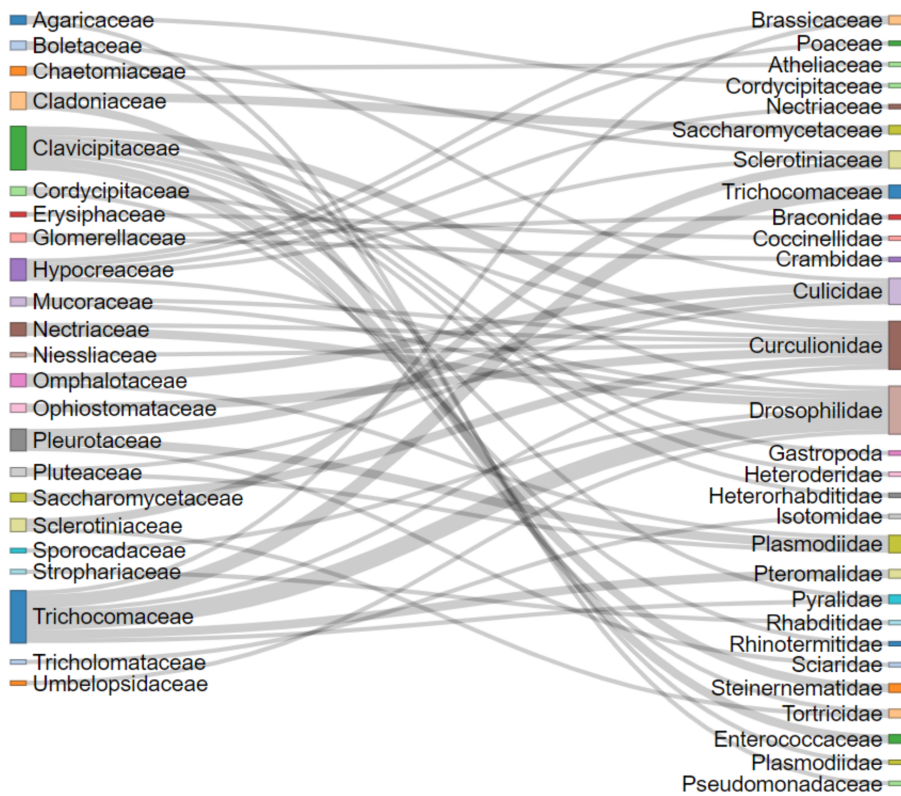


FIGURE 7 1-Octen-3-ol and 3-octanol mediated interactions between fungal sources and targets (recorded to taxonomic family) as identified within the literature of this review.

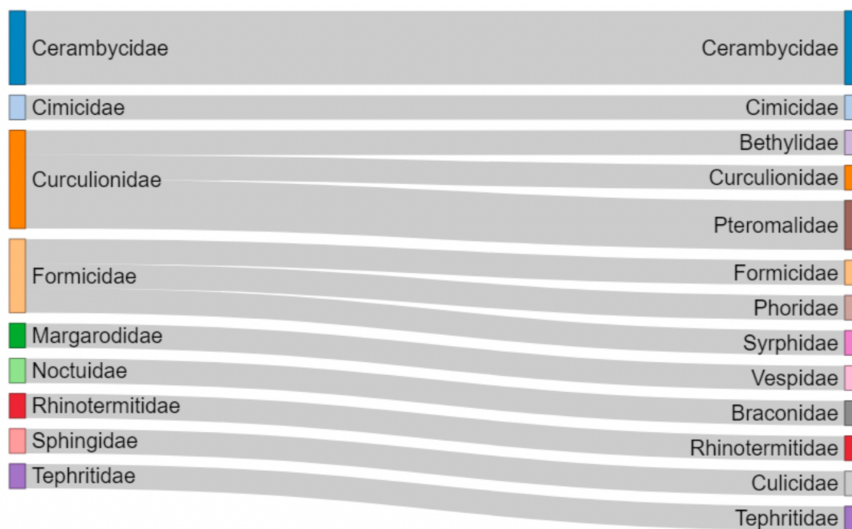


FIGURE 8 1-Octen-3-ol and 3-octanol mediated interactions between invertebrate sources and targets (recorded to taxonomic family) as identified within the literature of this review.

research exploring the interactions between fungi and invertebrates (14.29%, chemical ecology; 5.00%, animal protection; 16.67% crop protection) and interactions between plants and bacteria (16.67%; 10.00%; 2.78%).

3.5 | Interactions between taxonomic families

Alongside functional groups, interactions were also considered on a taxonomic family basis to identify key sources and targets within the existing research of all three categories. The most prominent sources of

1-octen-3-ol and/or 3-octanone explored in existing research are those from the families Lamiaceae, Fabaceae, Neckeraceae, Clavicipitaceae and Trichocomaceae. The targets/effectors with the highest number of interactions recorded within the research are the families Curculionidae, Culicidae and Drosophilidae (Figures 6–8).

4 | DISCUSSION

1-octen-3-ol and 3-octanone are VOCs that have been studied across a range of different biological science research categories over many

years. The diversity of this research has led to a large literature base that demonstrates the multi-functionality of these compounds and their importance in mediating chemical intra- and inter-specific interactions between organisms.

4.1 | Publication of records relating to the study of 1-octen-3-ol and 3-octanone

The rapid increase in publication of 1-octen-3-ol and 3-octanone associated crop protection research reflects the current need to develop new pest management tools. The 21st century has led to increased food insecurity globally and pressure on the agri-food industry, predominantly driven by rapid population increases (United Nations, 2022), global warming (Baker et al., 2000; Sarkar et al., 2020), greater public environmental awareness (Ahmed et al., 2021) and an ever-diminishing portfolio of effective synthetic chemical pesticides. There is also a bottleneck in the development of integrated pest management (IPM) compatible tools due to an over reliance on conventional synthetic pesticides. This need to develop new IPM tools is reflected in the increasing publication rates associated with 1-octen-3-ol and 3-octanone. Recent interest in exploiting natural products (e.g. biopesticides) has risen due to their compatibility with IPM programmes and perceived environmental safety. This has led to exploration of previously under-researched or unknown functions of natural products such as 1-octen-3-ol and 3-octanone. Clearly, further research into the potential of these compounds for crop protection is important, particularly when considering that the development of IPM tools is somewhat stagnating due to poorly implemented new to market product registration requirements. However, due to the relative novelty and diversity of research into these compounds, it is important to identify clear avenues for future research. By determining these areas, as well as others showing promise, research can be targeted to achieve optimal development of such compounds.

4.2 | Chemically mediated interactions between sources of 1-octen-3-ol and 3-octanone and target/ effectors

4.2.1 | Plant-derived interactions

Our systematic review shows that the largest proportion of researched interactions between 1-octen-3-ol and/or 3-octanone and a specified target/effector originate from plants. There are two dominant taxonomic plant families within which these compounds originate, the Lamiaceae (deadnettles) and Fabaceae (legumes). Both families are widely cultivated (Yuan et al., 2010) and therefore readily accessible for scientific research at a relatively low cost. Their diversity and availability may be an influencing factor in their regular inclusion within 1-octen-3-ol and 3-octanone research. Despite the prevalence of Lamiaceae and Fabaceae as a source of 1-octen-3-ol

and 3-octanone, many of their interactions within the literature are not concerned with invertebrates, the functional group recorded to have the largest number of interactions with plants. Rather, the evidence suggests that the majority of interactions originating from Lamiaceae and Fabaceae were with the bacteria functional group. There was little consistency between the bacteria families recorded to interact with both species including, but not limited to, Bacillaceae, Enterobacteriaceae, Pseudomonadaceae and Staphylococcaceae. Further increase in research exploring 1-octen-3-ol and 3-octanone interactions between these plants and invertebrate crop pests is predicted, with research into the use of other VOCs such as methyl jasmonate ($C_{13}H_{20}O_3$), benzyl alcohol ($C_6H_5CH_2OH$) and p-cymene ($C_{10}H_{14}$), and elicitors such as cis-jasmone ($C_{11}H_{16}O$) for pest management in Fabaceae crops (Ben-Issa et al., 2017; Mitra et al., 2021; Moraes et al., 2009).

One plant family which may be of future interest for animal protection was Cynomoriaceae. Whilst the number of researched interactions originating from this plant family were relatively low (total of 10 interactions), all recorded interactions focussed on targets/ effectors in the invertebrate functional group, including: Sarcophagidae, Muscidae, Calliphoridae and Anthomyiidae (Diptera). Many invertebrate species within these families are implicated in the spread of zoonotic disease amongst farmed livestock (Spradbery et al., 2019; Taylor et al., 2012). Such diseases include equine infectious anaemia, African swine fever and Rift Valley viruses (Baldacchino et al., 2013). Whilst production of 1-octen-3-ol and 3-octanone is abundant in the Cynomoriaceae (Wang et al., 2021), as a holoparasite many species are reliant on halophyte host plants for their survival. The requirement of a salt-loving host for survival may make the physical use of Cynomoriaceae within a traditional crop protection setting impractical, with most commercial crops requiring loamy soils for successful cultivation (Li et al., 2018). Therefore, it may be more valuable to explore the interactions of VOCs from Cynomoriaceae with economically important crop pests. Extraction of 1-octen-3-ol and 3-octanone from Cynomoriaceae could help to make this source effective in a range of cropping environments, removing barriers posed by the physical requirements of the plant. However, due to the global rarity of this plant family (Wang et al., 2021) synthesis of 1-octen-3-ol and 3-octanone, or extraction from a more common source may be of preference. This is important to consider when developing new crop protection methods derived from natural products, because for such tools to be commercially viable their source material must be abundant (E. Birch et al., 2011).

4.2.2 | Fungi-derived interactions

Fungi were the second most researched source of 1-octen-3-ol and 3-octanone in this systematic review. Families within the fungi were diverse, and included a wide range of readily cultivated, edible mushrooms such as the Botelaceae and Pleurotaceae (Talavera-Ortiz et al., 2020). Two fungi families were noted as being common in the records studied in this review, Trichocomaceae and Clavicipitaceae.

Trichocomaceae were noted as having the highest number of interactions recorded, with research predominantly focussing on

interactions with the Drosophilidae. Many Drosophilidae species are regarded as nuisance flies rather than pests, due to their attraction to decaying matter (Brake & Baechli, 2014). However, there are several economically important pests found within this family, including the spotted-wing Drosophila (*Drosophila suzukii*) (Lee et al., 2011). *Drosophila suzukii* was one of the species within the Drosophilidae researched within the literature, with the remaining research focusing on interactions targeting *D. melanogaster*. *Drosophila melanogaster* is not a crop pest, rather of interest amongst the scientific community as it is widely used as a model system for cellular and developmental processes found within higher eukaryotes (MacKay et al., 2012). Both *D. suzukii* and *D. melanogaster* are, consequently, two of the most extensively researched organisms across the biological sciences (Adams et al., 2000; Cini et al., 2012). Therefore, their prevalence amongst the literature in this review was expected. In terms of using 1-octen-3-ol and 3-octanone for use in crop protection, evidence would suggest that 1-octen-3-ol is an effective repellent against *D. suzukii*. Reher et al. (2019) found that in greenhouse cage tests, a treatment of 100 μ L \geq 98% 1-octen-3-ol at 50% v/v in paraffin oil significantly reduced larval infestation and oviposition in grape and strawberry crops. Similar results were obtained within the wider literature with the use of synthesised 1-octen-3-ol under laboratory conditions (Wallingford et al., 2018). However, naturally-derived 1-octen-3-ol had no repellent effect on *D. suzukii* in raspberry crops under field conditions (Reher et al., 2019). Contrastingly, several studies using synthesised 1-octen-3-ol reported to repel *D. suzukii* in raspberry (Wallingford et al., 2017; Wallingford, Connelly, et al., 2016; Wallingford, Hesler, et al., 2016), with 56.7% fewer eggs being recorded post-treatment compared to controls (Wallingford et al., 2018). As much of the existing research has been conducted within the same laboratory, there is a need for further research across a range of field and commercial cropping environments to further explore the potential of 1-octen-3-ol and clarify reasons behind the differences in efficacy of naturally occurring and synthesised variants of the compound.

Other fungi responsible for a large proportion of the interactions were those within the family Clavicipitaceae. All interactions originating from Clavicipitaceae targeted invertebrates, falling into the functional groups of moths (2), nematodes (4), gastropods (1), weevils (2) and Drosophilid flies (1). Target species in all cases were recognised crop pests. Efficacy in management of these pests varied between both family and species. The most effective use was seen against the garden snail (*Cornu aspersum*) and grey field slug (*Deroceras reticulatum*), with 100% mortality achieved within 1-hour post-treatment of 1-octen-3-ol and 3-octanone, and repellent/antifeedant properties being seen at lower doses (Khoja et al., 2019). Similar success was achieved in the management of the northern root-knot nematode (*Meloidogyne hapla*), with a cyclodextrin granular formulation 1-octen-3-ol leading to over 97% mortality within 4 days (Khoja et al., 2021). Alongside mortality from direct contact with 1-octen-3-ol and 3-octanone, research has explored the ability of these compounds in enhancing biological control using entomopathogenic nematodes (EPN; Hummadi et al., 2021). These compounds, sourced

from the entomopathogenic fungi (EPF) *Metarhizium brunneum*, have recorded toxicity at high doses to the EPN *Steinernema carpocapsae*, *S. feltiae* and *Heterorhabditis bacteriophora*. This study also identified the ability of these compounds to attract EPN at low concentrations, suggesting potential for further research to exploit these complex interactions between EPF and EPN for use in integrated pest management programmes. Despite research into the role of 1-octen-3-ol and 3-octanone being relatively novel, these records overall suggest that not only do these compounds show great potential for use in pest management, they also suggest that fungi within the family Clavicipitaceae may provide a diverse (Torres & White, 2009), effective and accessible (Yamanaka & Inatomi, 1997) source for the extraction of these compounds. Further research into non-target effects is required to facilitate optimal use of 1-octen-3-ol and 3-octanone within cropping environments.

4.2.3 | Invertebrate-derived interactions

Interactions originating from an invertebrate source were all concerned with target/effectors that were also invertebrates. There was no clear origin or target of focus within this area of research, and records explored both chemical ecology and crop protection. Of the crop protection records, research exploring invertebrate-invertebrate interactions formed a lot of the early literature (1991–2016), with no publications on this subject recorded as being published after 2016. As identified in this systematic review, much of the research into 1-octen-3-ol and 3-octanone applied to a crop protection context has been published post 2018. However, these publications focus on the interactions stemming from plant and fungal origins. Of the existing research exploring invertebrate–invertebrate interactions, little focus is placed on the repellent and insecticidal properties of 1-octen-3-ol and 3-octanone (as seen to be a focus in modern research). Rather, much of this research explored how volatile blends are used by parasitoids for habitat orientation (Morawo & Fadamiro, 2016; Steiner et al., 2007). With much of this research concerning the importance of volatile blends, this review indicates that existing research into invertebrate sources of 1-octen-3-ol and 3-octanone is of limited benefit to developing new crop protection tools.

4.2.4 | Development of literature

Since completion of the search conducted in this systematic review, as of August 2022 a further six records have been identified detailing chemically mediated interactions between 1-octen-3-ol and 3-octanone and specified target/effectors. Most of these records explored plant sourced interactions with invertebrate target/effectors (Ayelo et al., 2022; Jermakowicz et al., 2022; Liang et al., 2021; Zhuo et al., 2022). The remaining two records explored interactions between invertebrate and fungal sources with invertebrate targets/effectors (Bourdon et al., 2022; Shi et al., 2021).

4.3 | The future of crop protection

Whilst research into the development of 1-octen-3-ol and 3-octanone for use in commercial crop protection remains novel, it shows potential for success in the management of a broad range of invertebrate pests (Hummadi et al., 2021; Khoja et al., 2019; Watentena et al., 2019). This systematic review has identified several sources of naturally occurring 1-octen-3-ol and 3-octanone with potential for exploitation in crop pest management. Their use in crop protection has, historically, relied on laboratory-synthesised compounds as attractants in baits and lures (Takken & Kline, 1989; Watentena et al., 2019). However, identification of interactions between crop pests and naturally occurring compounds, alongside synthetic ones, may broaden the potential for application in crop protection. One way in which this may be utilised is through implementation of companion crops and/or trap crops with naturally high emissions of 1-octen-3-ol and 3-octanone or those that can be selectively bred to increase their emissions of these compounds. Exploiting VOCs in pest management through intercropping and trap cropping is not a novel concept. Globally, there have been many successful examples of using 'push–pull' approaches to pest management. Perhaps the most well-known is intercropping maize with tick clover (*Desmodium uncinatum*) and trap cropping with Napier grass (*Pennisetum purpureum*) in Africa to control fall armyworm (*Spodoptera frugiperda*) (Midega et al., 2018). By combining the repellent VOCs produced by *D. uncinatum* with the attractant VOCs produced by *P. purpureum*, it is possible to 'push' fall armyworm out of the maize crop whilst 'pulling' it toward the attractive trap crop (Hassanali et al., 2008). As many examples from this systematic review demonstrate, there are limited opportunities to incorporate plant-derived sources of 1-octen-3-ol and 3-octanone directly into integrated pest management programmes as studies are limited to plants from the Cynomoriaceae family. Fungi-derived sources of these VOCs are, however, much more likely to play a role in future integrated pest management programmes due to being naturally synthesised by market-ready biopesticide products.

Alongside exploitation of naturally occurring VOCs, synthesised VOCs have also shown potential in modifying invertebrate pest behaviour within the field. The four VOCs dimethyl disulfide, geraniol, eucalyptol and citronellol reduce oviposition by the cabbage root fly (*Delia radicum*) in field broccoli crops (Lamy et al., 2017). Similar success has been achieved with other invertebrate pests, including whitefly (*Trialeurodes vaporariorum*; Conboy et al., 2020) and entomopathogenic nematodes, *Steinernema feltiae*, *S. carpocapsae*, *S. kraussei* and *Heterorhabditis bacteriophora* (Laznik & Trdan, 2016). In some studies, mortality from exposure to synthetic VOCs has also been recorded (Feng et al., 2018). Considering this, it may be possible to directly utilise synthesised nature identical VOCs such as 1-octen-3-ol and 3-octanone as biopesticides. Using synthesised nature identical VOCs in this way has some advantages over naturally occurring ones as their dose and application frequency can be better controlled. This has potential for development into integrated pest management tools. One limitation of synthetic VOCs is the associated economic cost and time to development of future synthetic VOC pest management tools.

Whilst the generation of synthetic VOCs is recorded to be of relatively low economic cost compared to that of synthetic chemical insecticides (Singh et al., 2021), economic cost remains high in comparison to application of cultural preventative measures, such as intercropping. This is due to the requirement for synthetic VOC derived products to be registered as a pesticide. Such economic cost has potential to limit the global use of synthetic products, with potential for this solution being unsuitable in crops with low economic return. Economic cost should therefore be a consideration of future research and development into synthetic 1-octen-3-ol and 3-octanone, to optimise the creation and use of these pest management tools of the future.

5 | CONCLUSION

Research into chemically mediated interactions of 1-octen-3-ol and 3-octanone has been extensively researched across a range of biological sciences. However, only recently has focus been placed on the manipulation and use of these compounds outside of a natural context for human gain. When examining these interactions within the context of crop protection, research remains diverse in focus and a consensus has not been reached due to novelty of subject and low volumes of published literature at this time. There is, however, a clear drive toward crop protection focussed research in relation to 1-octen-3-ol and 3-octanone, with publication rates rapidly increasing. It is expected that this rise will continue throughout the next decade, with records published between January 2020 and July 2021 already reaching 37% of the total number of crop protection records published across the entirety of the last decade. It is important that new research is approached in a way which builds on the current scientific understanding of 1-octen-3-ol and 3-octanone in crop protection, as identified in this review. By identifying current understanding, research gaps and future avenues for exploration, it may be possible to exploit the functional diversity of 1-octen-3-ol and 3-octanone for optimal use within a wide range of crop protection settings.

Research suggests that, despite the compounds being chemically identical regardless of source, 1-octen-3-ol and 3-octanone from different sources exhibit different degrees of efficacy in pest management. It should be recognised that source does not alter the efficacy of 1-octen-3-ol and 3-octanone directly, rather may have an influence on overall interaction effect due to the presence of other associated compounds—a variable not widely considered within current research. Therefore, future research may be to explore the potential synergies of blended VOCs including 1-octen-3-ol and 3-octanone.

To achieve optimal use of 1-octen-3-ol and 3-octanone, two main research limitations need to be addressed. The first is the requirement for more crop protection focussed literature in relation to these compounds. At present a knowledge gap exists within the current literature. Whilst it is recognised that knowledge gaps are rare within scientific literature (Jacobs, 2011), this review confirms current reliance on knowledge from related research domains rather than within the field of crop protection directly. Therefore, the literature would

benefit from future studies developing on founding principles identified within more extensively researched areas such as chemical ecology and animal protection. The second research problem identified is an empirical gap (evaluation void; Müller-Bloch & Kranz, 2015). Upon the development of future research, a focus should be placed on attempting to evaluate the output of existing literature by confirming or challenging published theory. At present, research existing on a specific topic has often been conducted by a single laboratory or partnership, with little supporting research being conducted by external sources. As research and publication within the area of 1-octen-3-ol and 3-octanone in crop protection accelerates, it is important that theories are challenged and/or supported to ensure validity and repeatability of results prior to commercialisation. At present, commercial products based on 1-octen-3-ol and 3-octanone are predominantly targeted at the human pest market. However, there is increasing awareness for their potential application for the control of a much broader range of invertebrate pests. This review highlights the potential value of 1-octen-3-ol and 3-octanone for exploitation in a crop protection context. It identifies key invertebrate behaviour modifying interactions associated with a range of naturally biosynthesised sources, and their limitations for application in crop protection. Research into the effect of synthesised 1-octen-3-ol and 3-octanone is currently limited within the literature—an area which has been identified within this review as having future potential for commercialisation. Therefore, future reviews should consider the role of 1-octen-3-ol and 3-octanone in crop protection looking specifically at comparing effect strength of these volatiles as the literature on this subject continues to increase and diversify.

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CONFLICT OF INTEREST STATEMENT

The authors have no conflicts of interest to disclose.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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