Highlights

- Plant-associated bacteria interact with their environment through exchange of chemicals, including volatile compounds. Innovative agricultural technologies may exploit the inherent advantages of bacterial airborne signals, including diffusibility, independence from water availability and physical connection, and absence of pesticide residuals.

- Volatile compounds resulting from plant-pathogens interactions allow non-destructive disease diagnosis on bulk samples of asymptomatic plant material.

- Volatile compounds, expressing a direct biocidal activity, interfering with signalling, or stimulating plant host defences, contribute to biological control of pests and pathogens.

- Bacterial volatile compounds modulate plant hormones enhancing plant growth, stress tolerance, crop quality, aroma and nutraceutical characteristics, and reduce post-harvest losses.

Applications based on bacterial volatile compounds for crop management and quality

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Keywords

Abstract

Bacteria produce a huge diversity of metabolites, many of which mediate ecological relations. Among these, volatile compounds allow broad-range effects at low doses and may therefore be exploited for applications in plant defence and agricultural production. Such applications are still in their early development. Here we review the latest technologies involving the use of bacterial volatile compounds for phytosanitary inspection, biological control, plant growth promotion, and crop quality. We highlight a variety of effects with a potential applicative interest, based on either live biocontrol and/or biostimulant agents, or the isolated metabolites responsible for the interaction with hosts or competitors. Future agricultural technologies may benefit from the clarification of bacterial interactions with the environment, and the development of new analytical tools.

Bacterial volatile compounds in plant ecological interactions

Bacterial metabolic products characterised by low vapour pressure, high lipophylicity and a molecular weight below 300 Da are likely to be released as Volatile Organic Compounds (**VOCs**, see glossary). Considering the enormous metabolic diversity of bacteria, such compounds may derive from a large variety of chemical pathways, and are generally emitted as complex mixtures [1]. The composition of the bacterial **volatilome** (see glossary) is highly influenced by the growth conditions [2-5], including soil chemistry and structure, pH, availability of water and oxygen, presence of plant

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exudates or other organic compounds, and light irradiation. Translating such considerations into horticultural crop management, agricultural (tillage, cover cropping, fertilisation, watering, and plant protection) or post-harvest (refrigeration, atmosphere control, and ethylene modulation) practices that modify such parameters can influence BVC emissions as well [6].

Along with the characterisation of a growing number of bacterial volatile compounds (**BVCs**, see glossary) [3,4,7], their roles in intra- or inter-specific signalling or competition are being discovered (Figure 1). It should also be noted that the most commonly adopted analytical techniques in studies concerning bacterial volatile compounds are unable to detect molecules with a low molecular weight, such as CO_2, ethylene, nitrogen oxides, ethanol and H_2S (Box 1). Thus, part of the biological effects mediated by bacterial airborne signals may still be eluding the researchers' efforts. In comparison to water-soluble compounds, inherent advantages of VOCs in ecological interactions reside in their high diffusibility, enabling both above- and belowground action, the ability to diffuse through lipophilic barriers (such as cell membranes and plant cuticle), and the independence from water and physical connection among the VOC-producing organism and the signal recipient.

Technological applications based on the release or the exchange of VOCs are most likely to succeed, when they take advantage of these characteristics. Volatility is possibly one of the key points, as it allows a relative uniformity of the gas phase even in cases of poor accessibility of the target (for instance, in the soil, in stored bulk samples, or in internal plant tissues). In addition, biogenic VOCs do not pose problems with residues and environmental accumulation. By contrast, one should consider possible drawbacks deriving from the generally low concentration, impermanence, low target specificity, and difficult handling of VOCs used for plant treatment.

The above reasons may be responsible for the so-far limited enactment of VOC-based technologies. However, some work-arounds may be envisaged to reduce the weight of drawbacks. The use of microbes that form stable populations on plant hosts, exploiting naturally occurring resources and constantly delivering their bio-active function, or that survive harsh conditions (e.g. *Bacillus* spp. spores), may grant a durable effect of the treatment. In this light, the screening of bacterial species forming endophytic and/or specialised symbiosis offers a source of biological functions expressed in an efficient and highly focused way. Recent technological advancement in genomics, **metagenomics** and **gnotobiotics** (see glossary) has enabled breeding programs centered on the plant **holobiont** (see glossary), in which, in addition to plant genetic resources, microbial diversity (overlooked in traditional breeding, and even possibly lost during domestication or selection) is also explored [8-10]. Alternatively, when live bacteria cannot be used, their active principles could still

65 be considered for field application with encapsulation methods allowing a controlled release [11].

66 Caution should be taken for such treatments in dosing the active principle's release rates (as plant

67 stress may derive from its excess) and avoiding wastes due to volatilisation.

68

69 **VOC profiling for plant disease diagnosis**

70 Along with visual inspection, immunochemical and molecular methods represent the standard

71 techniques for disease diagnosis, due to their reliability, sensitivity, specificity, and reasonable

72 practicality in terms of costs and work effort [12,13]. However, these methods still pose a number

73 of issues. Since all of them are destructive, the assessment of plant or fruit health status causes an

74 economic loss and cannot be applied to unique samples. The development and production of

75 specific antibodies, and the design and validation of PCR primers require a laborious set-up and are

76 conditioned by the availability of sequence or protein data. Moreover, both PCR and

77 immunochemical methods are targeted to single organisms, and the screening for multiple

78 pathogens results consequently in a multiplication of work. Finally, representativity at the sampling

79 stage is a major constraint, particularly when pathogen populations are relatively small, and the

80 chance of false negatives must be minimised by increasing the sample size.

81 As a consequence of the bacterial metabolism and the concurrent activation of plant defences, the

82 VOC emission by pathogen-infected plants is, in principle, discernible from that of healthy ones [14].

83 Thus, the possibility of a VOC-assisted plant diagnosis has been put forward, and the recognition of

84 bacterial diseases by volatile fingerprinting has been attempted in several species and/or crops

85 (Table 1). VOC screening is non-destructive and can be applied to crops or live plants without

86 compromising their economic value or viability. Unlike molecular and immunochemical methods,

87 VOC-assisted plant diagnosis, in principle, allows the screening for multiple pathogens in the same

88 run [15,17,25,30,31]. Finally, bulk samples can be analysed as a whole with minimal risks of sampling

89 errors.

90

91 *Analytical technologies and methods*

92 **GC-MS**, **PTR-MS**, **SIFT-MS**, **E-NOSE** and **FAIMS** (see glossary) are among the technologies available

93 for VOC-based diagnosis (Table 2). A major distinction can be made between techniques allowing

94 the analytical determination of the chemical components of the VOC blend (e.g. GC-MS), and

95 techniques that only allow overall VOC profiling (e.g. most E-NOSE models), with in-between cases

96 of techniques with analytical power restricted to certain conditions. Techniques of the first class

97 may be used to identify distinctive marker compounds for determinate pathogens [15,17,18,20-

98 22,29]. Alternatively, the recognition of infected samples may be done through multivariate

99 statistical analysis or artificial neural networks. These recognition procedures may be applied to any

100 technique, but they are an obligate choice for non-analytical methods.

101 Based on the technology and the recognition method, several sampling systems are available.

102 Portable instruments may allow the direct application to ambient air. In these cases, the

103 instrumental sensitivty can be adjusted by regulating the input flow rate (i.e. the air volume

104 screened). Ambient air analysis or headspace sampling in odourless gas bags or canisters are the

105 simplest options, with the smallest chance of artifactual results. However, when such options are

106 not practical (e.g. gas samples are too small, or marker compounds are in trace amounts), the use

107 of VOC-sorbent materials may be envisaged to concentrate the VOC sample [14].

108

109 *Sample recognition and applicative perspectives*

110 Besides pathogen infection, other irrelevant factors (such as plant genotype, secondary microbial

111 colonisation, tissue age and environmental conditions during sampling) are predicted to influence

112 VOC emissions with additional levels of complexity. Furthermore, diagnostic power is influenced by

113 disease severity [15,32,33], thus latent infection stages or sporadic pathogen presence are harder

114 to detect. Physico-chemical factors influencing volatilisation and relative composition of air samples

115 (temperature, relative humidity, sorbent saturation or chemical affinity) also require to be

116 accounted for.

117 Thus, the main challenge for VOC-based diagnosis seems to be the development of feature

118 extraction methods, to isolate disease-related information from background noise. For this reason,

119 E-NOSE methods have not progressed beyond the proof-of-principle status so far. In fact,

120 discrimination power is related to the independence among the components of data variability [35],

121 while E-NOSE models tested for plant diagnosis include no more than 32 sensors with partially

122 overlapping chemical sensitivity [14]. Recent developments in E-NOSE construction, such as

123 coupling with chromatographic separation [36] and colorimetry [37] may overcome current

124 discrimination power limits.

125 With regard to techniques with high analytical power, methods based on unsupervised machine

126 learning and bacteria-VOCs association database were studied for human diagnostic purposes [38].

127 The implementation of such methods in plant health monitoring could be integrated with existing

128 microbial VOC databases [3]. An effort is required to expand such databases, currently limited in the

129 number of bacterial species covered.

130 The current technology readiness of VOC-based diagnostic systems may support standard

131 phytosanitary inspection by pre-screening plant material, to focus more in-depth, time- and

132 resource-consuming analyses on dubious cases. Significant advances may come in the future with

133 the development of more versatile instruments [36,37]. Whatever technology may become

134 dominant, coordination among researchers, field operators and industry is a requisite for the setting

135 of standards, databases and accepted practices.

136

137 **Bacterial volatile compounds in biological control**

138 Biological control has raised an interest over time, as a tool to achieve a stable level of disease

139 control by environmentally sustainable means. Biocontrol agents (**BCA**s, see glossary) are organisms

140 that reduce a pathogen's population size, or its chance to cause disease, by directly killing the

141 pathogen (with antibiotics, lytic enzymes and other toxic compounds), by interfering with its

142 signalling or regulatory metabolism, or by direct competition (i.e. better exploitation of resources,

143 determining the pathogen's starvation). These interactions contribute to microbial antagonism

144 (Figure 1). In this scenario, several BVCs have drawn attention as possible mediators of long-range

145 effects. While it may be expected that their gas-phase concentrations never reach biologically active

146 levels as they diffuse in the atmosphere, the competition among microbes in the phyllosphere takes

147 place in matrices (such as biofilms, mucilages, plant waxes) or sites (sub-stomatal chambers, soil

148 pores) where local BVC may attain substantial concentrations [39]. In this light, the identification of

149 BVC-releasing symbiotic endophytes may be desirable, as their beneficial effects would be delivered

150 close to their target and in a concentrated form.

151 Alternatively, BVCs can induce systemic plant defences (Box 2). Notably, such induction occurs at

152 low BVC rates, acts systemically and persists after the removal of the emitter bacterium, whereas

153 BVC-mediated microbial antagonism would require a local and continuous emission at higher rates.

154 Low BVC rates prime, rather than activate plant defences, i.e. responses are more prompt and

155 intense upon pathogen attack, but no phenotypic changes (including in yield and crop quality) are

156 expressed otherwise. In addition, the same plant may release pre-alert signals to neighbouring ones

157 [40]. Thus, even signals in low concentrations may lead to significant large-scale consequences.

158 BVCs may also influence plant-pest interactions, insect behaviour and survival rate, and thus could

159 be possibly used for pest control strategies (Box 3).

In spite of the potential applications, the use of BCAs presents some inherent difficulties, such as an inconstant effectiveness, depending on environmental, agricultural and ecological factors that may vary in different areas, plant species or growing seasons. In addition, the efficacy of BCAs depends on their population size, which usually decreases steeply after the release, and co-formulants are often required to extend the BCA's field life. For these reasons, BVCs have not yet found specific applications in biological control. As a promising perspective, the development of synthetic bacterial communities may overcome some of these drawbacks, by achieving a better stability or resilience of the microbial biocoenosis, along with the integration of multiple mechanisms of action [41,42].

Direct toxicity against pathogens

In exerting direct toxicity against plant pathogens, BVCs are influenced by several factors. Along with the chemical nature of the compound, its release rate, the occurrence of the conditions for its production, and the gas phase dynamics that regulate its volatility and stability all contribute to its ecological role and the technological usefulness [39]. The best-studied bacteria, in relation to characterisation of BVC toxicity, include several actinomycetes, *Pseudomonas*, *Bacillus*, *Serratia*, *Burkholderia*, *Xanthomonas* and *Erwinia* species.

Among the volatile compounds hindering the growth of competitors, ammonia, cyanide and sulfur-containing metabolites are believed to play a major role [43]. However, bacterial strains not releasing such compounds can still display antimicrobial properties, indicating that other BVCs substantially contribute to inhibition of microbial growth, and that synergistic effects exist between different compounds. Antimicrobial effects were described for alkanes, alkenes, alcohols, aldehydes, ketones, esters, terpenoids, pyrazines, phenolics, amines, quinolones, chlorine and sulfur compounds (Table 3) [44-57]. The most common molecular targets of toxic BVCs include metal cofactors, sulfhydryl groups, and protein folding.

Fungi and oomycetes often show a considerable sensitivity to BVCs, both for the elongation of mycelia and for spore germination [43,46-49]. In contrast, fewer cases are reported regarding BVC-mediated control of bacterial pathogens, namely, *Agrobacterium* species [48,58], *Clavibacter michiganensis* [59,60], *Xanthomonas oryzae* pv. *oryzae* [61] and *Ralstonia solanacearum* [62]. Reasons for such difference in susceptibility may reside in differences between bacteria and eukaryotic organisms, for instance in plasma membrane composition or gene expression.

The importance of BVC toxicity for interspecific competition in real conditions is debated [63], because of its dependence on BVC production rates and chances of accumulation. Thus, BVC-

mediated suppression of pathogens was not considered as a trait for selection of new biocontrol agents until recently [49,64]. Nonetheless, this mechanism has been documented for several commercial biocontrol agents, and some of the BVCs involved, such as benzothiazole and dimethyl sulfides [49,64] have been adopted as active principles in exogenous biocide treatments. Biomimicry, i.e. the simulation of biological processes and interactions for applicative purposes, may be advisable in field conditions for a number of reasons, including the caution in introducing organisms into a new environment with potentially irreversible effects, and the higher control of chemical nature, dosage and timing of the treatments [65]. Conditions for exogenous VOC treatments, however, include the technological feasibility of gas application to the target (soil, canopy, stored crops) and the low toxicity at the treatment dosages for the operator and for non-target organisms.

Disruption of quorum sensing

The complex of regulatory functions connecting the perception of intra- or inter-specific bacterial population density to the expression of 'social' phenotypes is termed Quorum Sensing (**QS**, see glossary). The typical QS signalling circuit consists of the production of a signal compound, along with the expression of specific receptors for the same signal(s). Among the traits governed by QS, bacterial motility, formation of biofilms, biosynthesis of secondary metabolites and virulence factors have been observed, implying their role in improving bacterial fitness in a crowded, diverse and competitive environment [66]. As a consequence, several species may form stable symbiotic consortia, based on the reciprocal exchange of nutrients and signals [67,68]. In the case of pathogenic bacteria, the full expression of virulence can require a stimulation by other microbial neighbours [69].

N-acyl-homoserine lactones (AHLs) are the best-studied example of QS signals, since they are employed by a wide array of Gram-negative bacteria, including plant pathogens such as *Pseudomonas*, *Erwinia/Pectobacterium* and *Agrobacterium* species. Other compounds mediating QS include peptide, aminoacid or fatty acid derivatives. While QS activity was only studied in aqueous solutions for most of these compounds, their semi-volatile nature presumably also allows airborne signalling.

The disruption of QS systems (Quorum Quenching, QQ) may be pursued to reduce the population of pathogens and/or to control the incidence and severity of plant diseases [70]. Interference in QS has been demonstrated for some BVCs. Among these, DMDS reduces the production of AHLs in *P.*

7

chlororaphis [71]. Linear ketones (2-heptanone, 2-nonanone, 2-undecanone) and 2-amino-acetophenone showed an activity on engineered AHL biosensors [72,73].

Indole and its derivatives may act as QS signals, being produced by some bacterial species in a population-dependent manner and eliciting specific responses. Non-producing pathogenic bacteria may also perceive it, possibly by means of AHL receptors [74]. Although auxin (indole-3-acetic acid) and indole are structurally related, in *Agrobacterium tumefaciens* (specialised in auxin biosynthesis, but not releasing indole) only indole can induce bacterial motility, biofilm formation, antibiotic resistance and expression of virulence genes, while reducing bacterial growth in the 0.2-1 mM concentration range [75].

Biostimulation

After the initial observation of plant growth promotion by 2,3-butanediol-emitting bacteria [76], it has become evident that BVC-mediated biostimulation is a widespread phenomenon involving numerous bacterial species and compounds [2,77], with potential applications still to be tested. The adaptive rationale of some biological effects promoted by plant-associated bacteria is, in many cases, evident. Symbiotic organisms, for instance, take benefit from increasing root growth and plant nutritional status. Conversely, pathogens can release BVCs to modify plant metabolism to their own advantage [78,79]. However, some methodological caveats should be pointed out in the study of influences of VOCs on complex plant traits. Several molecules of great importance for plant metabolism, but not easily detected in the most common experimental settings, for instance, may be neglected (Box 1).

Plant growth is the result of several factors, such as hormonal signalling, nutrition, stress tolerance (Figure 1). Thus, the observation of a plant growth-promoting effect by a bacterial strain in laboratory conditions, in absence of nutritional or cultural constraints, is possibly not indicative of the applicability of the same strain in field. Secondly, plant growth may not correlate (or even inversely correlate) with crop yield, for which not only carbon fixation, but also reallocation of photosynthates is relevant. Thirdly, the effects of BVCs are generally pleiotropic, i.e. they interact with multiple signalling pathways, and are not specific to a definite target organism [43].

Plant growth promotion and nutrition

Growth promotion by BVCs was shown on several cultivated species, including alfalfa, barley, basil, broccoli, lettuce, poplar, soybean, tobacco, tomato [43,77]. These effects have been related to

256 modulation of plant hormones, such as cytokinins [76], auxins, brassinosteroids [80], gibberellins,

257 ethylene [81] and strigolactones [82].

258 While hormonal effects may shape the allocation of resources within the plant and its phenological

259 progression [79], plant growth promotion and biomass increase should come with a corresponding

260 nutritional enhancement. The stimulation of auxin metabolism and/or signalling, for instance, leads

261 to changes in plant root architecture, which contributes to the uptake of water and nutrients [83].

262 Ethylene participates in the activation of mineral uptake systems [84]. BVCs were implied in

263 counteracting carbohydrate- and ABA-mediated inhibition of photosynthesis, thus enabling higher

264 CO_2 fixation rates [85], and stimulating iron uptake [86,87]. It should be noted that most research

265 was conducted in laboratory or controlled conditions, where nutrients and water are generally not

266 limiting.

267

268 *Abiotic stress tolerance*

269 Plant growth promotion by microbes can result from increased tolerance to environmental stresses.

270 Although mechanisms are often far from being elucidated [88], such effects are generally induced

271 by the release of volatile hormones by the microbes (notably ethylene, methyl-jasmonate and

272 methyl-salicylate), or involve the signalling cascade of plant hormones [89].

273 Current knowledge on BVC-induced tolerance refers mainly to osmotic, salt and/or water stress (Box

274 4). In addition, this research area may provide significant advancement to phytoremediation and to

275 the adaptation of crops to stresses related to climate change [90]. The recovery of marginal soils,

276 for instance, may be enhanced by the root branching stimulation, exerted by some symbiotic

277 bacteria to increase the release of organic carbon into the rhizosphere. Among the BVCs implicated

278 in this plant-microbe interaction, 1-butanol and the QS signal butyrolactone may play a role [91].

279

280 **Crop quality**

281 A list of examples of bacterial interactions with crops, influencing crop quality, is shown in Table 4.

282 In all the cases in which crop quality depends on secondary metabolites, such as essential oils and

283 aromas, a close link between the elicitation of plant defences and an increased crop value is easily

284 explained. In fact, essential oils form one of the first lines of plant defence and inter-plant

285 communication, and their contents are raised by BVCs from several defence-inducing bacteria. Thus,

286 an increased essential oil content was obtained by exposing aromatic plants, including peppermint

287 and basil [92,93], or medicinal plants such as *Atractylodes lancea* [94], to BVCs emitted by several

288 *Pseudomonas*, *Bacillus* and *Azospirillum* spp.

289 In the determination of the aromatic profiles of fruit, a remarkable role has been observed for the

290 associated microflora. *Methylobacterium* spp. include endophytic species expressing alcohol

291 dehydrogenase (ADH) activity, which converts plant-derived alcohols to the corresponding

292 aldehydes or ketones [95,96]. The substrate-specificity of bacterial ADH is low, but distinct from that

293 of plant ADH, thus explaining the diversity, along with the higher intensity, of VOC emissions from

294 microbe-colonised plants.

295 During post-harvest storage, crops may incur in spoilage by pathogens, with consequent loss of

296 produce and/or contamination by mycotoxins. Because of the use of controlled atmosphere on a

297 large variety of crops, VOC-based technologies may fit well in post-harvest disease control. In fact,

298 on one hand, relatively high concentrations of bioactive volatiles can be obtained in a closed storage

299 cell; on the other hand, in comparison to synthetic fungicides, the application of biogenic VOCs and

300 BVC-emitting bacteria to products for human consumption poses lower concerns. Several *Bacillus*

301 spp. strains releasing antifungal BVCs were identified and tested on citrus, mango, cherry, litchi and

302 peach [97-102], while *Streptomyces* spp. were tested on strawberry, citrus, tomato and chili [103-

303 107]. Some compounds mediating antifungal effects, such as cedrol, 2-pentylfuran [102] and

304 acetophenone [107], are commonly found among fruit aromas, and their efficacy was proved on a

305 large spectrum of pathogens. Therefore, their technical use may encounter few restrictions by

306 policy-makers, and possibly even higher appreciation by consumers.

307 The microbial population living on grapevine berries (including *Paenibacillus* spp.) produces volatile

308 compounds possibly improving the quality of wine [108]. Thus, while fruit technology has been so

309 far oriented to the limitation of microbial populations on the crop, future work should address and

310 exploit the contribution of the microflora to aromatic properties of fruit or derivate products.

311

312 **Concluding remarks**

313 Despite the great diversity of bacterial metabolites and of biological relations mediated by them,

314 which form a huge reservoir of resources with a potential applicative interest, BVC applications have

315 been explored so far only marginally, and their practical use is at its dawn especially for improving

316 crop tolerance and quality [95]. The present overview was limited to volatile compounds emitted

317 by bacteria, but other organisms (including fungi, moulds and, to some extent, plants) also release

318 bioactive compounds. In addition, biogenic inorganic volatile compounds were only marginally

considered. Thus, future agricultural and environmental engineering applications may benefit from the study of a wider range of biological relations, or by the development of new analytical tools and protocols.

In modern agricultural systems, there is a growing interest in finding environmentally sustainable, effective and inexpensive solutions for the problems encountered at each step of the production chain. The diffusion of biological control methods, and the programs for phytoremediation or recovery of marginal soils are examples of such dynamics. However, the novelty of these solutions also poses some legislation and registration issues [113,114]. In addition, live biostimulant or biocontrol agents may not adapt to all cultural conditions [90], and promising biological functions may come along with potential risks for human health or environmental equilibrium.

Therefore, the mechanisms of interaction among different bacterial species and with their eukaryotic (plant, insect) hosts deserve in-depth investigation, to develop more efficient and flexible solutions for emerging problems. Volatile compounds may show inherent advantages related to their diffusibility, low dose of action and absence of toxic residues [89]. Extensive field testing is required as a key step to the commercial and industrial application of technologies based on BVCs (see also the outstanding questions).

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Box 1. Low molecular weight volatile compounds

Some volatile compounds, characterised by a small and simple chemical structure, interact directly with plant metabolism or signalling cascades. However, these molecules have received, in explorative studies, only marginal attention, because of technical limits, including the impossibility of a correct identification by GC-MS (due to short retention times and/or scarcely indicative spectral profiles), or the occurrence of artifacts (such as accumulation effects in sealed cuvets, or interference with growing media) linked with the experimental setting.

Carbon dioxide fuels photosynthesis and it is often the most important limiting factor of this process. CO_2 regulates stomata opening and, consequently, photosynthesis and transpiration [115]. CO_2 may contribute to the growth and resistance promoting effects observed in plants treated with bacterial VOCs [116]. CO_2 produced by respiration of bacterial endophytic symbionts can reenter the photosynthetic pathway, not being limited by stomata opening, and has been estimated to be able to provide up to 57% of total CO_2 photo-assimilated by the plant [117]. In this view, plants colonised by endosymbionts may have a better water use efficiency and a higher availability of photoassimilates for growth and defences.

Ethylene is a gaseous plant hormone playing a central role in plant development and resistance response to abiotic and biotic stresses [118], also interacting with salicylic acid- and jasmonic acid-dependent signalling pathways. Ethylene and its precursor 1-aminocyclopropane-1-carboxylate (ACC) are subjected to sophisticated co-regulation by plants and associated microbes, thus shaping the plant microbiome [119,120]. In fact, bacteria can actively produce ethylene, or reduce its biosynthesis in plants subtracting ACC by ACC-deaminase activity, thus lowering plant ethylene levels and promoting plant growth.

Nitric oxide (NO) is a radical gas mediating a large variety of physiological responses in plants. Plant-associated bacteria can produce NO, as a result of denitrification, by enzymatic conversion of L-arginine or by release from siderophores [121,122]. One important effect of bacterial NO, observed e.g. in *Azospirillum* spp. [123], is the enhancement of root branching, promoting both plant nutritional status and bacterial colonisation.

While commonly regarded as a toxic and/or defence compound, hydrogen sulfide (H_2S) also has a regulative role in plants by interacting with NO and thiols [124,125]. Plant-associated bacteria synthesise H_2S through cysteine desulfhydrylation or sulfite reduction.

727 Ethanol and methanol are common products of fermentation, originated by both plants and
728 bacteria under anoxic conditions, and have been implied in the activation of plant stress responses
729 [126].

730

731 **Box 2. BVC-elicited induction of plant defences**

732 Since the discovery of induced systemic resistance (**ISR**, see glossary) by 2,3-butanediol [127], the
733 potential application of BVCs for the elicitation of plant defences has drawn attention. Notably,
734 induction of plant defences is one of the very few measures that can be adopted against viral
735 diseases [128]. ISR is often stimulated as the result of a specific symbiotic interaction between the
736 host plant and bacteria, which also promote plant nutrition and growth. Thus, the two aspects of
737 defence and growth promotion coexist in the same symbiotic relation and are somewhat difficult to
738 tell apart (e.g. activation of stress responses in Figure 1). However, relevant details for plant defence
739 engineering, including mechanisms of signal perception and decoding (i.e., how relatively simple
740 molecules drive specific responses), remain obscure [88].

741 2,3-butanediol biosynthesis, for instance, was observed both in defence-eliciting (*Bacillus* and
742 *Serratia* spp., *Pseudomonas chlororaphis*) and pathogenic (*Erwinia*/*Pectobacterium*, *Dickeya* spp.)
743 bacteria [127,129-131]. In different pathosystems, the action of 2,3-butanediol and related
744 compounds (acetoin, 2,3-butanedione) has been connected to different combinations of salicylic
745 acid, jasmonate and/or ethylene signal cascades [127,128,132]. According to the relative
746 stimulation of these pathways, specific subsets of plant defensive responses may be activated.

747 While 2,3-butanediol and related compounds are the best-studied example of defence-inducing
748 BVCs, other molecules [43,133] were identified which could stimulate plant defences. In some cases,
749 such as for DMDS and benzothiazole, direct antimicrobial and plant defence induction effects may
750 coexist [134]. One advantage of these compounds is that, although acting through plant hormone
751 signal cascades, they are less prone than hormones to cause drastic physiological reprogramming.
752 For instance, ISR is expressed only after pathogen challenge, and is not generally associated to
753 changes in plant phenotype or crop yield [40,135].

754 Synergism of BVCs in complex mixtures may also occur in natural conditions [88]. By modulating the
755 simultaneous activation of several signal cascades (ethylene, jasmonate, salicylate, and other
756 hormones), BVC mixtures could attain protection against a broader range of pathogens [135].

757

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Box 3. Pest management by BVCs

Survival and replication rate of pests (including *Drosophila suzukii* and several nematodes) were reduced by means of bacterial volatile emissions [48,136]. However, the use of toxic BVCs seems impractical against most motile animal species, due to limitations in exposure time and concentration. Instead, microbial biocontrol agents releasing toxic compounds may act as effective biopesticides for soil-borne or sessile pests, with a significantly reduced environmental impact.

Insects and nematodes use a variety of semiochemicals to coordinate their life functions, including feeding, mating, oviposing and alarm behaviour. Pest- or plant-associated bacteria contribute to the production of biologically active BVCs (Figure 1), and many cases of attraction to microbes associated to the host have been observed [137]. Fruit flies (*Drosophila* spp.), for instance, are attracted by BVCs from symbiotic *Lactobacillus* spp. acting as aggregation pheromones [138], and are repelled by the common BVCs, 1-octen-3-ol and geosmin [139]. Locusts use guaiacol derivatives, produced by *Pantoea agglomerans* residing in their intestines, as an aggregation pheromone [140]. Finally, the association with certain bacteria may determine the insect's preference for BVCs emitted by those microbes, by effect of conditioning or learning [141]. Parasitoid recruitment can be mediated by BVCs, either by direct attraction to microbes indicating a food source [142], or indirectly by eliciting a more intense release of plant VOCs [143]. Concerning nematodes, experiments on the model organism *Caenorhabditis elegans* showed that attractive BVCs produced by *Bacillus nematocida*, such as benzyl benzoate, benzaldehyde, 2-heptanone, and acetophenone, stimulate bacterial swallowing by the host. Thus, the bacterium colonises the worm's intestines, leading to its death [144].

BVCs may, therefore, find an application in pest management. VOC-based technologies, employing attractants, deterrents and pheromone-like compounds have been applied to lure-and-kill, push-pull and sexual confusion control strategies. However, information concerning semiochemicals for such technologies is currently restricted to a relatively small number of species (mostly Lepidoptera, Diptera and Coleoptera). New impulse, in this sense, may derive from metagenomic analyses performed either on the insect or on its hosts [145]. With the exception of specialised symbiotic relations, insect guts have often been demonstrated to host relatively simple microbiota, dominated by Enterobacteriaceae (notably *Enterobacter*/*Pantoea* and *Klebsiella* spp.), to be highly influenced by the diet, and possibly transmitted by parents [141,146,147]. This body of knowledge may provide useful information for the selection of effective and persistent biocontrol agents interacting with insects.

Box 4. Examples of abiotic stress tolerance induced by BVCs

Abiotic stresses elicit NO and ethylene production in plants, which exert several and multifaceted physiological effects. Plant-associated bacteria may indirectly influence plant NO and ethylene emission or produce these bioactive compounds (Box 1).

Water deficiency, osmotic stress and salt toxicity are partially interconnected and overlapping both in causes and in the induction of plant responses. 2,3-butanediol, or total BVCs from 2,3-butanediol-emitting bacteria *Bacillus subtilis* GB03 and *Pseudomonas chlororaphis* O6, increased Arabidopsis tolerance to water deficiency and osmotic stress. Abscisic acid, salicylic acid, ethylene, and jasmonic acid signaling pathways were implicated in *P. chlororaphis* O6- and 2,3-butanediol-induced stomata closure, increasing tolerance to drought [148]. *B. subtilis* GB03 stimulates the biosynthesis of osmoprotectants (choline, glycine-betaine) in the plant, enhancing its growth under water withholding and osmotic treatment [149].

Several cases of improved plant tolerance to salt stress have been observed after interaction with BVC-releasing bacteria. *B. subtilis* GB03 and its main volatile, acetoin, enhance peppermint tolerance to salt stress by stimulating SA biosynthesis and reducing ABA [150]. Another mechanism of induction of Na^+ stress tolerance in Arabidopsis consists of the tissue-specific modulation of HKT ion transporters [151]. Such transporters are downregulated in roots to reduce Na^+ uptake and upregulated in shoots to promote internal recirculation. NO, produced by salt-stressed plants, was also implicated in the enhanced colonisation of the rhizosphere by *Pseudomonas simiae* strain AU, which in turn elicits antioxidant defences, osmoprotection and expression of ion transporters in soybean [152]. Other salt tolerance-inducing BVCs (namely, 2-undecanone, 1-heptanol and 3-methyl-butanol) were identified from *Parabulkholderia phytofirmans* [153].

Drought stress and high temperature promote isoprene emission by plants [154]. Isoprene is the most abundantly produced biogenic VOC on Earth, with an estimated emission of more than 2% of all photoassimilates. Isoprene has a likely a role in protection from reactive oxygen and nitrogen species formed under diverse stress conditions [155]. Many Proteobacteria, Actinobacteria and Firmicutes produce isoprene. *Bacillus* and related genera are among the terrestrial bacteria accounting for the highest production of isoprene. Interestingly, isoprene emission by *Bacillus subtilis* is enhanced by supra-optimal temperature and salinity [156], suggesting that also plant-associated *B. subitlis* may mediate the plant reactions to these stresses. Soil and phyllosphere bacteria may also directly influence the host isoprene metabolism by using plant-derived isoprene as carbon source [155].

Table 1. Applications of VOC-based recognition of bacterial pathogens in different plant species and organs, indicating the diagnostic techniques and the VOCs marker/s

Crop species and conditions	Bacterial pathogen/contaminant	Methods	Distinctive features and remarks	Reference
Apple, dormant plants	*Erwinia amylovora* *Pseudomonas syringae* pv. *syringae*	GC-MS E-NOSE PTR-MS	Multiple pathogen discrimination Dilution effects Markers: acetoin, 2,3-butanediol, 2-hexenal, phenylethanol (*E. amylovora*)	[15]
Bell pepper-derived medium	*Leuconostoc gelidum* ssp. *gasicomitatum* and *Lactococcus piscium*	GC-MS SIFT-MS	Control of spoilage off-odours by controlled atmosphere	[16]
Carrot, roots	*Pectobacterium carotovorum*	GC-MS	Multiple pathogen discrimination Markers: 3-methyl-butan-1-ol, 1-propanol, 2,3-butanedione	[17]
Citrus sinensis, asymptomatic plant	*C. liberibacter*	GS-MS FAIMS	Correct identification of PCR-false negatives Severity-dependent markers: methyl-salicylate (severe), geranyl acetone, linalool (mild)	[18]
Ficus benjamina and *Spathiphyllum wallisii*, *in vitro* cultures	*Escherichia coli* contamination	SIFT-MS		[19]
Grapefruit, leaves	*Xanthomonas axonopodis* pv. *citri*	GC-MS	Marker: phenylacetaldehyde O-methyloxime	[20]
Grapevine, rootstock cuts	*Agrobacterium vitis*	GC-MS E-NOSE	Marker: styrene	[21]
Kiwifruit, *in vitro* explants	*Pseudomonas syringae* pv. *actinidiae*	GC-MS E-NOSE PTR-MS	Marker: 1-undecene	[22]
Lettuce	Resident microflora (mainly *Pseudomonas* spp.)	GC-MS SIFT-MS	Control of spoilage off-odours by packaging	[23]
Onion, bulbs	*Burkholderia cepacia*	GC-MS E-NOSE	Markers: 2-nonanone, 2-octyl-5-methyl-3(2H)-furanone	[24]
Onion, bulbs	*Pectobacterium carotovorum*	GC-MS	Multiple pathogen interaction Marker: 3-bromo-furan	[25]
Onion, bulbs	*Burkholderia cepacia*	FAIMS		[26,27]
Poplar, wood	Bacterial wetwood (non-determined species)	E-NOSE		[28]
Potato, tubers	*Clavibacter michiganensis* ssp. *sepedonicus*	GC-MS PTR-MS	Marker: 2-propanol	[29]
Potato, tubers	*Pectobacterium carotovorum* *Bacillus polymyxa* *Arthrobacter* sp.	GC-MS	Markers: 2-propenal, DMDS, 1-alkenes, branched alkanes, octanal, naphtalene, butanoic acid (*P. carotovorum*); N,N-dimethylformamide, 1-pentadecene (*B. polymyxa*); 2,3-dihydrofuran (*Arthrobacter* sp.)	[30]
Potato, tubers	*Pectobacterium carotovorum*	GC	Multiple pathogen discrimination	[31]
Potato, tubers	*Ralstonia solanacearum*, *Clavibacter michiganensis* ssp. *sepedonicus*	E-NOSE	Lab- to real scale Threshold of disease severity for recognition	[32]
Potato, tubers	*Pectobacterium carotovorum*	E-NOSE	Pre-symptomatic recognition	[33]
Potato, tubers	*Pectobacterium carotovorum*	FAIMS	Early detection (1 d post inoculation)	[34]
Potato, tubers	*Pectobacterium carotovorum*	FAIMS		[26]

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Table 2. Overview of analytical techniques employed for VOC-based plant diagnosis, with working principles and potential advantages and drawbacks

Analytical technique	Working principle	Operative features	Diagnostic principle
GC-MS	Differential retention time and fragmentation profile of VOCs	+ High analytical power (identification of single compounds) + May use sample concentration on sorbents (e.g. SPME)	Recognition of markers Multivariate statistical analysis
PTR-MS SIFT-MS	Fragmentation profile of VOCs	+ Partial analytical power + Quick response	Partial recognition of markers Multivariate statistical analysis
Electronic nose	Electric properties of the overall VOC mixture	+ Simple operation, portability + Quick response + May adjust sensitivity by regulating flow - Interference by water - No analytical power - Instrumental drift	Multivariate statistical analysis Neural network machine learning
FAIMS	Differential mobility of ion fragments in electric field	+ Partial analytical power + Portability	Partial recognition of markers Multivariate statistical analysis

Table 3. Volatile organic compounds exerting direct toxicity against plant pathogens

Compound(s)	Emitting species	Target organism(s)	Reference
Hydrogen cyanide Ammonia 1-Undecene	*Pseudomonas* spp. *Bacillus* spp. others	*Phytophthora infestans* *Rhizoctonia solani* *Helminthosporium solani* *Fusarium oxysporum* *Dickeya dianthicola*	[49]
2-(2'-heptyl)-3-methyl-4-quinolone	*Burkholderia cepacia*	*Aspergillus niger* and other fungi	[44]
Alkylated benzene derivatives Phenol derivatives Naphthalene derivatives Benzothiazole 2-Ethyl-1-hexanol 2-Undecanol 2-Nonanone 2-Decanone 2-Undecanone Nonanal Decanal	*Bacillus amyloliquefaciens* NJN-6	*Fusarium oxysporum f.* sp. *cubense*	[45]
N,N-dimethyl- hexadecanamine	*Arthrobacter agilis* UMCV2	*Botrytis cinerea* *Phytophthora cinnammomi*	[46]
2-methyl-isoborneol	*Streptomyces alboflavus* TD-1	*Fusarium moniliforme*	[47]
1-Undecene 2-Nonanone 2-Undecanone	*Pseudomonas chlororaphis*	*Agrobacterium tumefaciens* *Synechococcus* spp. *Rhizoctonia solani*	[48]
Dimethyl disulfide 2-Heptanone	*Serratia proteamaculans*	*Agrobacterium tumefaciens* *Synechococcus* spp. *Rhizoctonia solani*	[48]
3-hexanone 1-dodecene isovaleric acid S-methyl-butanethioate S-methyl-methanethiosulfonate furfuryl alcohol acetophenone phenylpropanedione 2- acetylthiazole nitropentane	*Pseudomonas* spp.	*Phytophthora infestans*	[49]

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2-(2-Methylpropyl)-3-(1-methylethyl) pyrazine 2- Isopropylpyrazine 2- methyl-1-butanol Hexadecanal Isoamyl acetate	*Paenibacillus polymyxa* Sb3-1	*Verticillium longisporum*	[51]
Phenylethyl alcohol Methyl salicylate Ethyl phenylacetate Methyl anthranilate α-Copaene Caryophyllene 4-Ethylphenol Humulene	*Streptomyces fimicarius* BWL-H1	*Peronophythora litchii*	[52]
2,3,5-Trimethylpyrazine 2-Nonanone 2-Decanone 2-Dodecanone Dimethyl disulfide Dimethyl trisulfide	*Bacillus* spp. *Pseudomonas* spp.	*Fusarium* spp. *Colletotrichum gloeosporioides*	[53]
Hexanedioic acid, bis(2-ethylhexyl) ester Octadecane 1-Hexadecanol Docosane Chloroacetic acid, tetradecyl ester	*Bacillus atrophaeus* HAB-5	*Colletotrichum gloeosporioides*	[54]
2-methyl-1-butanol ethyl hexanoate 3-methyl-1-butanol ethyl octanoate phenylethyl acetate phenylethyl alcohol	*Pseudomonas chlororaphis* subsp. *aureofaciens* SPS-41	*Ceratocystis fimbriata*	[55]
2-methylbutyrate 2-phenylethanol	*Streptomyces yanglinensis* 3-10	*Aspergillus flavus* *A. parasiticus*	[56]
Isooctanol Linalool 3-Octanone 2-Naphthalene methanol 3-Undecanone 2-Tridecanone	*Corrallococcus* sp. EGB	*Fusarium oxysporum f.* sp. *cucumerinum* *Penicillium digitatum*	[57]
Dimethyl disulfide	*Pseudomonas fluorescens* B-4117 *P. fluorescens* Q8r1-96 Serratia plymuthica IC1270	*Agrobacterium tumefaciens* *A. vitis*	[58]
2,4-diacetylphloroglucinol Hydrogen cyanide	*Pseudomonas* sp. LBUM300	*Clavibacter michiganensis* ssp. *michiganensis*	[59]
Benzaldehyde Nonanal Benzothiazole Acetophenone	*Bacillus subtilis* FA26	*Clavibacter michiganensis* ssp. *sepedonicus*	[60]
3,5,5-trimethylhexanol Decyl alcohol	*Bacillus cereus* D13	*Xanthomonas oryzae* pv. *oryzae*	[61]
Toluene Ethyl benzene m-xylene Benzothiazole 2-decanol 2-tridecanol 1-undecanol Dimethyl disulfide Benzaldehyde 1-Methyl naphthalene	*Pseudomonas fluorescens* WR-1	*Ralstonia solanacearum*	[62]

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833 **Table 4. Examples of bacterial interactions with crops influencing quality parameters**

Crop plant	Bacterial species	Quality parameter(s)	Mechanism of interaction	Reference
Sweet basil	*Bacillus subtilis* GB03	Increased production of essential oils		[92]
Peppermint	*Pseudomonas fluorescens* WCS417r, *Bacillus subtilis* GB03, *Azospirillum brasilense* SP7	Increased production of essential oils		[93]
Atractylodes lancea	*Pseudomonas fluorescens* ALEB7B	Increased production of essential oils	Benzaldehyde mediates the effect	[94]
Strawberry	*Methylobacter* spp.	Production of aromatic compounds (furanones)	Bacterial alcohol dehydrogenase	[95,96]
Raspberry	*Methylobacter* spp., *Bacillus* spp.	Production of aromatic compounds (frambinone)		[109,110]
Strawberry	*Bacillus megaterium*	Production of aromatic compounds (2,3-dialkylacroleins)	Conversion of linear aldehydes	[111]
Basmati rice	*Acinetobacter* spp.	Production of aromatic compounds (2-acetyl-1-pyrroline)		[112]
Citrus, mango, cherry, litchi, peach	*Bacillus* spp.	Protection from spoliage	Antifungal action of cedrol and 2-pentylfuran	[97-102]
Strawberry, citrus, tomato, chili	*Streptomyces* spp.	Protection from spoliage	Antifungal action of acetophenone	[103-107]
Grapevine	*Paenibacillus* spp.	Production of aromatic compounds in wine production		[108]

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835 **Figure 1. Summary of VOC-mediated biological functions of plant-associated bacteria.**

836 Biological effects of plant-associated bacteria and their mechanisms of interaction with the host

837 plant and the environment can be exploited in the agricultural practice. The resident bacteria may

838 increase the availability of certain mineral nutrients, or stimulate plant growth and stress responses

839 by means of hormones or other signalling compounds. As a result, a better nutritional status and a

840 better ability to cope with stresses is achieved in the host plant. In their interaction with pests and

841 pathogens, plant-associated bacteria may act as direct competitors and/or predators with a biocidal

842 action, or exert a disturbance in long-range signalling, possibly influencing the pest's behaviour, its

843 recognition by natural enemies, and the expression of «social» phenotypes related to virulence in

844 pathogens.

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846 **Glossary**

847 **BCA**: Biological Control Agent, an organism exerting directly (e.g. by killing or predating) or indirectly

848 (by competition for resources, or through the action of other organisms) a limiting effect on the

849 population of a pest or pathogen.

850 **BVCs**: Bacterial Volatile Compounds, including organic (i.e. carbon-containing) and inorganic (e.g.

851 H_2S, nitrogen oxides) compounds.

852 **E-NOSE**: Electronic nose, a device including an array of electric sensors with differential affinity for

853 different chemical classes, and variating their electric conductance upon interaction with the

854 components of a gas blend. Used to compare gas samples, has good portability and ease of

855 operation, allows real-time analysis, but not chemical identification.

856 **FAIMS**: Field Asymmetric Ion Mobility Spectrometry, analytical method based on the separation of

857 ions in an oscillating electric field. Allows real-time analysis of gas profiles with good portability, and

858 can be coupled to GC-MS for chemical identification.

859 **GC-MS**: Gas Chromatography-Mass Spectrometry, analytical technique based on separation of

860 molecules in a gas mixture according to affinity to a chromatographic column, followed by their

861 fragmentation to yield a typical spectrum. Most used technique for identification of volatile

862 compounds.

863 **Gnotobiotics**: study of test organisms, in which the resident microbial community is artificial,

864 controlled and/or completely characterised.

865 **Holobiont**: the complex formed by a host organism and its associated microflora.

ISR: Induced Systemic Resistance, condition of increased and generalised plant resistance to potential pathogens and pests, activated after interactions with microbes (including beneficial symbionts).

Metagenomics: study of the complex of genomes associated in one super-organism, such as a plant with its associated microflora.

PTR-MS: Proton Transfer Reaction-Mass Spectrometry, analytical technique based on fragmentation of gas compounds in an electric field. Allows highly sensitive real-time detection and tentative identification of compounds.

QS: Quorum Sensing, bacterial communication system allowing the coordination of 'social' phenotypes (motility, biofilm formation, etc.) according to population density.

SIFT-MS: Selected Ion Flow Tube-Mass Spectrometry, analytical technique based on fragmentation of gas compounds in an air flow. Allows real-time detection and tentative identification of compounds.

VOCs: Volatile organic compounds, organic molecules characterised by low vapour pressure, high lipophylicity and low molecular weight, normally found in the gas phase in standard conditions.

Volatilome: the complete set of volatile compounds originating from an organism or biological system.

Bacterial function

Mechanism of action

Effects

availability of nutrients

hormonal effects

ecological signalling

pathogenesis

QS interference

direct toxicity

improved nutrition

shaping of plant architecture

activation of stress responses

efficient use of water

stimulation of plant defences

pest aggregation/deterrence recruitment of parasitoids

microbial antagonism

pest/pathogen population control

lower pathogen virulence

improved plant growth and crop yield

plant health protection