Volatiles in the Rhizosphere: Bioprospecting for Sustainable Agriculture and Food Security

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Abstract

Volatile organic compounds are low molecular weight lipophilic molecules with low boiling points and an appreciable vapor pressure under ambient conditions and constitute a small proportion of the total number of metabolites produced by living organisms. Volatiles are important aromatic compounds found in foods that evoke gustatory response in humans and animals. In addition they have important role in mediating communication between living organisms. Due to their roles as signaling molecules, within and between organisms, studies with regard to structural and functional diversities of these compounds are essential for an improved understanding of cellular and organismal communications in living systems. Since plant–microbe interactions are one of the most fascinating ecological phenomena that help to sustain the food cycle, ecological balance, and environmental stability, this chapter highlights the diversity of volatiles present in the plant rhizosphere. The rhizovolatiles discussed here include those produced by plants as well as by microorganisms inhabiting the rhizosphere. This chapter focuses on the role of these volatiles in the establishment of successful association between plants and other organisms and their beneficial effects on plant growth and development. This will value-add to our present understanding of the chemical cues defining the complexity and dynamism of rhizosphere functioning. At the end, this synthesis emphasizes on the potentiality of these volatiles for sustainable agriculture and food production to ensure food security.

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5.1   Introduction

Volatiles are defined as the group of chemical elements or compounds with low boiling point. These compounds could be naturally occurring or produced by activities of microorganisms, plants, animals, and humans (Abdullah et al. 2015a). The definition of volatile organic compounds (VOCs) depends on the frame in which this term is used (http://www.eurofins.com/voc.aspx). According to the World Health Organization (WHO), VOC is any organic compound whose boiling point ranges from 50 to 260 °C with saturation vapor pressure greater than 100 kPa at 25 °C (ISO 16000-6). Compared to the anthropogenic sources which emit an estimated 142 Tg of carbon per year, biological sources emit in much higher amount (1,150 Tg of carbon per year) (Goldstein and Galbally 2007). The majority of naturally occurring VOC is produced by plants (1 pg of carbon in the form of VOC annually), and the rest is produced by animals, microbes, and fungi, such as molds (Pichersky and Gershenzon 2002). VOCs include a wide range of ubiquitous aromatic compounds such as hydrocarbons, alcohols, aldehydes, acids, esters, amines, thiols, xylene, and monoterpenes, for example, α-pinene and trace amounts of insect pheromones. These compounds chiefly correspond to compounds responsible for flavors detectable by humans at below part per trillion (ppt) levels and are endowed with diverse physical properties (Table 5.1; Rowan 2011). Few mammalian pheromones, androstenone (5α-androst-16-en-3-one) and fecal indolic compounds, and skatole (3-methylindole) which have higher molecular weights and sufficient vapor pressure that can be clearly perceived by humans are also considered as VOC (Liberles 2014; Moore et al.1987). In particular, volatile compounds with low molecular weight (500 Daltons, Da) and high vapor pressure can diffuse in gaseous phase and hence serve as important signaling molecules (semiochemicals) within and between organisms. Although VOCs constitute only a small fraction of the total metabolites produced by an organism (1 % of the total metabolites), they take part in a wide range of biological processes (Dudareva et al. 2004; Rowan 2011). Thus measurement of the amount of the VOC produced and determination of their functional role are essential to understand the functioning of living systems.

The advent of technologies has led to the identification of volatile metabolites from different living organisms. Few databases have so far been developed that describe the volatiles and their biological functions (Abdullah et al. 2015a). The information on VOCs and their interactions with the organisms and contribution in the benefits of mankind pertaining to health, food, and industry are not well organized (Abdullah et al. 2015a; Dudareva et al. 2004, 2006). Although an extensive volume of literature exists on VOCs and their biosynthesis, our knowledge about their biological functioning and mechanism of action is still limiting (Holopainen

Table 5.1 Properties and source of different types of volatile organic compounds (VOCs)

Volatile	Source	Chemical class/ biosynthesis	Boiling point (°C) under 780 mm Hg
Androstenone	Mammalian pheromone	Steroid	372
α-Farnesene ($C_{15}H_{24}$)	Flower volatile and flavor precursor	Sesquiterpene	280
δ-Octalactone ($C_8H_{14}O_2$)	Microbial, dairy foods	Fatty acid oxidation	238
Dimethyl disulfide (CH_3SSCH_3)	Onion, garlic, coffee	Disulfide	109
Ethanol (C_2H_5OH)	Anaerobic respiration	Hydrocarbon	−102
Ethylene (C_2H_4)	Plant hormone	Alcohol	78
Hexanal ($C_6H_{12}O$)	Green leaf volatile	Aldehyde (lipoxygenase)	131
Isoprene (C_5H_8)	Plants (oxidative stress)	Terpenoid	265
Methanethiole (CH_3SH)	Biogenic	Sulfide	6
Skatole ($C_9H_9N_2$)	Feces	Aromatic heterocycle	78

and Blande 2012). This chapter highlights the biological activities of VOC associated with plant's rhizosphere which is an extremely ecologically important niche housing many of the complex interactions that occur between plant roots and microorganisms. A major part of this chapter provides a comprehensive description of the types of VOC produced by different plants and how these compounds mediate interactions between plants and microorganisms and macroorganisms residing in the vicinity of the roots. The second part of this chapter focuses on the functional relevance of the isolated rhizo-VOC from different plants with respect to agriculture and food production. Finally, we close this chapter by describing the limitations of the production of these volatiles and possible direction to solve the problems. In conclusion, we also highlight the plausible applications of these molecules in future economic benefits.

5.2   Volatiles Observed in the Rhizosphere

5.2.1   Rhizovolatiles of Plant Origin

An organism's interaction with its environment is fundamental to the survival of that organism and the performance of the ecosystem as a whole (Elton 1927). The association among the species includes four main types of two-way interactions: mutualism, commensalism, competition, and predation (herbivory and parasitism). Following the colonization in the terrestrial ecosystem, the "plants" as sessile organisms develop such interactions with innumerable micro- and macroorganisms for their survival and systemic functioning. The communication between plants and organisms is mediated through the exchange of chemicals which are synthesized and exuded by both plants and the partner-organisms. These chemicals lead to the development of a complex signaling network that culminates into the establishment

of a strong beneficial association between them. Rhizosphere, the narrow zone surrounding the plant roots, represents one of the most diverse habitats on the planet and houses many such interactions (Trabelsi and Mhamdi 2013). The dynamicity of the rhizosphere ecology is defined by the physicochemical and biological events defined by the host plant itself through uptake of water and minerals and subsequent release of nutrients and carbon dioxide, exudation, and secretion of an array of chemical compounds altogether defined as "rhizosphere processes" (Philippot et al. 2013). An amount of 5–20 % of all photosynthetically fixed carbon is released by the plants in the rhizosphere to create a carbon-rich environment for numerous beneficial and pathogenic micro- and macroorganisms (Steeghs et al. 2004).

5.3   Structural Diversity

VOCs form an important component of the host of compounds released by the plant through their roots in the rhizosphere. The important characteristics of plant VOC include their structural diversity, species-specific property, and tissue specificity (Wei et al. 2016). Some of these secondary metabolites are restricted to certain plant taxa at high concentration and have no apparent roles in plants' primary metabolism (Schoonhoven et al. 2005). They are secreted only at certain stages of development or under specific circumstances to provide signals for the physiological state of plant cells. It has been shown that a given tissue has similar VOC fingerprints at a particular stage of developmental (Wei et al. 2016). VOC secreted from plants, in general, have molecular weight less than 300 Da and boiling points lower than 260 °C (Dong et al. 2016). Till date, more than 1700 volatiles have been recognized from the aerial and non-aerial parts of plants. These constitute more than 90 families, comprising approximately 1 % of all currently known plant specialized metabolites (Pichersky and Gershenzon 2002; Dudareva et al. 2004). Ethylene, the potent activator of plant defense responses, was the first gaseous hormone discovered in nature (Bleecker and Kende 2000).

Plant VOC has been classified on the bases of their chemical structures, physiological functions, and biosynthetic pathways. They can act as endogenous hormones (e.g., ethylene, methyl jasmonate (MeJA), and methyl salicylate (MeSA)) or can mediate the interactions between cospecific and heterospecific plant species and with organisms of higher trophic levels (herbivores; pollinators; enemies of herbivores). The following are few major biosynthetic pathways that produce plant VOC. These include (1) *mevalonate (MVA)/2-C-methyl-D-erythritol 4-phosphate pathway (MEP)* producing terpenoids and carotenoid derivatives, (2) *shikimate and phenylpropanoids pathway* producing benzenoids and phenylpropanoids from aromatic amino acids (such as phenylalanine), and (3) *lipoxygenase (LOX) pathway* producing green leaf volatiles (GLV), methyl jasmonate, and fatty acid derivatives like alcohols and aldehydes (Figs. 5.1 and 5.2; Wei et al. 2016). VOCs are produced by the removal of hydrophilic moieties and oxidation, hydroxylation, reduction, methylation, and acylation reactions (Pichersky et al. 2006; Tzin and Galili 2010; Becker et al. 2015).

Methanol (cell wall expansion & maintenance) →Formaldehyde (oxidative demethylation; dissociation of 5,10- methylene-THF) → Formic acid (photorespiration & oxidation of glyoxalic acid) → CO_2

Ethanol (stress) → Acetaldehyde (pyruvic acid decarboxylation; wound responce) → Acetic acid (carbohydrate & fat decomposition) → Fatty acids, steroids, terpenoids, carotenoids.

Isoprene (oxidative stress) → Methyl venyl ketone(oxidative stress – drought, radiation)

Stored monoterpenes (ionization of GDP) → Ethanol (anoxic condition – root flooding)

Fig. 5.1 Production and metabolism of plant VOC. *GDP* geranyl diphosphate, *THF* tetrahydrofolate, *VOC* volatile organic compound

Herbivore-induced plant volatiles (HIPV) and oviposition-induced plant volatiles (OIPV) are by far the most studied plant VOC, specifically produced in response to arthropod herbivore feeding, damage, and oviposition (Becker et al. 2015). In intact plants, VOC with glycosidic linkage and the enzyme beta-glycosidase which degrades the glycosidic bonds are located in vacuoles and cell walls, respectively. This enzyme–substrate compartmentalization inhibits the hydrolysis. However, the exogenous beta-glucosidase from the herbivores during piercing–sucking–chewing of plant parts can hydrolyze the glycosidically bound VOC and release the VOC (Dong et al. 2015). Herbivore attack generates superoxide by the action of nicotinamide adenine dinucleotide phosphate complex. This superoxide is converted to H_2O_2 which induces activation signaling by VOC like jasmonic acid, salicylic acid, and ethylene that stimulates production of phytohormone (Dong et al. 2015).

HIPV can be broadly classified into two categories. Some are emitted constitutively, and the remaining are induced only upon herbivore attack. Hemiterpenes like isoprene, linalool, and *β*-myrcene belong to monoterpenes, (E)- *β*-caryophyllene from sesquiterpenes, and eugenol from phenylpropanoids and (E)-2-hexenol; a type of GLV is constitutively expressed. However, the levels of these VOCs are increased upon attack by the herbivores (Becker et al. 2015). On the other hand, (E)- *β*-ocimene, (E)- *β*-farnesene, methyl salicylate, methyl jasmonate, and (Z)-3-hexenyl acetate belonging to monoterpenes, sesquiterpenes, benzenoids, fatty acid derivatives, and GLV, respectively, are induced only due to herbivore attack (Becker et al. 2015). HIPV attract parasitoids and predators which feed upon herbivore arthropods as a defense response in the neighboring plants in addition to exerting toxic effects on the herbivores directly (Ode 2013; Gols 2014; Becker et al. 2015). This indirect defense mechanism through HIPV is evident in as many as 49 plant species belonging to 25 different families and insects from five different orders till date (Mumm and Dicke 2010). Through protection from the insects, HIPV also increases plant strength and fitness (Becker et al. 2015).

Secretion of sulfur-containing VOC by plant following attacks by herbivores constitutes a multi-trophic interaction between plants and parasitoids. Roots emit
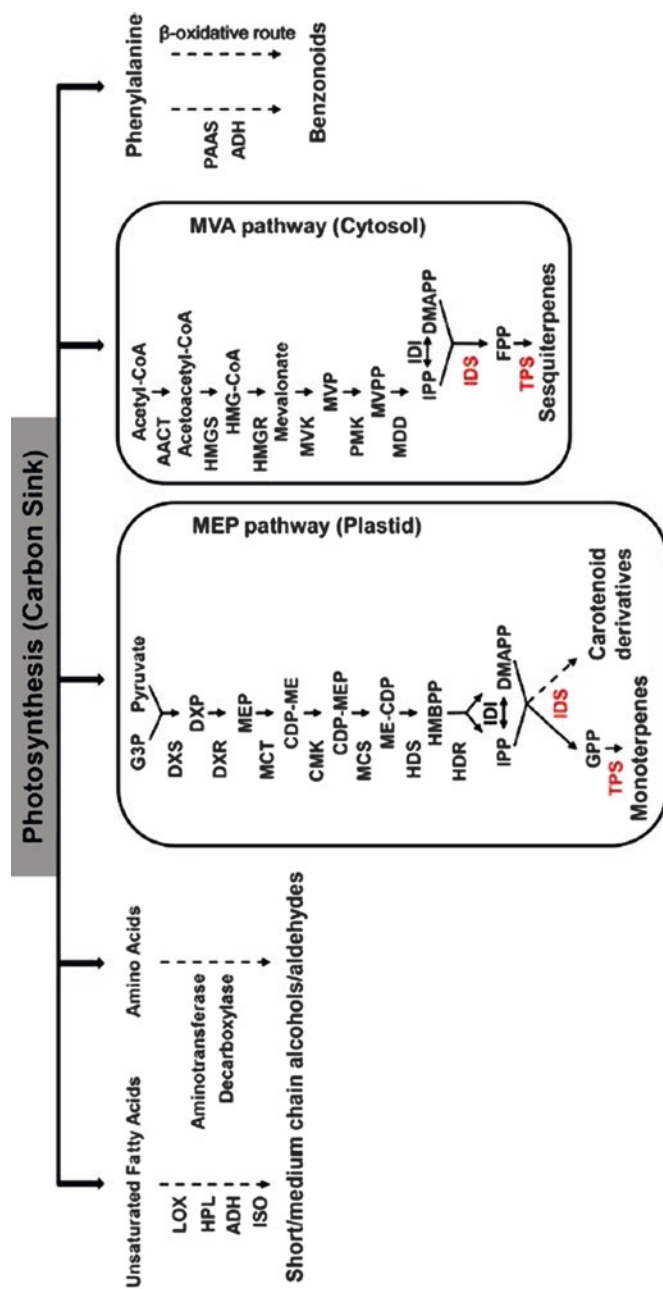
Fig. 5.2 Different pathways for synthesis of plant volatile compounds

higher amounts of sulfur-containing VOCs per gram dry mass than that of shoots (Kergunteuil et al. 2015). In this regard, the local emission of sulfur-containing VOC is more pronounced and temporarily dynamic in roots (Kergunteuil et al. 2015). Van Dam et al. analyzed the emission of sulfur-containing VOCs from herbivore-damaged roots of six *Brassica* species and correlated the findings with the composition of root glucosinolate which is a typical secondary metabolite involved in plant defense (van Dam et al. 2012). Upon root damage, glucosinolate is hydrolyzed to other VOCs such as thiocyanates, isothiocyanates (ITC), nitriles, and epithionitriles which act as signaling cues by the predators and parasitoids to trace the herbivorous hosts. This study showed that the emission of sulfide VOC is species and time dependent but not influenced by the type of damage or glucosinolate composition in the roots.

5.4   Functional Significance

VOCs are not directly involved in mediating growth, development, and reproduction in plant but participate in important ecological functions including inter- and/or intraspecies cross-talks, antimicrobial activities, and defense strategies against pests and pathogens (Abdullah et al. 2015a). They represent an important indicator for biological processes such as cell to cell communication, regulation of physiological processes, and modulation of interactions among a wide variety of organisms to maintain ecological equilibrium and environmental integrity (Patti et al. 2012; Fall et al. 1999). These semiochemicals function as hormones in the identification of mates, cospecifics, competitors, and predators (Abdullah et al. 2015b; Pichersky et al. 2006; Pichersky and Gershenzon 2002).

VOCs along with the nonvolatile compounds basically assist plants to adapt to the environment (Wei et al. 2016). They are emitted to act as attractants/repellants to/against the neighboring plants and other micro- and macroorganisms including herbivores, pathogens, pests, pollinators, and parasitoids, to assuage the heat and oxidative stresses, and to regulate the levels of systemic acquired resistance (SAR) to various diseases (Pichersky and Gershenzon 2002; Dicke et al. 2009; Frost et al. 2008; Schwarz et al. 2009). VOCs thus represent a key component in a plant's chemotype and have imperative roles in plant's ecosystem (Wei et al. 2016).

Application of high-throughput techniques such as proteomics and metabolomics has allowed to gather enormous information about the biochemical and molecular aspects of VOC, the mechanism of synthesis, and emission and explication of the probable functions of VOC. One of the frequently addressed questions is that why do plants emit volatiles. Investigations have proved that several factors such as endogenous circadian clock; various biotic stressors, e.g., pathogens and herbivore feeding; and abiotic stresses such as drought, heat stress, and ozone actually induce the release of VOC from plants (Dong et al. 2016; Holopainen and Blande 2012). The herbivorous-invertebrate feeding is considered to be one of the major triggers for VOC emission by plants (Holopainen and Blande 2012). The damaged roots transmit signals to distant parts and neighboring plants via VOC

(Holopainen and Blande 2012). The amount and proportion of VOC emitted allow the plant to send complex signals which then carry out assorted ecological functions including plant-plant communication and communication with second (herbivores and pollinators) and third (enemies of herbivores) trophic level organisms (Holopainen and Blande 2012).

In general, the communication in the root systems is based on nonvolatile hydrophilic exudates as water films shield the root surfaces and the soil particles, thereby allowing the free flow of air within the soil pores. Recent evidences imply that VOC are involved in root–root and root–microbial/pest interaction belowground as well (Schenkel et al. 2015). The alkaloids and phenolic compounds are the major signaling molecules found in the roots of the terrestrial plants grown in wet soil. These compounds mediate self-inhibition, avoidance of underground obstacles, and allelopathy. Studies with different varieties of barley cultivars demonstrated that VOC from one variety significantly allocated more biomass to the roots of the other varieties. This indicates that the phenomenon of coadaptation among different cultivars may be implicated for harnessing adaptation under various environmental conditions (Ninkovic 2003).

5.5 Mediators of Plant–Plant Communication

Peñuelas et al. have proposed plausible ecological roles of root-secreted VOC (Peñuelas et al. 2014). Volatiles emitted by underground roots regulate plant to plant communication mostly in the rhizosphere. This communication is important to distinguish between self-plants from the nonself ones. However the exact mechanism that differentiates different types of signals is not totally understood (Holopainen and Blande 2012). Experiments have shown that there is an increase in number and size of root branches when a number of nonself-plants grow together relative to that when the plants of same species are grown in the same place. This is possibly attributed to the increased availability of different kinds of nutrients for the plants growing in competition. Allogenetic recognition and physiological coordination among the roots also result in allocation of greater amount of resources for growth of the roots. This is believed to be mediated by VOC secreted by the plant roots. VOC, thus, functions in recognition of kins among the plants grown together (Holopainen and Blande 2012).

Volatiles such as sesquiterpene (E)-b-caryophyllene are induced in the roots to deal with heat stress and damage caused by insect feeding. (E)-b-caryophyllene forms 70 % of the total sesquiterpene secreted from the roots of *Copaifera officinalis* indicating the specificity of this compound in the legume's roots (Chen et al. 2009). In in vitro experiments in sand-filled olfactometer, (E)-b-caryophyllene was also produced from the damaged maize roots due to the rootworm (*Diabrotica virgifera*) feeding. It was also demonstrated that (E)b-caryophyllene evaporated and moved in humid sandy soil more swiftly. This latter observation indicates the rapid movement and transmission of signals by VOC among the neighboring roots.

5.6   Role in Plant Defense

In systemic acquired resistance (SAR) for various plants, viz., *Arabidopsis thaliana* and *Nicotiana tabacum* (tobacco), salicylic acid (SA)-binding proteins possessing esterase activity release the active defense volatile phytohormone SA through hydrolysis of methyl salicylate (MeSA) (Slaymaker et al. 2002; Vlot et al. 2008). The released SA is perceived by the receptors from the distant parts of the same plant or on the conspecific or heterospecific neighboring plants. In addition to this, neighboring plants might as well adsorb VOC and store them in the epidermis layers and release them to the atmosphere as and when needed.

   In a study, Wei et al. threw light on diverse composition of VOC and chief VOC synthesizing enzymes from different tissues including roots in cucumbers. An abundance of aromatic benzenoids particularly oxidized monoterpenes was detected in the roots of the cucumbers. TPS11 and TPS14 were the two *terpene synthase* genes identified to be involved in the synthesis of terpenoids in the roots of cucumber. This study provides a solid foundation for future investigations of both the physiological functions of VOC with respect to improvement of flavor in cucumber plants (Wei et al. 2016). Proton-transfer-reaction mass spectrometry (PTR-MS) analyses revealed that ethanol, acetaldehyde, acetic acid, ethyl acetate, 2-butanone, 2,3,-butanedione, acetone and the monoterpene, and 1,8-cineole are the major VOCs released from *Arabidopsis* ecotype Columbia (Col-0) during interactions with *Pseudomonas syringae* DC3000 and the aphid *Diuraphis noxia* (Steeghs et al. 2004). The interactions between the pathogenic fungus *Alternaria brassicicola* with cultured *Arabidopsis* roots showed a distinct pattern of VOC emission with a release of high abundance of ethanol in addition to acetic acid, acetone, ethyl acetate, and 1,8-cineole indicating a rapid switching to alcoholic fermentation mode of metabolism induced by pathogen. This suggests that the plant roots are proficient enough to adapt to the changing scenario in the rhizosphere. Fingerprinting of VOC with functional genomics thus establishes a link between gene regulation with metabolic pathways and synthesis of bioactive volatile synthesis in response to pathogenic invasion in particular plant species (Steeghs et al. 2004). A few studies have been reported that VOCs are secreted from plant roots in the presence of insects (Neveu et al. 2002). Methyl jasmonate (MeJA) is an example of such insect-induced VOC that triggers the release of proteinase inhibitors and polyphenol oxidase in undamaged neighboring plants. In another study, in response to contact with parasites, accumulation of phytoalexin was observed in bean and barley plants (Farag et al. 2013).

5.7   Diversity of Rhizovolatiles of Bacterial Origin

Microorganisms colonizing in plant rhizosphere produce a large battery of VOC which manipulate the assembly and activity of rhizobacteria/fungi in the host and neighboring plants. Microbial activities include mineral sequestration, nutrient assimilation, metal sorption, substance solubilization, toxin removal, pathogen

repulsion, and disease suppression (Bailly and Weisskopf 2012; Kai et al. 2016). Effects of microbial VOC on plants vary within a particular combination of plant and microbial species as well as other biotic and abiotic factors (Schmidt et al. 2015).

Plant-associated microbiome practically covers the entire plant surface. They are especially profuse in the nutrient-rich rhizosphere where the competition between the different organisms is high (De Vrieze et al. 2015). Approximately 400 of the 10,000 described microbial species have been shown to produce VOC (Ortíz-Castro et al. 2008). Till date, 1,088 VOCs identified from 517 microorganisms have been clustered in KNApSAcK Metabolite Ecology Database (Abdullah et al. 2015a). A total of 77 species of these are "pathogenic bacteria" that can be grouped into six clusters, of which again three clusters contain 100 % pathogenic species including *Pseudomonas aeruginosa*, *Klebsiella pneumoniae*, and *Escherichia coli*, while the remaining three clusters contain both pathogenic and nonpathogenic bacteria. Among 517 microorganisms, 92 species emit only one type of VOC, while 14 have been reported to emit 50 different types of VOC (Abdullah et al. 2015a). This statistical data confirms that a few microbial VOCs can act as its odor fingerprint. A total of 341 bacterial VOC from 1,044 species were reported to be associated with 11 types of biological activities. Of these, 57.3 % of the biological activities are related to chemical ecology which includes plant growth enhancement, antimicrobial, antifungal, attractant, defense, root growth inhibition, and repellent activities (Figs. 5.3 and 5.4; Table 5.2; Abdullah et al. 2015a). It is noteworthy to mention that the chemical structure of VOC determines their biological activities. Isoprenes, terpenes, alkanes, alkenes, alcohols, esters, carbonyls, and acids are volatiles that help in communication between microbes in a rhizo-consortium and the plants (Kai et al. 2007; Vespermann et al. 2007).
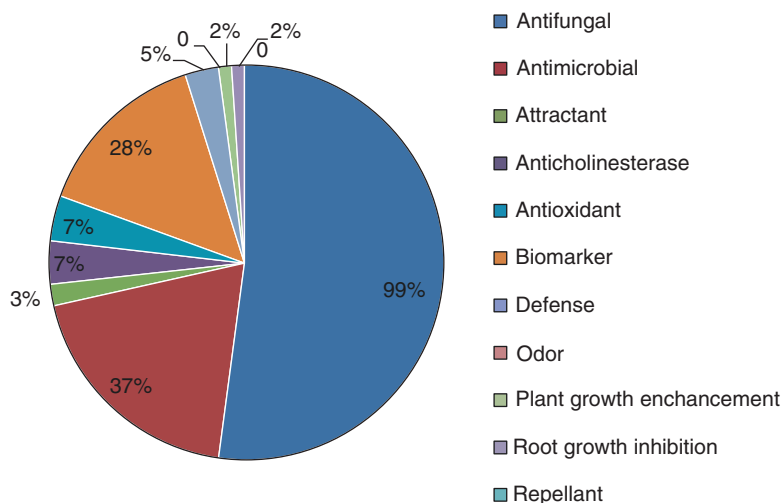

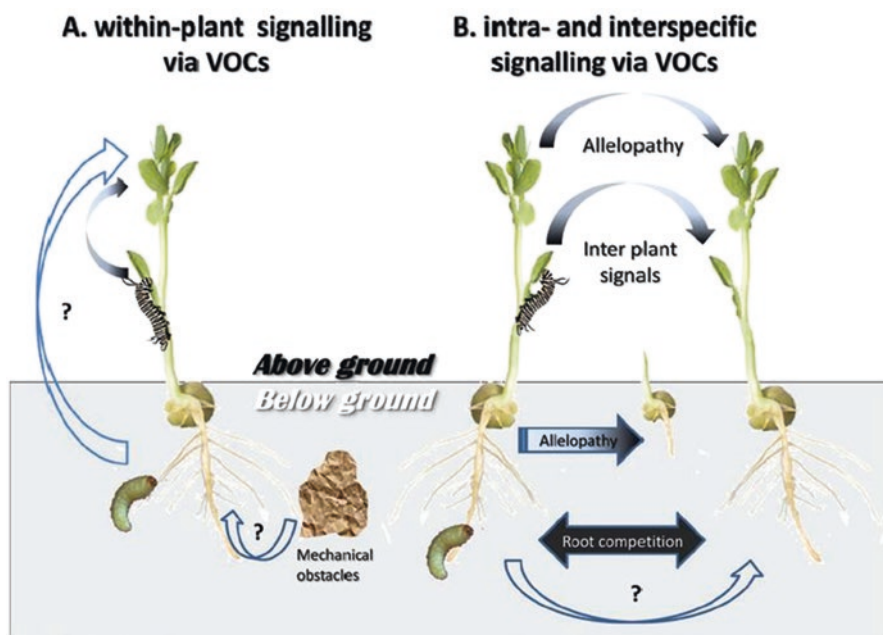**Fig. 5.3** Proportion of bacterial species producing different volatiles with different functions

Fig. 5.4   Role of plant volatiles in aboveground and belowground signaling

Table 5.2   Bacterial volatiles and their functions

Cluster ID (count of VOCs)	Chemical structure	Related biological activities
Cluster 1 (55)	Terpenoids	Antimicrobial; anticholinesterase; defense; antioxidant
Cluster 2 (33)	Hydrocarbons	Antimicrobial; anticholinesterase; antioxidant
Cluster 3 (41)	Alkanes	Biomarker
Cluster 4 (18)	Alkenes	Antifungal
Cluster 5 (21)	Aldehydes, esters, carboxylic acid, ketone	Antimicrobial; antioxidant; biomarker; anticholinesterase; repellant
Cluster 6 (25)	Alcohol and alkanes	Plant growth enhancement; root elongation inhibition; odor
Cluster 7 (47)	Ester, carboxylic acid, ketone	Attractant; biomarker
Cluster 8 (15)	Epoxide, ether, ester, alcohol	
Cluster 9 (42)	Aromatic alcohol, carboxylic acid, ester, ketone, ether	Attractant
Cluster 10 (14)	Aromatic compound	Biomarker
Cluster 11 (30)	Diverse (C0-C6 molecules)	Biomarker

5.8 Beneficial Roles of Bacterial VOC

We are beginning to understand the effects of bacterial VOC on the growth and development of plants. The effects of bacterial VOC on plant growth (promotion and/or inhibition) have been nicely reviewed by Bailly and Weisskopf (2012). In general, bacterial VOCs mediate multiple functions of intra- and interspecies communication such as bacterial quorum sensing, growth and differentiation, inhibition of phytopathogenic fungal growth and differentiation, plant health and growth promotion (direct/indirectly), and antibiotic and stress resistance (De Vrieze et al. 2015).

Bacterial volatiles contribute in mineral utilization of plants. One notable example is during iron homeostasis in plants under iron-limiting conditions (Zamioudis et al. 2015). VOC from ISR-inducing *Rhizobacteria* like *Pseudomonas putida* WCS358 (recently renamed *Pseudomonas capeferrum* WCS358; Berendsen et al. 2015) was found to efficiently activate the expression of root transcription factor MYB7 and iron uptake-related genes including ferric reduction oxidase (FRO2) and iron-regulated transporter1 (IRT1) in *Arabidopsis* independent of the iron availability in the vicinity of the roots (Zamioudis et al. 2015).

This observation suggested that VOCs interact with cellular processes of plants that rapidly utilize the iron from the internal iron storage of plants and enhance the need for iron acquisition. Besides WCS358, seven other strains from the genus *Pseudomonas* and the phylum *Actinobacteria* could also potently activate the promoter of MYB72 gene suggesting that the members of the natural root microbiota play an important role in upregulating the capacity for iron uptake in the plant roots. To investigate the mechanisms of action of VOC from *Bacillus subtilis* in promotion of plant growth, Meldau et al. showed that B55 strain contributed to sulfur nutrition in *Nicotiana attenuata* (coyote tobacco) roots by increasing the sulfur absorption ability of the plants (Meldau et al. 2013). Other VOCs, viz., 13-tetradecadien-1-ol, 2-butanone, and 2-methyl-n-1-tridecene identified from *Pseudomonas fluorescens* SS101, were found to increase the number of lateral roots (Park et al. 2015).

VOC function is one of the chief determinants of induced systemic resistance [ISR] and induced systemic tolerance [IST] to abiotic stresses, such as drought and heavy metals in variety of plants including *Arabidopsis thaliana* (Zamioudis et al. 2015). With the help of VOC, plant growth-promoting rhizobacteria (PGPR) elicit ISR and plant growth promotion even in the absence of physical contact with plants. Initial research was conducted on the emission of VOC from plant growth-promoting bacteria (PGPB), *Bacillus* sp., which evoked ISR and also enhanced plant growth and development by improving plant mineral nutrition (Ryu et al. 2003, 2004a, b). VOC from *Bacillus subtilis* strain GB03 was shown to stimulate iron uptake mechanisms in *Arabidopsis*, thereby improving the iron content of the plants (Zamioudis et al. 2015). Following this discovery, numerous researches were undertaken to identify VOC from different species belonging to *Bacillus* and non-*Bacillus* genera and to study their role in plant growth promotion and disease suppression

(Yi et al. 2016). A number of in vitro culture-plate assays have been performed with different plant species incubated with PGPR, and the VOCs secreted from the bacterial species were identified. Petri dish bipartite studies have shown that acetoin and 2,3- butanediol secreted from *Enterobacter cloacae* JM22, *Pseudomonas fluorescens* 89B61, and *Pseudomonas chlororaphis* O6 could promote *Arabidopsis* growth through ISR (Kai et al. 2016). 2,3-Butanediol is one of the most well-characterized compounds isolated from a host of Gram-positive and Gram-negative bacteria, namely, *Aerobacter* sp., *Bacillus* sp., *Enterobacter* sp., *Klebsiella* sp., and *Serratia* sp. (Yi et al. 2016). Yi et al. demonstrated that 2,3-butanediol secreted by *Bacillus subtilis* has protective role both for the plants and the microbes with the subsequent development of ISR via ethylene and auxin homeostasis (Yi et al. 2016; Kanchiswamy et al. 2015). In another study, exogenous applications of 2,3-butanediol and its precursor 3-hydroxy-2-butanone (syn. acetoin) isolated from *Bacillus subtilis* GB03, *Bacillus pumilus* SE34, and *Bacillus amyloliquefaciens* IN937a were found to promote the growth of *Arabidopsis* plants (Farag et al. 2013; Kai et al. 2016). 2,3-Butanediol suppressed the growth of soilborne pathogen *Rhizoctonia solanacearum* and enhanced the growth of biocontrol *Pseudomonas protegens* Pf-5. The composition of root exudates is modified by 2,3-butanediol which in turn influenced the selectivity of the bacterial species in the rhizosphere. Thus in short 2,3-butanediol plays a role in the recruitment of the bacterial species at the junction of plant roots. It also activated the synthesis and secretion of defense molecules such as salicylic acid and ethylene from the plant roots and thereby enhanced the plant immunity. A study had shown that 2,3-butanediol promoted the robustness of the bacteria by protecting them against low pH of the rhizosphere by creating an alkaline environment during multiplication of bacterial cells. These together explained the role of 2,3-butanediol in promoting bacterial fitness and stability in the rhizosphere. In addition to this, 2,3-butanediol ensures optimal functions of the cell wall-degrading enzymes such as cellulase, pectinase, and protease and acts as an important factor responsible for virulence of *Pectobacterium* sp. and *Dicheya* sp., the causative agents for soft-rot disease (Kwan et al. 2013). VOC from *Pseudomonas chlororaphis* promoted growth by eliciting systemic resistance against the bacterial pathogen *Erwinia carotovora* in tobacco (*Nicotiana tabacum*) plants via GacS kinase-dependent production of 2,3-butanediol (Han et al. 2006). *Pseudomonas chlororaphis* also increased drought tolerance by stimulating the synthesis of jasmonic and salicylic acids in plants (Kanchiswamy et al. 2015). Numerous other bacterial VOCs such as those secreted from *Burkholderia cepacia* and *Staphylococcus* sp. have also been detected in the plant rhizosphere. These compounds have shown to improve plant growth. Along with *Bacillus* sp., volatiles from *Stenotrophomonas* and *Serratia* inhibited the growth of mycelia of pathogenic fungus *Rhizoctonia solani* and promoted growth in *Arabidopsis thaliana* seedlings, while the volatiles from *Burkholderia cepacia* and *Pseudomonas* sp. retarded the growth of the fungus to an extent.

5.9   Regulation of Secretion of Bacterial Volatiles

Secretion of VOC by the bacteria in the rhizosphere is greatly influenced by exact nature of multi-trophic interaction taking place in the rhizosphere. Following is an example of how quorum sensing may be modulated by VOC. It has been noticed that 2,3-butanediol stimulates GacS kinases which regulate the synthesis acyl-homoserine lactones (AHLs), a key molecule utilized by the bacteria to communicate with neighboring organisms (Han et al. 2006). Emission of the volatile metabolite 2-aminoacetophenone by *Burkholderia ambifaria*, *Pseudomonas aeruginosa*, and *Streptomyces* sp., on the other hand, is found to be regulated by the quorum sensing signals (Kai et al. 2016). This actually culminates into a nonrandom loss in bacterial communities and hence the pattern of metabolite secretion (Hol et al. 2015; Schulz-Bohm et al. 2015). Fungal VOCs have been shown to alter thermostability of *Collimonas pratensis* and *S. plymuthica* PRI-2C (Schmidt et al. 2015). In a study, de Vriez et al. identified a series of compounds such as dimethyl trisulfide (DMTS), S-methyl methanethiosulfonate (MMTS), nitropentane, isovaleric acid, undecanal, phenylpropanedione, propiophenone, and the simple ketones 3-hexanone, 2-decanone, and 2-undecanone secreted from different strains of *Pseudomonas* to elicit anti-oomycete potential against *Phytophthora infestans* in potato plants (De Vrieze et al. 2015). These compounds inhibited the growth of mycelium in *Phytophthora infestans* in addition to harboring sporicidal activities (De Vrieze et al. 2015).

5.10   Bioprospecting of Volatiles

A large number of VOC obtained from microbes and plants are used by humans as food additives or flavors, drugs, and fragrances and in agriculture (Schenkel et al. 2015). The use of VOC as an alternative novel strategy in sustainable agriculture and crop production has only recently been explored (Kanchiswamy et al. 2015). A large body of literature has already documented in vitro effects of VOC in plant growth promotion. Studies are ongoing to examine the suitability of several HIPVs to enhance the efficacy of biological control agents (reviewed in Peñaflor and Bento 2013). The strategies using plant VOC may be classified under four major categories. These include (1) selection and growing of plant cultivars that can release HIPV to attract natural enemies, (2) application of exogenous elicitors in the plants for induction of defense response, (3) release of synthetic HIPV to recruit natural enemies for the crops directly, and (4) manipulation of target genes of HIPV to enhance the production and release of volatiles and also to hasten the induced defense responses.

Studies with various inbred lines of corn and cotton crops have revealed the blends of HIPV vary among plant cultivars affect natural enemy foraging (Peñaflor and Bento 2013). Keeping in line, (E)-β-caryophyllene secreted by European varieties helps the host to find entomopathogenic nematodes more efficiently than the North American varieties, making the former a better biological control of the

nematode (Rasmann et al. 2005). Therefore, selection of cultivars is important for improving biological control.

To develop crop plants with better pest resistance, plant metabolism may be engineered to target the pathways involved in VOC synthesis and regulation. The strategies usually involve manipulation of expression of genes related to terpenoid synthesis (TPs) and have been employed in model plants like *Arabidopsis* and crop plants like cotton and rice (Peñaflor and Bento 2013). The transgenic lines (Bt cotton and Bt rice) with manipulated synthesis and secretion of terpenoids are capable of attracting natural enemies better, which eventually affect the tripartite interactions of the plant with the insects and nematodes. Jasmonic acid, salicylic acid, and their metabolites such as methyl jasmonate, cis-jasmonate, and methyl salicylate are widely used as exogenous elicitors. These molecules function as fake signals to trigger the emission of a blend of toxins and HIPV even from the undamaged plants. As a result of these signals, the undamaged crops become more resistant to herbivore damage and begin to recruit natural enemies to both herbivore-infected and noninfected plants. Methyl salicylate (MeSA) is one of the strongest candidates often used as a synthetic plant volatile. It attracts a wide range of natural enemies in the field and aids to biological control by suppressing herbivore populations. Dimethylhexadecylamine, secreted by *Arthrobacter agilis* strain UMCV2, was found to modulate the morphogenesis in *Medicago sativa* in vitro by increasing the plant biomass and the length of the stem and the roots (Aviles-Garcia et al. 2016). In petri plate assays, it enhanced the formation of lateral roots indicating the role of this compound in plant growth and development. The racemic mixture of (RR) and (SS) isomers of 2,3-butanediol isolated from *Bacillus subtilis* GB03 and *Bacillus amyloliquefaciens* IN937a was found to trigger ISR when applied exogenously in *Arabidopsis* seedlings and also reduced the severity of the pathogenesis caused by *Erwinia carotovora* subsp. carotovora. Acetoin and 2,3-butanediol produced by different strains of *Bacillus subtilis* GB03 have been shown to affect the protective strategies of *Arabidopsis* upon infection. Both the transgenic and mutant lines of *Arabidopsis* showed stimulated defense response against *Bacillus subtilis* through increased production of ethylene. These studies highlight the role of bacterial VOC as plant defense stimulators, an observation which may be applied in agricultural field studies in future. In fact, VOCs have been applied in open-field studies very recently for sustainable protection of crops (Song and Ryu 2013). Application of VOC in open field thus remains a promising area to explore.

5.11   Conclusion

Small VOC emitted from microorganisms and the plants form important signaling molecules and have dramatic effects on plant development and thereby might be of help in better crop production and sustainable agriculture. However, the lack of techniques to isolate and identify VOC has resulted in gaps in knowledge regarding the functioning of VOC in rhizosphere. Therefore, to study the potentiality of VOC in situ, modeling of native rhizosphere system and developing rhizosphere

platforms by combining various sets of microorganisms and plant species, is very much essential. This artificial system will mimic the functions and interactions of VOC actually occurring in an environmental niche and will provide a better understanding of the functionality of VOC. The elucidation of probable functions of VOC will provide solutions to exploit VOC toward developing cost-effective and eco-friendly strategies in agricultural practices worldwide by replacing the necessity for genetic modification and use of harmful pesticides, fungicides, and bactericides. The knowledge on VOC composition from plants will help to engineer hypersensitive genetically modified crops with better VOC secreting capabilities. The use of these plants in agricultural fields will confer enhanced protection in the neighboring plants through long-distance SAR via the released VOC. VOC may also be used to direct the plants toward the applied biological control agents (BCA) in field studies. In addition, VOC might have a great application toward development of trap crops to attract pests. Thus, volatiles may provide solutions for the development of ecologically feasible and environmental friendly approach toward crop protection in the future, thereby minimizing pest attacks and subsequent agricultural and economic losses. However, the strategies need to be developed for the appropriate use of volatiles in accordance to the geographical location and climatic conditions of a region, also considering the flora and the fauna constituency of the country. This can empower the biological control of harmful crop pests worldwide consequently leading to successful biological control programs.

Highlights
- Volatile organic compounds (VOCs) are small lipophilic compounds with low boiling points and high vapor pressure and produced as secondary metabolites from both micro- and macroorganisms.
- VOCs are important factors for aromatization of foods as well as key signaling molecules for inter- and intraspecies communications, taking part in plant–microbe and microbe–microbe interactions in rhizosphere.
- Plant VOCs have been classified on the basis of their chemical structures, physiological functions, and biosynthetic pathways and are mostly characterized by their structural diversity, species-specific property, and tissue specificity.
- Endogenous circadian clock, biotic stressors like pathogens and herbivore feeding, and abiotic stresses like drought, heat stress, and ozone actually induce the release of VOC from plants, the most important being the herbivore-induced plant volatiles (HIPV).
- VOCs from plants are the chief molecules for underground communication between neighboring plants and the other micro- and macroorganisms, helping in kin recognition, self-avoidance, systemic acquired resistance (SAR), long-distance signaling, defense response, and allelopathy.

- Bacterial VOCs (BVOCs) mediate multiple functions of intra- and interspecies communication such as bacterial quorum sensing, growth and differentiation, inhibition of phytopathogenic fungal growth and differentiation, direct or indirect plant health and growth promotion, induced systemic resistance (ISR), development of antibiotic, and stress responses.
- 2,3-Butanediol is one of the most well-characterized BVOCs isolated from a host of Gram-positive and Gram-negative bacterial groups including *Aerobacter* sp., *Bacillus* sp., *Enterobacter* sp., *Klebsiella* sp., *Pseudomonas* sp., and *Serratia* sp.
- The methods practiced for sustainable agriculture can be grouped under four major functional categories, namely, selection of plant cultivars with high defense response, application of exogenous elicitors and synthetic HIPV, and genetical manipulation of target genes of HIPV to enhance the production and release of volatiles and also to hasten the induced defense responses.
- In vitro and a few field-based studies on the use of BVOC in crop plants have elucidated upon the application of VOC as an alternative novel strategy for sustainable agriculture and crop production by replacing the chemical fertilizers and pesticides.

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