

Allelopathy

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Contributor: Xu Han

Allelopathy is an ecological phenomenon in which organisms interfere with each other. As a management strategy in agricultural systems, allelopathy can be mainly used to control weeds, resist pests, and disease and improve the interaction of soil nutrition and microorganisms. Volatile organic compounds (VOCs) are allelochemicals volatilized from plants and have been widely demonstrated to have different ecological functions.

allelochemicals

VOCs properties

VOCs action

VOCs detection

green agriculture

1. Introduction

The concept of “allelopathy” was first proposed by Austrian scientist Hans Molisch in 1937 and mainly referred to the chemical relationship of plant interaction. Allelopathy is an ecological phenomenon and plays an important role in the ecological adaptation of plants [1][2]. The allelopathic effects have both positive and negative effects. Various studies have reported the advantages of allelopathic effects in agricultural systems, such as weed control [3][4][5][6], inhibition of pests [7][8][9][10], disease [11][12], improvement of soil nutrition [13][14], and microbial interactions [15][16]. Ultimately, allelopathy of most plants has effect on plant growth [10][17][18]. Plants can synthesize various secondary metabolites during growth and development. Plant Volatile organic compounds (VOCs) vary by species, and they are related to the abundance of neighboring plant species and plant species composition [19][20]. These secondary metabolites can be beneficial or harmful to other organisms when stored or released into the environment, such as secondary metabolites stored in plants that can prevent animal feeding and microbial infestation, while volatiles released into the air can attract insect pollinators [21]. Plants communicate with organisms in the environment through VOCs, thereby achieving a wide range of ecological functions, such as affecting their growth, development, defense, reproduction, and life cycle [22]. In 1984, allelopathy was defined as “any direct or indirect harmful effect by one plant (including microorganisms) on another through production of chemical compounds released into the environment” by Rice [23]. These products of secondary metabolism, called allelochemicals, can be found in any organ of the plant (leaves, stems, flowers, seeds, fruits, and/or roots) and can be released from the producing plant by different routes: volatilization, foliar leaching, root exudations, and decomposition of plant residue (**Figure 1**).

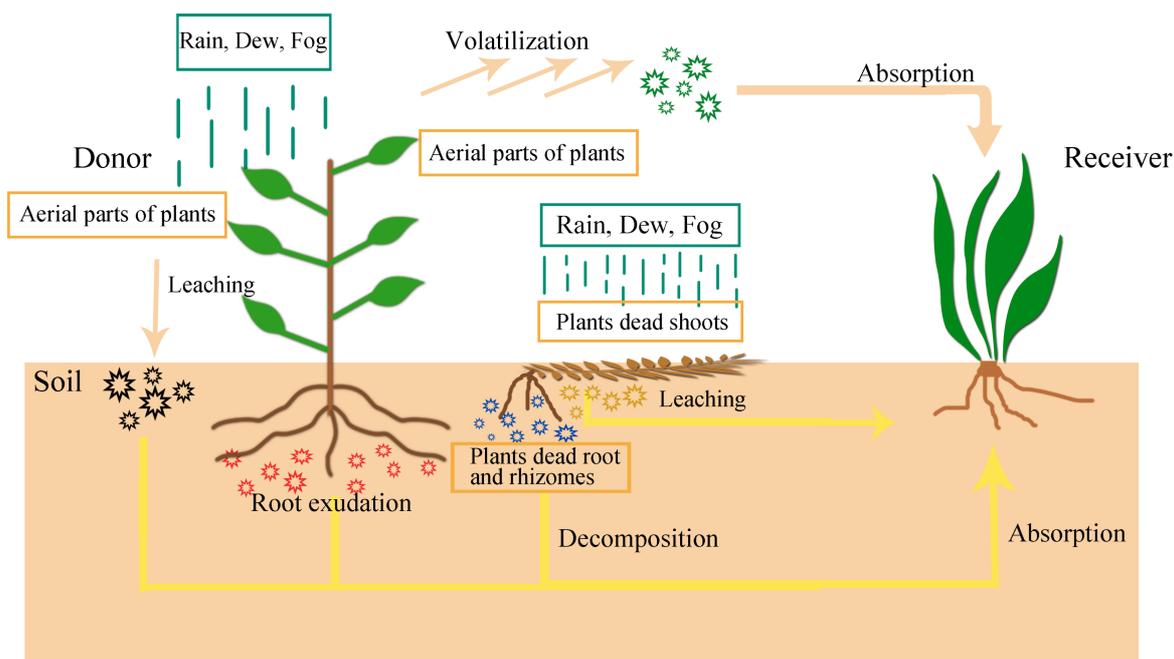


Figure 1. The allelopathy pathways of plants.

VOCs are secondary metabolites volatilized by plants and ubiquitous allelochemicals of plants [24]. Shikimate/phenylalanine, the mevalonic acid (MVA), the methylerythritol phosphate (MEP), and lipoxygenase (LOX) pathways are the four main synthesis pathways of VOCs, and plants can synthesize and release various VOCs including terpenoids, phenylpropanoids/benzenoids, and fatty acid derivatives [25]. The VOCs released by these plants often have different ecological functions, such as chemical communication, kin recognition, attracting or repelling insects, and many other effects [21][26][27][28][29]. Although the researches of plants VOCs are mainly aboveground some chemical signal, more and more studies show that VOCs also play an integral part in belowground plant–plant interactions [30]. In fact, the phenomenon that plants release allelochemicals through the volatile pathway has been noticed for a long time. One of the first empirical studies of allelopathy involving VOCs was researched by Molisch, who found that VOCs released by apples and pears could inhibit potato germination [31]. VOCs have been widely demonstrated to defend primarily against herbivorous insects [32][33], microbes, and pathogens [34][35][36], thereby reducing extreme environmental stress [37][38] and promoting nutritional acquisition [11]. Muller et al. [39] researched the volatiles of annual grassland species in *Salvia leucophylla* Greene and *Artemisia californica* communities, and this revealed that volatile allelochemicals had the interspecific allelopathic effects on the woody herbaceous plants, which would negatively affected the recipient plant species [40][41] and changed soil microorganisms [42][43]. Besides, in addition to VOCs released from plant shoots, root volatiles may also have allelopathic effects on neighboring plants; for example, VOCs from big sagebrush (*Artemisia tridentata* Nutt.) root inhibited seed germination of wild tobacco (*Nicotiana attenuata*) [44]. Most allelochemicals produced by plant roots are considered as “root exudates” [45], but the few allelochemicals released by volatilization of roots are called VOCs, which play an important ecological role in the soil ecosystem and have not been studied thoroughly [46][47].

Allelopathy has received high attention and become one of the central scientific problems in ecology [48]. Allelopathy is forming an independent scientific system, and we are conducting in-depth and extensive research from both theoretical and practical aspects. VOCs released by plants are one of the main ways to achieve allelopathic effects. It is a more economical, environmentally friendly, and effective measure to use the allelopathic effect of plant natural products to develop the agricultural production [49]. Several excellent reviews have summarized the relevant research on potential applications of VOCs [20][22][49], but the studies on allelopathy of plants VOCs have not been systematically reviewed and reported. VOCs are a kind of natural and environmentally friendly chemical substances that volatilize from plants and are used as natural herbicides and fungicides to protect neighboring plants from stress and increase crop yields [49]. We think VOCs have a much broader range of the potential applications. So, in this context, study on the allelopathy of VOCs is particularly important to the future development of green agriculture. The review mainly focuses on the recent studies of allelopathy of plants VOCs, regarding resisting diseases and preventing pests of plant, impacting on competition (inhibiting weed hazards), breaking dormancy, regulating plant growth, affecting reactive oxygen species (ROS) content and enzyme activity, modulating plant respiration and photosynthesis, and their role as a signal conducting substance. We present the evidence from the references to illustrate these roles to deepen the understanding of allelopathy of plants VOCs.

2. Method of VOCs Collection and Identification

The allelopathy of VOCs has attracted widespread attention in recent years and a lot of research work has been done. With the advancement of organic separation and identification technology and the participation of more and more experts, the collection and identification technology of plants VOCs is no longer a difficult issue in research.

2.1. Collection of Plants VOCs

The volatiles mostly are organic compounds with a molecular weight between 100 and 200, such as hydrocarbons, alcohols, ketones, organic acids, nitrogen compounds, and organic sulfur [50]. Most of them have high chemical activity. Different collection methods may directly affect the type and proportion of VOCs, so it is particularly important to choose the appropriate method.

Traditional distillation collection techniques include steam distillation (SD), simultaneous distillation and solvent extraction (SDE), microwave-assisted hydrodistillation extraction (MWHD), ultrasound-assisted extraction (USE), and solid-phase trapping solvent extraction (SPTE). They have certain disadvantages in the isolation and purification of chemical constituents from plants tissues, such as long extraction time, high volumes solvent, and low efficiency [51]. In addition, many natural products are thermally unstable and may degrade during thermal extraction or distillation.

The most mainstream approach is headspace solid-phase microextraction (HS-SPME). It has some advantages over SD, SDE, and SPTE, such as rapid solvent-free extraction, no apparent thermal degradation, less laborious manipulation and sample requirement, and so on [52]. Moreover, due to the relatively low temperature and short headspace solid-phase extraction time, the risk of thermal artifacts is extremely low compared to other techniques

[53]. Additionally, it is easy to standardize and fully integrate into the analysis system [54]. Thus, HS-SPME is an ideal technology of plants' VOC collection.

2.2. Identification of Plants VOCs

Identification of allelochemicals involves both quantitative and qualitative measurement. Qualitative identification is the identification of the type and structure of the allelochemicals. Qualitative identification involves methods such as gas chromatography (GC), mass spectrometry (MS), nuclear magnetic resonance (NMR), Fourier transform infrared (FT-IR) spectroscopy, and many other methods [55][56][57]. These are the analysis methods of VOCs, but the analytical difficulties and required instruments are completely different. Quantitative identification means the determination of the concentration of allelochemicals on the premise of clarifying the type of them. The method of chromatography is used to detect the concentration of known substances. Different methods should be selected for qualitative and quantitative identification, and the selection criteria are determined according to the characteristics of VOCs.

The existing identification techniques include gas chromatography mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), proton-transfer-reaction mass spectrometry (PTR-MS), and so on. PTR-MS has the potential to sample VOCs on-line and make quantitative analysis fast without any sample preparation [58][59]. The most widely used of these identification techniques is GC-MS [60]. Although PTR-MS can better achieve quantitative identification, most of the volatiles identified are preliminary [61]. GC-MS has a higher selectivity and sensitivity in the identification of VOCs and efficient separation and identification of the analytes.

3. Conclusions

Herein summarizes the allelopathy of VOCs of plants including growth, competition, dormancy, resistance of pests and diseases, respiration, photosynthesis, ROS content, enzyme activity, and signaling. It also summarizes the main methods of collection and identification of VOCs. The study of allelopathy is quite a complicated work, because it involves a variety of disciplines such as chemistry, ecology, biology, microbiology, and so on. Scientists in these fields need to work together to conduct research. The study of allelopathy on plants VOCs is still a new field. Most of the researches still focus on the expression of the allelopathic phenomenon, but the depth and breadth of them are far from enough, such as the lack of research on allelopathy mechanisms of plants, the relationship between chemical recognition and communication mechanisms and allelopathy mechanisms, and so on. In recent years, we have seen more and more reports on VOCs. VOC transmission, emission, and accumulation are also hot topics in research, which deserve more research attention. There are still many issues that need to be further explored. Plant VOCs deserve more research attention.

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