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Review

Crop Allelopathy for Sustainable Weed Management in Agroecosystems: Knowing the Present with a View to the Future

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Abstract: In the face of yield losses caused by weeds, especially in low-input agricultural systems, and environmental pollution due to the excessive use of synthetic herbicides, sustainable weed management has become mandatory. To address these issues, allelopathy, i.e., the biochemical phenomenon of chemical interactions between plants through the release of secondary metabolites into the environment, is gaining popularity. Although many important crops are known for their allelopathic potential, farmers are still reluctant to use such knowledge practically. It is therefore important to assist advisors and farmers in assessing whether allelopathy can be effectively implemented into an eco-friendly weed management strategy. Here, we aim to give a comprehensive and updated review on the herbicidal potential of allelopathy. The major findings are the following: (1) Crops from different botanical families show allelopathic properties and can be cultivated alone or in combination with other non-allelopathic crops. (2) Many allelopathic tools can be adopted (crop rotation, intercropping, cover cropping as living or dead mulches, green manuring, use of allelochemical-based bioherbicides). (3) These methods are highly flexible and feature increased efficiency when combined into an integrated weed management strategy. (4) Recent advances in the chemistry of allelopathy are facilitating the use of allelochemicals for bioherbicide production. (5) Several biotechnologies, such as stress induction and genetic engineering techniques, can enhance the allelopathic potential of crops or introduce allelopathic traits de novo. This review shows how important the role of allelopathy for sustainable weed management is and, at the same time, indicates the need for field experiments, mainly under an integrated approach. Finally, we recommend the combination of transgenic allelopathy with the aforementioned allelopathic tools to increase the weed-suppressive efficacy of allelopathy.

Keywords: allelopathy; weed management; crop rotation; cover crops; intercropping; bioherbicides

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1. Introduction

Weeds are considered the most serious biotic constraint on crop production, with yield losses ranging from 45–95%, depending on environmental conditions and agronomic practices [1]. The reduction of yields is not the only harmful effect associated with weeds; a decrease in the quality and market value of agricultural products is also reported. For many years, weed control in agroecosystems has been pursued almost exclusively mechanically and chemically, keeping weed pressure and management costs low and crop productivity high. Nowadays, agriculture is facing the negative effects derived from the improper use of tillage and synthetic herbicides: depletion of soil organic matter, disruption of soil structure, acceleration of soil erosion, increase in herbicide-resistant weeds, development of a substitution weed flora, herbicides persistence in vegetables, and contamination of food and the environment. Furthermore, in organic farming, an exponentially increasing sector throughout Europe (~13.7 million ha) and the world (~71.4 million ha of total organic area) [2], chemical control is avoided and both hand weeding and mechanical tools alone are not agronomically or economically sufficient. As a consequence, the search for alternative and sustainable weed control practices has become an imperative. Among the low-input and environmentally-friendly available methods for weed management, the manipulation of allelopathic mechanisms plays a central role, as demonstrated by the increasing interest of the scientific community [3]. In the past 11 years (late 2020-early 2010), 3257 articles have been published in the field of allelopathy (this number refers to the Scopus® database using the keyword "allelopathy"), 53% of which were focused on weed control.

Allelopathy is a biochemical phenomenon with ecological implications involving any harmful or beneficial effect, either direct or indirect, by one plant (donor) on another (target) through the production of chemical compounds that escape into the environment [4]. Allelochemicals, i.e., the defensive secondary metabolites involved in the allelopathic interactions, can have negative effects on conspecific (autoallelopathy or autotoxicity) and/or heterospecific species (heterotoxicity). They encompass a very wide range of chemical classes, the most representative of which are phenolic compounds (simple phenols, flavonoids, quinones, coumarins, etc.), terpenoids (mono-, di- and triterpenes, sesquiterpenes and steroids) and compounds containing a nitrogen atom (e.g., benzoxazinoids) [5]. The mechanisms of action of allelochemicals are the most varied, considering that the visible effects on target plants (e.g., inhibition of seed germination, reduction of seedling growth) are often secondary signs of primary changes (inhibition of cell division and elongation, interference with cell membrane permeability, enzymatic activities, respiration and photosynthesis, etc.) [3]. Furthermore, in field conditions, the allelopathic effects are generally caused by the joint action of mixtures of allelochemicals. The role of allelochemicals in acting as biopesticides in agricultural pest management against weeds, insects and diseases has been examined and reviewed [6,7]. In this review, only the detrimental effects of allelopathy and the plant–plant interactions will be considered, with special reference to crop–crop and weed–crop allelopathic interference. Nevertheless, even in this case, there is a large literature on how allelopathy could be exploited for weed control [8,9]. However, in the past 5 years more than 1000 papers have been published on this topic, thus an updated review of them is needed. After discussing the allelopathic behavior of the main crops and the allelochemicals involved, this article reviews the recent advances in weed management through allelopathy by reporting practical applications of crop rotation, cover cropping and bioherbicides, also under an integrated approach. The last chapter focuses on the role of modern biotechnologies in plant allelopathy. The goal of the review is to find new possible applicative solutions in the allelopathy field by using the acquired knowledge to make weed management more sustainable.

2. Crop Allelopathy

Although the ability of certain plants to negatively affect other plants is an ancient concept, and was well-documented 2000 years ago (e.g., by Demokritus, Theophrastus, Pliny the Elder, Columella, etc.) [10], allelopathy in the narrow sense has been demonstrated only in the past four decades [11,12]. Over these years, several eminent scientists in the field of allelopathy have proposed guidelines for the suspected cases of crop allelopathy [13,14]. Summarizing, an allelopathic crop should present (i) vegetation patterns around itself, (ii) affect the growth of other crops or the same crop growth when cultivated in succession, (iii) cause problems of soil sickness due to the build-up of allelochemicals in the soil, (iv) synthesize and release into the environment bioactive allelochemicals. A large number of plant species are known to possess allelopathic properties, mainly weeds. The latest estimation found ~240 allelopathic weeds [15], but many other weed species were found in the past 20 years to show allelopathic effects. In addition to weeds, many herbaceous and woody crops have allelopathic traits both on other crops and weeds [16]. Most allelopathic crops belong to the Asteraceae and Poaceae families, but Brassicaceae and Fabaceae are also well-represented (Table 1).

Table 1. List of main crops showing allelopathic properties with corresponding allelochemicals involved.

Botanical Family	Binomial Name	Allelochemicals	References
Amaryllidaceae	*Allium cepa* L. *A. sativum* *A. ursinum*	S-containing compounds (alliin, isoalliin, methiin, allicin, ajoene, sulfenic acid, methyl propenyl disulfate, methylpropyl trisulfate) and phenolic acids (ferulic, *p*-coumaric, *p*-hydroxybenzoic, syringic, vanillic)	[17]
Asteraceae	*Artemisia absinthium* L.	Tannins, terpenes and alkaloids (absinthium)	[18]
	Carthamus tinctorius L.	Sesquiterpene lactones (dehydrocostuslactone, costunolide) and strigolactones (solanacol, GR24 and abacyl acetate)	[19]
	Cichorium intybus L.	Sesquiterpene lactones (8α-angeloyloxycichoralexin, lactupicrin) and guaianolides (cichoralexin, 10α-hydroxycichopumilide)	[20]
	Cynara cardunculus L.	Sesquiterpene lactones (cynaropicrin, deacylcynaropicrin, 11,13-dihydro-deacylcynaropicrin, grosheimin, 11,13-dihydroxi-8-deoxygrosheimin, aguerin B, cynaratriol), pinoresinol and polyphenols (caffeoylquinic and dicaffeoylquinic acids, luteolin and apigenin derivatives)	[21–23]
	Helianthus annuus L.	Sesquiterpene lactones (helivypolide D, leptocarpin, helivypolide E, annuolide F, annuolide H, helivypolides F, helivypolides H, helivypolides J, helieudesmanolide A, 8β-angeloiloxicumambranolide), heliannuoles (heliannuol J), bisnorsesquiterpenes (annuionone D, (+)-dehydrovomifoliol), flavonoids (heliannone A, kukulkanine B, heliannone B, tambuline) and (+)-loliolide	[24]
	H. tuberosus	Sesquiterpene lactones (1,10-epoxidized heliangolides, 1-keto-2,3-unsaturated-furanoheliangolides, 4,15-isoatriplicolide angelate, 4,15-isoatriplicolide methylacrylate), diterpenes (*ent*-17-oxokaur-15(16)-en-19-oic acid, *ent*-17-hydroxykaur-15(16)-en-19-oic acid, *ent*-15β-hydroxykaur-16(17)-en-19-oic acid methyl ester and *ent*-15-*nor*-14-oxolabda-8(17),12E-dien-18-oic acid), phenolic compounds (*p*-hydroxybenzoic acid, *p*-hydroxybenzaldehyde, salicylic acid, coumarin, *o*-coumarinic acid, and *p*-coumaric acid) and (+)- pinoresinol	[25,26]
	Lactuca sativa L.	Phenolic acids (coumarin, *trans*-cinnamic acid, *o*-coumaric acid, *p*-coumaric acid and chlorogenic acid)	[27]
Brassicaceae	*Brassica juncea* (L.) Czern. *B. napus* *B. nigra* *B. oleracea*	Glucosinolates [isothiocyanates (allyl-ITC, 2-phenylethyl, 3-butenyl, 4-pentenyl, 4-methylthiobutyl, 5-methylthiopentyl), nitriles (5-methylthiopentanenitrile, 6-methylthiohexanenitrile), oxazolidinethione (goitrin)] and brassinosteroids (brassinolide, 24-epibrassinolide, 28-homobrassinolide)	[28]
	Capparis spinosa L.	Flavonoids (quercetin-3-*O*-β-D-glucopyranoside, quercetin, kaempferol 3-*O*-β-D-glucopyranoside, rhamnetin, isorhamnetin, rhamnozin, thomnocitirin), carotenoids (β-carotene, lutein, neoxanthin and violaxanthin), tocopherols (α- and γ-tocopherol) and glucosinates	[29,30]

Table 1. *Cont.*

Botanical Family	Binomial Name	Allelochemicals	References
Cannabaceae	*Cannabis sativa* L.	Glycosides, alkaloids, flavonoids, flavones, steroids, tannins, phenols and saponins	[31]
Convolvulaceae	*Ipomea batatas* (L.) Lam.	Polyphenols (coumarin, trans-cinnamic acid, hydroxycinnamic acid, *p*- and *o*-coumaric acid, caffeic acid, chlorogenic acid)	[32]
Cucurbitaceae	*Citrullus lanatus* (Thunb.) Matsum and Nakai	Phenolic acids (ρ-hydrobenzoic, vanillic, syringic, ρ-coumaric and frulic acids)	[33]
Cucurbitaceae	*Cucumis sativus* L.	Phenolic acids (benzoic, *p*-hydroxybenzoic, 2,5-dihydroxybenzoic, 3-phenylpropionic, cinnamic, *p*-hydroxycinnamic, gallic, vanillic, caffeic, hydrocaffeic, *p*-coumaric, ferulic, sinapic, *p*-thiocyanatophenol and 2-hydroxybenzothiazole) and fatty acids (myristic, palmitic, and stearic)	[34]
Fabaceae	*Arachis hypogaea* L.	Phenolic acids (*p*-coumaric and benzoic) and fatty acids (tetradecanoic, hexadecanoic, octadecanoic)	[35]
	Glycyrrhiza uralensis Fisch.	Flavonones (liquiritin, isoliquiritigenin) and triterpenes (glycyrrhizic acid, dodecanoic acid)	[36]
	Medicago sativa L.	Phenolic compounds (salicylic acid, *p*-hydroxybenzoic acid, *trans*-cinnamic acid, *o*-coumaric acid, *p*-coumaric acid, ferulic acid, vanillic acid, chlorogenic acid, caffeic acid, coumarin, rutin, quercetin, scopoletin, medicarpin, sativan, 4-methoxymedicarpin, 5-methoxy-sativan)	[37,38]
	Phaseolus vulgaris L.	Phenolic acids (benzoic, salicylic, and malonic)	[39]
	Pisum sativum L.	Phenolic acids (benzoic, cinnamic, *p*-hydroxybenzoic, 3,4-dihydrobenzoic, vanillic, *p*-coumaric, sinapic) and pisatin	[40]
	Vicia faba L.	Phenolic acids (lactic, benzoic, *p*-hydroxybenzoic, vanillic, adipic, succinic, malic, glycolic, *p*-hydroxyphenylacetic, salicylic)	[39]
	Tamarindus indica L.	Phenolic acids (caffeic), methyl-2,3,4-trihydroxyhexanoate and organic acids (citric, malic, oxalic, and tartaric)	[41,42]
Juglandaceae	*Juglans nigra* L. *J. regia*	Naphthoquinones (juglone, 1,4-naphthoquinone, plumbagin, 2-methyl-1,4-naphthoquinone), triterpenoids (lupenone, lupeol, squalene) fatty acids (n-hexadecanoic, 9,12-octadecadienoic, 8-octadecenoic, palmitic, stearic), phenolic acids (chlorogenic, *p*-coumaric, *o*-coumaric, ferulic, tannic, caffeic, vanillic, syringic), flavonoides (catechin, epicatechin and myricetin), flavonoids (quercetin and quercetin derivatives), hydroxybenzoic acids (gallic, ellagic, protocatechuic), and steroids (γ-sitosterol, sitostenone)	[43,44]
Labiateae	*Rosmarinus officinalis* Schleid.	Monoterpenoids (α-pinene, myrcene, α-terpinene, β-cymene, 1,8-cineole, camphene, α-limonene, sabinene) and polyphenols (caffeic, ferulic, gallic, rosmarinic, carnosic, and chlorogenic acids)	[45,46]

Table 1. *Cont.*

Botanical Family	Binomial Name	Allelochemicals	References
Moraceae	*Ficus carica* L.	Phenolic acids (3-*O*-caffeoylquinic acid, 5-*O*-caffeoylquinic acid, dihydroxybenzoic acid, caffeoylmalic acid) and flavonoids (rutin, isoquercetin, catechin and astragalin)	[47]
Myrtaceae	*Eucalyptus globulus* Labill. *E. urograndis* *E. urophylla*	Phenolic compounds (chlorogenic acid, ρ-coumaric acid, ellagic acid, hyperoside, rutin, quercitrin and kaempferol 3-*O*-glucoside) and organic acids (citric, malic, shikimic, succinic and fumaric)	[48]
Poaceae	*Avena sativa* L.	Flavonoids (2-*O*-glucoside, isovitexin 2″-*O*-arabinoside), phenolic acids (caffeic, ferulic, coumaric, salicylic, coumarin, cynnamic and derivatives) and saponins (avenacoside A, avenacoside B, 26-desglucoavenacoside A, 26-desglucoavenacoside B)	[49,50]
Poaceae	*Hordeum vulgare* L.	Phenolic acids (benzoic, caffeic, chlorogenic, coumaric, coumarin, ferulic, *p*-hydroxybenzoic, ferulic, gentisic, salicylic, sinapic, syringic, vanillic, cinnamic, hydroxycinnamic, scopoletin), benzoxazinoids (DIBOA, DIMBOA), alkaloids (gramine, hordenine), flavonoids (saponarin, apigenin, lutonarin, catechin, cyanidin, isovitexin) and cyanoglucosides (heterodendrin, epidermin, epiheterodendrin, sutherlandin, osmaronin, dihydroosmaronin)	[51]
	Oryza sativa L.	Diterpenes (momilactones and oryzalexins), phenolic acids (caffeic, ferulic, coumaric, salicylic, syringic, *p*-hydroxybenzoic, coumarin, cynnamic and derivatives), flavones (5,7,4′-trihydroxy-3′,5′-dimethoxyflavone) and cyclohexenones (3-isopropyl-5-acetoxycyclohexene-2-one-1)	[13,49,52]
	Secale cereale L.	Benzoxazinoids (DIBOA, HMBOA, BOA, DIMBOA, MBOA) and phenolic acids (caffeic, ferulic, coumaric, salicylic, coumarin, cynnamic and derivatives)	[49]
	Sorghum bicolor (L.) Moench *S. bicolor* × *S. sudanense* *S. halepense*	Benzoxazinoids (DIBOA, HMBOA, BOA, DIMBOA, MBOA), benzoquinones (sorgoleone), cyanogenic glycosides (dhurrin), phenolic acids (*p*-hydroxybenzoic, *p*-hydroxybenzaldehyde, coumaric, ferulic)	[53]
	Triticum aestivum L. *T. durum*	Benzoxazinoids (DIBOA, DIMBOA-Glc, HMBOA, BOA, DIMBOA, MBOA), phenolic acids (*trans*-ρ-coumaric, *cis*-ρ-coumaric ferulic, vanillic, syringic, ρ-hydroxybenzoic), fatty acids (acetic, propionic and butyric), triterpenoids (cycloart-5-ene-3β,25-diol and cycloart-3β,25-diol) and steroids (cholesterol, ergosterol, campesterol, stigmasterol, sitosterol, spinasterol and stigmastanol)	[54–56]
Rubiaceae	*Coffea arabica* L.	Alkaloids (caffeine, theobromine, theophylline, paraxanthine), coumarins (scopoletin) and phenolic acids (chlorogenic, ferulic, *p*-coumaric, *p*-hydroxybenzoic, caffeic and vanillic)	[57]

Table 1. *Cont.*

Botanical Family	Binomial Name	Allelochemicals	References
Solanaceae	*Capsicum annuum* L.	Phthalate esters (N-phenyl-2-naphthylamine, dibutyl phthalate, butyl cyclohexyl ester), dicarboxylic acids (phthalic acid, 1,2-benzenedicarboxylic acid) and phenols anilines (diphenylamine, 4,4′-(1-methylethylidene) bis-phenol, 1-naphthalenamine, n-phenyl-1-naphthylamine)	[58,59]
	Nicotiana tabacum L.	Alkaloids (nicotine), sucrose esters (fluoro derivatives of sucrose) and diterpenes (duvatrienediol and duvatrienediol derivatives)	[60]
	Solanum lycopersicum L.	Alkaloids (α-tomatine), steroids (stigmasterol), furocoumarins (bergapten) and strigolactones (7-oxoorobanchylacetate, solanacol, orobanchol, strigol, fabacyl acetate, orobanchyl acetate and 5-deoxysrtrigol)	[61]

As regards the Asteraceae, the most studied allelopathic crop is sunflower (*Helianthus annuus* L.). In Asteraceae members including sunflower, the main allelochemicals are sesquiterpenes, especially heliannuoles, sesquiterpene lactones and bisnorsesquiterpenes, in addition to triterpenes and flavonoids [24]. Its allelopathic effects have been tested on both other crops and weeds, in field conditions and in vitro bioassays [62]. In recent years, the allelopathic potential of *Cynara cardunculus* L., an herbaceous perennial species belonging to the Mediterranean basin [63], was assessed on seed germination and seedling growth of some weeds and target crops [21,64,65]. Allelochemicals responsible for *C. cardunculus* allelopathy are the sesquiterpene lactones cynaropicrin, deacylcynaropicrin, 11,13-dihydro-deacylcynaropicrin, aguerin B, grosheimin, 11,13-dihydroxy-8-deoxygrosheimin and cynaratriol, as well as polyphenols such as caffeoylquinic and dicaffeoylquinic acids, luteolin and apigenin derivatives [21–23]. Recently, Rial et al. [19] demonstrated the phytotoxicity of safflower (*Carthamus tinctorius* L.), a thistle-like herbaceous plant cultivated in regions with arid or semiarid climate for industrial applications (oil production, pigments and human consumption), indicating the sesquiterpene lactones dehydrocostuslactone and costunolide and several strigolactones as the main allelochemicals released by root exudation.

Allelopathy in Poaceae plants has been widely described. Rice (*Oryza sativa* L.), rye (*Secale cereale* L.), common (*Triticum aestivum* L.) and durum wheat (*T. durum*), sorghum (*Sorghum* spp.), barley (*Hordeum vulgare* L.) and oat (*Avena sativa* L.) are probably the most studied allelopathic crops. The spectrum of their allelochemicals has been investigated in depth, with benzoxazinoids (DIBOA, HMBOA, BOA, DIMBOA, MBOA), phenolic acids, flavonoids and terpenoids recognized as major allelochemicals [49,53,55]. Moreover, the biosynthetic pathways of some of these allelochemicals have been sequenced, such as in the case of sorgoleone [66]. Given the considerable knowledge of this family and chemicals involved, the recent research has focused on the utilization of their allelopathic mechanisms for weed control.

The Brassicaceae family comprises more than 3200 species, of which the *Brassica* genus includes several highly allelopathic crops such as canola (*Brassica napus* L.), Indian mustard (*B. juncea*), black mustard (*B. nigra*) and cabbage (*B. oleracea*). Rehman et al. [28] reviewed the use of *Brassica* allelopathy for weed management and documented that glucosinolates (mainly isothiocyanates and nitriles) and the endogenous steroidal compounds brassinosteroids (e.g., brassinolide, 24-epibrassinolide, 28-homobrassinolide) are responsible for their phytotoxicity. Significant evidence of allelopathic effects has been reported in some leguminous crops. The best known example is alfalfa (*Medicago sativa* L.), commonly used as living or dead mulch for weed management, and widely studied also as a plant model in autoallelopathy [37,38]. Other examples of allelopathic Fabaceae plants are the common bean (*Phaseolus vulgaris* L.), faba bean (*Vicia faba* L.), peanut (*Arachis hypogaea* L.) and, recently, liquorice (*Glycyrrhiza uralensis* Fisch.) [35,36,39]. Fabaceae allelopathy is mainly due to phenolic acids such as benzoic, cinnamic, *p*-hydroxybenzoic, vanillic, coumaric, ferulic, caffeic, salicylic, etc.

The Solanaceae family is gaining in interest for the allelopathic potential shown by some important members. Rial et al. [61], for example, investigated the allelopathic traits of tomato (*Solanum lycopersicum* L.) and identified its major root allelochemicals as the alkaloid α-tomatine, the steroid stigmasterol, the furocoumarin bergapten and the strigolactones solanacol, orobanchol, strigol, etc. Important phytochemical advances were also made in the discovery and identification of tobacco (*Nicotiana tabacum* L.) [60] and red pepper (*Capsicum annuum* L.) allelochemicals [59].

3. Allelopathic Practices Involved in Weed Management

Allelopathic crops can be employed to manage weeds in agroecosystems by (i) including them in rotational sequences or (ii) intercropping in close proximity with a cash crop, (iii) cover cropping as living or dead mulches, (iv) crop residue incorporation into the soil and (v) by using their allelochemicals as bioherbicides [6–9]. The adoption of allelopathy for weed management is highly flexible, varying site by site depending on the specific characteristics of the context: pedo-climatic conditions, weed species, agricultural practices used, economic constraints and farmer's expectations. Allelopathy can be exploited in different cropping systems, but it certainly plays more beneficial roles in organic farming, and in conservative, minimum and no-tillage agricultural systems, where weed control is often problematic. Moreover, the abovementioned allelopathic weed control tools can be individually applied or combined into an integrated weed management strategy (IWMS) to increase their efficiency [67].

3.1. Crop Rotation

Planting different crops in sequence in the same field is a traditional agricultural tactic allowing many benefits in cropping systems: weed and pest control, reduction of autoallelopathy or soil sickness related to monoculture, reduction of nutrient leaching, improvement of soil organic matter and soil microorganisms, enhancement of soil fertility and crop yields [68]. Crop rotation offers the best results when considered within an IWMS as prevention against weed establishment and reduction of the soil seedbank [67]. Indeed, such techniques avoid the development of specialized and invasive weed flora, while allowing a multifaceted weed community characterized by low densities for each species [69]. It does not eradicate troublesome weeds, but limits their reproduction and reduces the impact of subsequent direct control methods. Including an allelopathic crop within rotational sequences can help to control weeds both in the current and next crops by releasing allelochemicals into the soil through root exudation, decomposition of plant residues and leaching from plant foliage. Once released into the rhizosphere, allelochemicals can directly or indirectly—by microbial transformation into more active, less active or entirely inactive compounds—inhibit seed germination and reduce weed density and biomass [70]. The positive effects of allelopathic crops within crop rotations are often exacerbated in conservative agricultural systems. For example, studying the impact of five tillage systems and five crop rotations, Shahzad et al. [71] found that sorghum-wheat rotation had the strongest weed-suppressive effect in terms of density and dry biomass reduction in all tillage systems, especially during the second year, thanks to the accumulation of sorghum allelochemicals (sorgoleone) in the soil. In another study, Scherner et al. [72] examined the combined 11-year-long effects of tillage and crop rotations on weed flora and reported that, among the four crop sequences under study, the most diversified sequence (winter wheat–spring barley–peas rotation) had the lowest density of grass weeds, while tillage effects did not differ within rotations. Similarly, Hunt et al. [73] compared the environmental and agronomic impact of three crop rotation systems and integrated mechanical–chemical weed control tactics. A 4-year rotation based on corn–soybean–oat/alfalfa–alfalfa combined with mechanical and chemical weed control returned similar results to a conventionally managed less diverse system in terms of grain yields and weed suppression, while also achieving a significant reduction in herbicide use and water contamination. Overall, the scientific literature agrees in promoting the diversification of crop rotations to suppress weeds while limiting the adoption of herbicides. In this regard, Weisberger et al. [74] conducted a meta-analysis across studies involving simple and more diverse crop rotations. They found that diversifying crop rotations, often involving allelopathic crops such as wheat, oat, corn, alfalfa, sunflower, etc., reduced weed density by 49% compared to simple sequences, while no significant effects were observed on weed biomass, likely due to the lower number of studies. Furthermore, they indicated that the effect of crop rotation on the size and structure of weed communities was markedly influenced by tillage systems. In particular, crop rotation showed the best results in zero-tillage systems where, in addition to weed control, it reduced or eliminated the yield losses and improved soil conservation. Therefore, the authors demonstrated the high synergism between zero-tillage and crop rotation for weed management.

Recently, Scavo et al. [75] suggested the inclusion of cultivated cardoon or globe artichoke for 2–3 years in Mediterranean crop rotations to reduce the size of the weed seedbank and stimulate the soil eubacterial communities. Sometimes, the combination of crop allelopathy and crop rotation can produce negative effects on the cash crop. For instance, Karkanis et al. [76] indicated that the inclusion of spearmint (*Mentha* × *piperita*) or peppermint (*Mentha spicata* L.) in rotational sequences decreased the dry biomass, photosynthetic rate and grain yield of corn as the succeeding crop. Demonstrating the direct allelopathic effect of crop rotation in field experiments is very complex, since it is often confused with the role of competition and other indirect disturbances. For this reason, a multidisciplinary approach in such experiments is needed.

3.2. Cover Cropping

Cover cropping is the mono- or intercropping of herbaceous plants either for part of or an entire year with the aim of enhancing yields [77]. Cover crops are grown for their numerous ecosystem services: protection from soil erosion, reduction of nutrient leaching (especially nitrates), enhancement of soil organic matter levels and microbial activities, improvement of soil structure and hydraulic properties, conservation of soil moisture, pest management and weed control [78,79]. Altogether, these benefits result in higher yields for the subsequent crops. Cover cropping, mulching, intercropping and green manuring are often indicated as distinct and separate techniques, but they can be considered as synonymous [67,79]. Indeed, cover crops can be used as living mulches when intercropped with the cash crop, as dead mulches by leaving plant residues on the soil surface or green manures by incorporating the residues into the soil (Table 2).

Table 2. Exploitation of cover cropping for the allelopathic management of weeds.

Cover Cropping Type	Allelopathic Cover Crop	Main Crop	Target Weeds	References
Dead mulching	*Helianthus annuus* L., *Zea mays* L., *Oryza sativa* L., *Sorghum bicolor* L.	Wheat	*Phalaris minor* Retz.	[80]
	Trifolium subterraneum L.	Apricot	Several monocots and dicots	[81]
	Fagopyrum esculentum Moench., *Sinapis alba* L., *T. subterraneum*, *H. annuus*, *Linum usitatissimum* L., *Raphanus sativus* L., *Vicia sativa* L., *Avena strigosa* Schreb., *Cannabis sativa* L. and mixtures	Sugar beet	*Stellaria media* (L.) Vill., *Chenopodium album* L., *Matricaria chamomilla* L.	[82]
Green manuring	*Eucalyptus globulus* Labill.	Corn	*Digitaria sanguinalis* (L.) Scop., *C. album*	[83]
	S. alba and *S. alba* + *F. esculentum*	Red clover, wheat, pea, barley rotation with red clover as a undersown crop	*Cirsium arvense* (L.) Scop., *Sonchus arvensis* L., *Galium aparine* L., *Lamium purpureum* L., *Fallopia convolvulus* (L.) Á. Löve, *C. album*, *S. media*	[84]
	V. faba	Corn	*A. retroflexus*, *C. album*, *Solanum nigrum*, *D. sanguinalis*, *Cyperus rotundus* L.	[85]
	Hordeum vulgare L., *V. sativa*	Corn, sunflower	*Xanthium spinosum* L. and other broadleaf species	[86]
Intercropping	*Crotalaria juncea* L.	Cotton	*C. rotundus*, *Alternanthera paronychioides* A. St.-Hil.	[87]
	Trigonella foenum-graecum L.	Coriander	Several monocots and dicots	[88]
	F. esculentum, *Lens culinaris* Medik., *S. bicolor*, *H. annuus*	Soybean	*C. album*, *Polygonum persicaria* L.	[89]
	T. repens	Wheat	*A. fatua*, *S. media*, *M. recutica*	[90]

As observed for crop rotation, cover cropping is commonly adopted in low-input agriculture and organic farming, mainly in IWMS to control the soil weed seedbank and prevent weed emergence [67]. The weed-suppressive ability of cover crops is a result of physical and allelopathic effects, which in the field often act in synergism [91].

Root development, rapid growth, length of biological cycle and biomass production are factors determining the competitive capacity of cover crops for light, water, nutrients and space. Generally, the greater the biomass production and biological length, the higher the cover crop phytotoxicity [92]. Both cover crops and mulches can indirectly affect weed density by favouring predators that eat seeds [93]. Moreover, surface-applied or soil-incorporated mulches obstruct weed seed germination and reduce weed emergence by acting as physical barriers [78]. In addition to such kinds of physical interference, living and dead mulches of allelopathic species directly exude into the rhizosphere or release allelochemicals by residues' decomposition that, once present in the soil solution, must reach the target plants to exert phytotoxic effects [70]. The efficacy of this allelopathic weed suppression is mediated by climatic conditions, soil properties, cover crop genotype, quantity, duration and placement of cover crop residues, and biological characteristics of the weed communities (Figure 1).

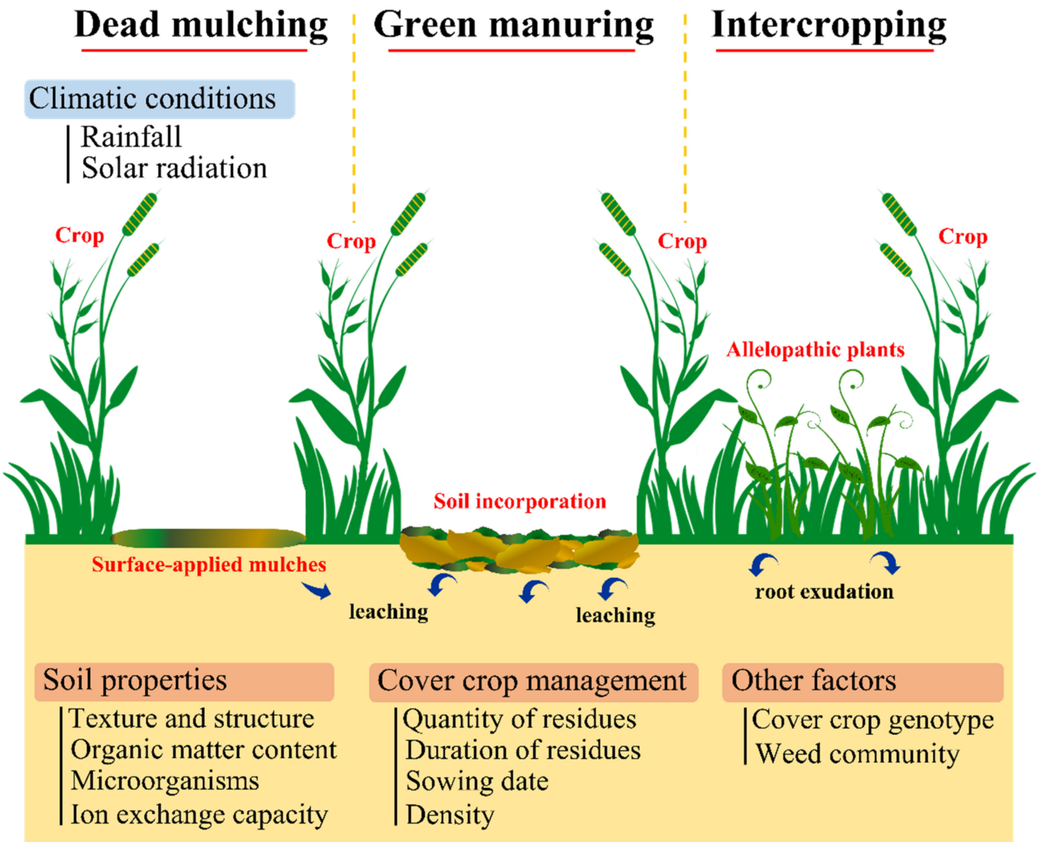

Figure 1. Practical applications of allelopathic cover cropping by intercropping, surface-application (dead mulching) and soil incorporation (green manuring) of crop residues. Allelopathic effects are due to the release of active allelochemicals into the soil through root exudation from living mulches and leaching from decomposing residues. The level of phytotoxicity is closely influenced by climatic conditions (rainfall, solar radiation), soil properties (texture, structure, organic matter content, pH, cation exchange capacity and microorganisms), characteristics of the weed community, cover crop genotype and management (quantity and duration of residues, sowing date and density).

For example, Kruidhof et al. [94] reported an increased allelopathic activity of lucerne (*M. sativa*), winter oilseed rape (*B. napus*) or winter rye (*S. cereale*) with increasing rainfall level, probably due to the higher leaching of allelochemicals. The same authors also indicated that the larger the weed seed size, the higher its resistance and detoxification capacity, especially with respect to surface-applied dead mulch, highlighting the importance of weed community composition. The role of soil properties (e.g., texture, structure, pH, organic matter level, ion exchange capacity, etc.) in affecting allelochemicals retention, transport and availability in the soil has been examined in depth by Scavo et al. [70]. Concerning cover crop management, the extent of an effective weed control increases with increasing seeding rate, amount and duration of plant residues [8,79]. These aspects of cover cropping allelopathy are exacerbated in no-tillage systems. Some important cover crops with allelopathic potential include the cereals rye, sorghum, wheat, barley, oat, buckwheat (*Fagopyrum esculentum* Moench.), the Brassicaceae black mustard, field mustard (*B. rapa*), rapeseed (*B. napus*) and white mustard (*Sinapis alba* L.), and the legumes alfalfa, hairy vetch (*Vicia villosa* Roth), common vetch (*V. sativa*), velvet bean (*Mucuna pruriens* ((L.)) DC.), cowpea (*Vigna unguiculata* ((L.)) Walp.), crimson clover (*Trifolium incarnatum* L.), subterranean clover (*T. subterraneum*), red clover (*T. pratense*) and Egyptian clover (*T. alexandrinum*).

3.2.1. Dead Mulching

Surface-applied mulches are recognized to act as preventive weed control by affecting the soil weed seedbank, weed emergence and establishment [67]. In a two-year field trial, Abbas et al. [80] noted a significant decay of the soil weed seedbank and an increased wheat yield after the application of sunflower, rice, corn and sorghum mulches. Moreover, the integrated use of allelopathic crop mulches and post-emergence herbicide mixtures at low doses provided an effective control of *Phalaris minor* Retz., thus reducing the herbicide-resistance development in *P. minor* and the herbicide selection pressure. Sturm et al. [82] evaluated ten different cover crop mulches and mixtures in a sugar beet cultivation, obtaining different results in relation to cover crop type and target weed. In particular, a significant reduction of weed density by all cover crops compared to untreated control was observed, with the highest reduction caused by cover crop mixtures, likely due to a synergistic effect of allelochemicals. The release of allelochemicals into the soil largely depends on the decomposability of the residues (C/N ratio) and residue management, particularly pre-treatment [95]. Dead mulching is often less efficient in suppressing weeds than incorporating plant residues into the soil, likely due to the higher release rate mediated by soil microorganisms and to the longer persistence of released allelochemicals [91]. Scavo et al. [81] studied the effect of *T. subterraneum* cover cropping, with or without burying dead mulches into the soil, on the quali-quantitative composition of the soil weed seedbank in an apricot (*Prunus armeniaca* L.) orchard. *Trifolium subterraneum* green manuring was more effective than dead mulching in decreasing the size of the soil weed seedbank, although both have significantly reduced it compared to spontaneous flora cover cropping and conventional apricot management. In contrast, Kruidhof et al. [95] reported a genotype-dependent effect, where winter rye dead mulching inhibited weed emergence more so than green manuring, while an opposite trend was observed for winter oilseed rape.

3.2.2. Green Manuring

In recent years, several reports have been made on incorporating allelopathic plant residues into the soil (i.e., green manuring) for weed control under field conditions. Puig et al. [83] evaluated the allelopathic potential of *Eucalyptus globulus* Labill. leaf green manure in corn fields for two seasons and in two different locations. *Eucalyptus* green manure significantly reduced weed biomass, especially that of *Digitaria sanguinalis* (L.) Scop. and *Chenopodium album* L., and mainly at early stages of corn establishment, while corn was not negatively affected. Soil pH, cation exchange capacity and microbial biomass carbon were also increased by *E. globulus* green manure. In previous research, Puig et al. [48] reported that *Eucalyptus* leaf green manure continuously releases different phenolic acids (chlorogenic acid, ellagic acid, hyperoside and rutin) and volatile compounds (the monoterpenes α-pinene, β-pinene, α-phellandrene, eucalyptol, β-cis-ocimene, γ-terpinene, terpinen-4-ol, terpineol and the sesquiterpene longifolene and β-caryophyllene) during a 30-day period of decomposition. In another study, Álvarez-Iglesias et al. [85] reported that faba bean (*V. faba*) green manure suppressed both density (from −14.8% to −69.8%) and biomass (from −46.9% to −78.5%) of some dicotyledon and monocotyledon weeds in correspondence with the early critical period of corn, thus reducing the need for post-emergence herbicides.

Investigating the weed-suppressive capacity of different cover crops cultivated for green manure in a 6-year field experiment, Masilionyte et al. [84] found that white mustard (*S. alba*), especially when combined with buckwheat (*F. esculentum*), showed a higher reduction of the number of weeds and weed biomass than narrow-leafed lupine (*Lupinus angustifolius* L.) in a mixture with oil radish (*Raphanus sativus* L.), thanks to its biomass production and release of allelochemicals into the soil. Alonso-Ayuso et al. [86] studied barley (*H. vulgare*) and vetch (*V. sativa*) green manure in a long-term field experiment involving two cash crops: corn and sunflower. Overall, replacing a winter fallow by cover crops had positive effects on weed density, diversity and soil seedbank, with both cover crops showing a weed density reduction of 51–63% in spring, while barley green manure suppressed winter weeds better than vetch. However, the weed seedbank size was not affected after 10 years of cover cropping. Additionally, only during 1 year did the weed control efficacy increase as the cover crop termination date was delayed.

3.2.3. Intercropping

Intercropping, i.e., growing multiple crop species together in the same field during a growing season, has been widely used throughout history to maximize ecosystem services per unit area per unit of time. It still remains a common agricultural practice in small farms, conservative agriculture and resource-limited agricultural systems, although it is increasingly used also in modern intensive agriculture. Many studies describe intercropping as a means to address weed control in an economical and environmentally friendly way [96]. The genotypes of both cash and cover crop, plant density, plant arrangement, etc., closely affect the level of weed suppression. On this point, it is possible to distinguish three main types of intercropping: fully mixed (without a specific arrangement), relay (with a temporal separation between crops) and strip (two or more crops are separated in the space by cultivating them in strips) [96]. Strip intercropping is the most adopted in allelopathic field experiments, since it allows more interactions between crops and facilitates their cultivation. Allelopathic crops, when included in intercropping systems, release allelochemicals into the environment through root exudation, volatilization from aboveground plant parts and leaching from rainfall or decay of plant debris [3]. Intercropping is reported to enhance the allelopathic weed–cover crop interactions and, consequently, the phytotoxic effects by improving soil microbial diversity and facilitating allelochemicals' transport into the soil [96]. Barto et al. [97] described the ability of common mycorrhizal networks in acting as 'superhighways' directly connecting the plants belowground and delivering allelochemicals to target plants.

Cereal–legume intercropping is the most common example of allelopathic intercropping due to the high numbers of allelopathic crops suitable for cover cropping both in the Poaceae and Fabaceae families. Rad et al. [98] investigated the effect of *S. bicolor* intercropping with different ratios of hairy vetch (*V. villosa*) and lathyrus (*Lathyrus sativus* L.), and three weed management strategies (no weed control, full weed control, hand-weeding). The selection of appropriate intercropping ratios played a key role in enhancing the weed control and improving the quali-quantitative traits of sorghum forage. Sorghum with 100% lathyrus showed the highest weeding efficacy, but good results in terms of forage yields were obtained by adding a minimum of 33–66% of hairy vetch to intercropping under no weeding conditions. Analyzing the trade-off between wheat yield, protein content and weed control, Vrignon-Brenas et al. [90] indicated that combining simultaneous white clover (*T. repens*) intercropping with high N availability significantly increased cover crop biomass, decreased weed shoots' dry matter and improved N accumulation while maintaining high wheat yields and protein content. Intercropping has also been applied for the control of parasitic weeds by using allelopathic species as trap crops. For instance, after 3 years of field experimentation, Fernández-Aparicio et al. [99] suggested intercropping grain legumes such as faba bean and pea with Egyptian clover (*T. alexandrinum*) to reduce the infection of the holoparasitic plant *Orobanche crenata* Forssk.

Research involving other cover crop species has also been published in recent years. Blaise et al. [87], evaluating twelve different intercrops over 5 years in cotton and found an average reduction of 43–71% of weed emergence and a 91–96% reduction of weed biomass compared to the control. Among intercrops, sun hemp (*Crotalaria juncea* L.) on one hand, showed the highest phytotoxicity with a significant suppression of purple nutsedge (*Cyperus rotundus* L.) and smooth joyweed (*Alternanthera paronychioides* A. St.-Hil.), while on the other, it allowed the highest cotton yield levels. Cheriere et al. [89] compared the combinations of different allelopathic crop species and spatial arrangements on grain production and weed control in soybean. A trade-off between soybean production and weed control was found, with sunflower allowing the lowest yield but, at the same time, the highest weed control level. The authors concluded that this trade-off could be managed by farmers by combining associated species choice and spatial arrangement; for example, planting alternate rows in sorghum and buckwheat intercrops. Intercropping density can also affect the weed–crop allelopathic interactions and the levels of weed control. For instance, Pouryousef et al. [88] studied five fenugreek (*Trigonella foenum-graecum* L.) densities of intercropping with coriander (*Coriandrum sativum* L.) and reported an increased reduction in weed biomass at increasing density, even if the weed control level was not entirely adequate, likely due to the low allelopathic potential of this cover crop. The authors suggested that this issue could be solved by using mixtures of different cover crops.

Much evidence has been reported about the increase in weed control when using mixtures of cover crops [100]. Kunz et al. [101], for instance, evaluated the weed suppressive effects of four cover crops in single and two mixed cultivations in three different locations. On average, both cover crop mixtures performed better than single cover crops and reduced weed density by 66% during the fallow period. The authors hypothesized the synergisms between allelochemicals (glucosinolates) and the additive allelopathic + competitive effects as an explanation. Similar results were also obtained by Florence et al. [100], according to which cover crop mixtures are able to compensate for the temporal and spatial variations in growing conditions, thus outperforming single species in the long term. Therefore, the combination of both allelopathic and competitive traits in cover crop species may help in increasing their weed-suppressive capacity. Several attempts were carried out with the goal of shifting allelopathy from competition in cover cropping experiments [78]. Using active carbon for allelochemicals' immobilization in a glasshouse experiment, Sturm et al. [102] found that allelopathic effects were species-specific, with the weed *Stellaria media* (L.) Vill. showing a greater sensitivity to allelopathy than *Alopecurus myosuroides* Huds. and volunteer wheat (*T. aestivum*). Allelopathy played an important role on overall weed suppression, although a greater contribution was played by competition. The authors concluded that an allelopathic cover crop should have competitive prerequisites (rapid germination, fast development, dense canopy and high soil coverage) to enhance the efficiency of its weed control.

3.3. Bioherbicides

Bioherbicides are broadly defined as natural products of biological origin derived either from living organisms or their secondary metabolites to suppress target weed populations without harming the environment [103]. For the purpose of this review, only plant-derived allelochemicals will be considered. With the aim of reducing the use of synthetic herbicides, overcoming weed-resistance phenomena and minimizing their environmental impact, plant-based allelochemical bioherbicides are gaining in popularity by virtue of the numerous advantages provided: water solubility, environmentally-friendly chemical structure (low amounts of 'heavy atoms', absence of 'unnatural' rings, high number of oxygen-, nitrogen- and sp^3-hybridized carbon molecules), high degradability in soil and water, possibility of new molecular targets in weeds, public acceptance [104]. Some of these benefits, however, in certain situations could represent a drawback. Their structural complexity, indeed, generates more stereocenters than synthetic molecules, making them unstable and rapidly degradable, thus reducing their environmental half-life.

Nevertheless, the chemical characteristics of allelochemicals lead to an increase in the costs for their synthesis, also considering that their discovery and set-up as bioherbicides is more complicated than that of synthetic herbicides [105] (Figure 2). In this regard, the recent advances in metabolomic techniques and chemical analytic instrumentations (e.g., liquid or gas chromatography combined with mass spectrometry) are simplifying the rediscovery of allelochemicals and their identification and quantification directly in crude plant extracts. As a result, tens of articles have been published in the past 10 years on the chemistry of crop allelopathy and, nowadays, we have a wide knowledge of the secondary metabolites involved in the phytotoxic effects of the most important crop species [5].

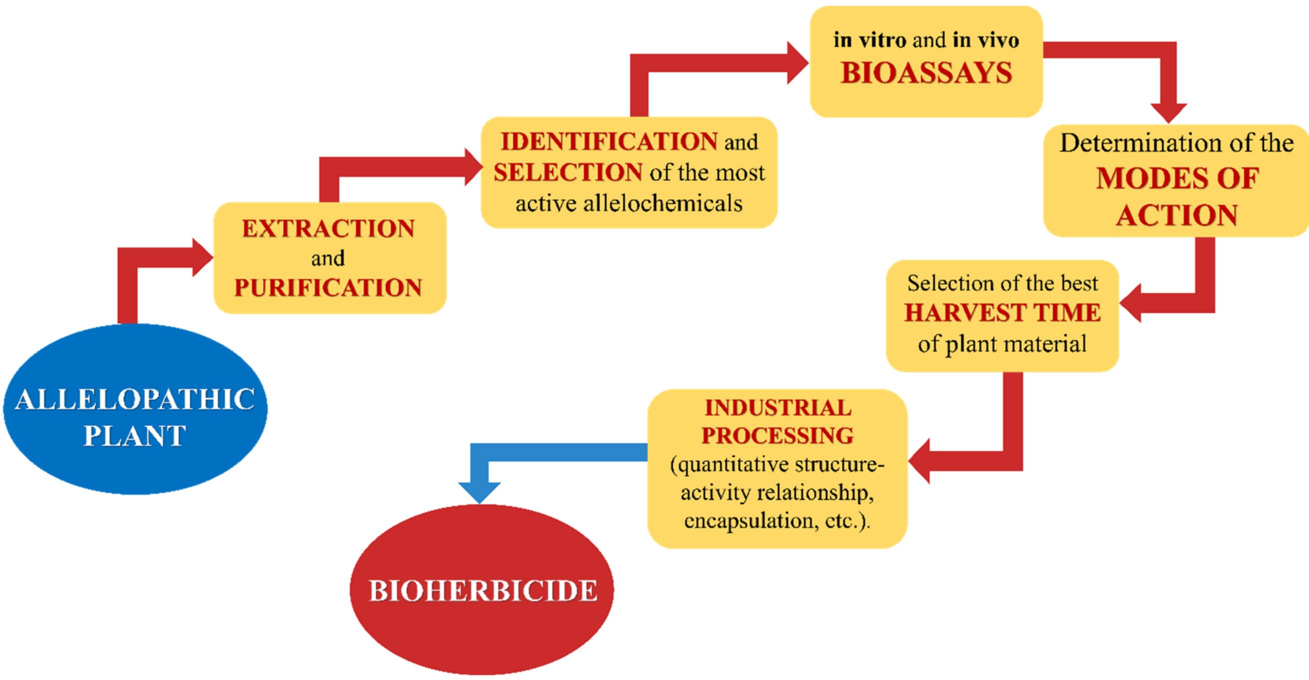

Figure 2. Steps for producing a commercial bioherbicide. After allelopathic potential is established and the best allelopathic genotype selected, allelochemicals need to be extracted, purified and identified. Then, allelopathic effects need to be checked both in vitro and in field conditions on a wide range of different weeds. Once the choice of the harvest time (i.e., maximum concentration of allelochemicals in plant tissues) has been made, a number of industrial processes such as quantitative structure-activity relationship (QSAR), chemical stabilization, encapsulation, etc., complete the whole process.

The application of plant extracts from various plant parts for weed control is well-documented, especially under laboratory conditions by using organic solvents for allelochemicals' extraction and detection (commonly methanol, ethanol, ethyl acetate and dichloromethane) [22] (Table 3).

Table 3. Application of plant water extracts for weed management in field conditions.

Donor Plant (Dose)	Extract Concentration	Main Crop (Yield)	Target Weeds	Weed Control	References
Sorghum ($0.0006\ L\ m^{-2}$)	10%	Wheat (+39%)	*Avena fatua* L., *Phalaris minor* Retz.	−31% and −32% of DW	[106]
Sorghum + sunflower ($0.0012\ L\ m^{-2}$)		Wheat (+49.5%)		−52% and −45.5% of DW	
Sorghum + sunflower ($0.0006\ L\ m^{-2}$)		Wheat (+62%)		−31.5% and −32.5% of DW	
Sunflower ($0.1\ L\ m^{-2}$)	10%	Wheat (no yield losses)	*Chenopodium album* L.	−70% of biomass	[107]
Chinese cabbage ($0.002\ L\ m^{-2}$)	10%	Mung bean	*Trianthema portulacastrum* L., *Cyperus rotundus* L.	−14.6% of density and DW	[108]

Table 3. *Cont.*

Donor Plant (Dose)	Extract Concentration	Main Crop (Yield)	Target Weeds	Weed Control	References
Tree wormwood (4 L m^{-2})	18.82%	Wheat (−52.9%)	Several monocots and dicots, mainly *A. fatua* and *P. paradoxa*	~30% of weed suppression	[109]
Sicilian sumac (4 L m^{-2})	8.75%	Wheat (+9%)		50.8% of weed suppression	
Common thyme (4 L m^{-2})	22.33%	Wheat (−7.2%)		~35% of weed suppression	
Common lantana (4 L m^{-2})	6.14%	Wheat (+16.5%)		16% of weed suppression	
Mediterranean spurge (4 L m^{-2})	2.27%	Wheat (−2.3%)		~40% of weed suppression	
Tree of heaven (0.001–0.002 g L^{-1})	20%	Sage, rosemary, carnation	*Lepidium sativum* L., *Raphanus sativus* L.	0% weed presence in sage and rosemary, ~24% in carnation	[110]

Several studies have examined the allelopathic effects of plant water extracts under field conditions in important crops such as wheat, corn, cotton, etc. [7], with phytotoxic results expressed in terms of weed density and biomass reduction. Sorghum and sunflower are the best known examples of plant water extracts applied in field trials for weed control. Anjum and Bajwa [107] studied the bioherbicidal activity of sunflower leaf extracts (at 100 mL m^{-2}) applied three times in post-emergence at 7-day intervals, reporting that extracts at the highest concentration decreased lambsquarters (*C. album*) by 70% and increased wheat biomass and harvest index, compared to a weedy control, thanks to the overcoming of weed–crop competition. Jamil et al. [106] tested the water extracts of sorghum alone (at 12 L ha^{-1}) and in combination with sunflower, Chinese cabbage, eucalyptus, tobacco and sesame (at 6 L ha^{-1}) for weed control in wheat fields, following the hypothesis of a greater effectiveness of different allelochemicals when acting in synergism. Among treatments under study, sorghum + sunflower at 12 L ha^{-1} was the most effective in reducing wild oat (*Avena fatua* L.) and canary grass (*Phalaris minor* Retz.) dry weight, while sorghum + sunflower at 6 L ha^{-1} was the most economically viable treatment. In another 2-year field experiment carried out by Carrubba et al. [109] on wheat, aqueous extracts from *Rhus coriaria* L., *Lantana camara* L., *Thymus vulgaris* L. and *Euphorbia characias* L. were used in post-emergence as bioherbicides. The authors reported season-dependent results, with none of the tested extracts showing an eradication capacity of weeds. Overall, *R. coriaria* showed the most positive effect on wheat yield and weed suppression, although total weed biomass was not correlated to grain production. Application of *B. campestris* water extracts at 20 L ha^{-1} was found to significantly reduce horse purslane (*Trianthema portulacastrum* L.) and purple nutsedge (*C. rotundus*) density and dry weight in mung bean (*V. radiata*), with a 10.5% increase of yield [108]. In a nursery production system involving three horticultural crops (i.e., *Salvia officinalis* L., *S. rosmarinus* and *Dianthus caryophyllus* L.), *Ailanthus altissima* (Mill.) Swingle extracts at 100 and 200 mg L^{-1} were evaluated on the weeds *Lepidium sativum* L. and *R. sativus*. Use of *A. altissima* leaf extracts as post-emergence bioherbicides eradicated the two indicator weeds in *S. officinalis* and *S. rosmarinus*, while increased the percentage of weed presence in *D. caryophyllus*. The authors suggested applying the extract directly to the soil or growth media in order to alleviate phytotoxicity on the cash crops [110]. The chemical effects caused by the application of plant extracts were investigated in detail and can be summarized in: increase of reactive oxygen species (ROS), inhibition of gibberellin pathway and accumulation of abscisic, salicylic and jasmonic acid, alteration of cell membrane permeability and deregulation of nutrient uptake (Ca, K, Mg, Fe), alteration of photosynthesis and respiration [3,111]. Radhakrishnan et al. [112] reviewed the effects of plant-based bioherbicides on weed physiology, highlighting significant metabolic processes, resulting in the inhibition of seed germination and seedling growth.

Another strategy consists in the combined application of plant water extracts and synthetic herbicides with the aim of reducing herbicide doses. The reviews by Alsaadawi et al. [113], Farooq et al. [7] and Soltys et al. [105] involved a compendium of many articles prepared under this integrated approach, while in the past 5 years no significant steps forward have been made. Bioherbicides and synthetic herbicides can be combined by applying them at the same time or with different times of application: one in pre-emergence and the other one in post-emergence. Encouraging results were obtained in wheat, rice, corn and cotton without affecting crop yields, but further studies are necessary to evaluate the synergism between bioherbicides and synthetic herbicides.

Despite these findings on allelopathic water extracts, there is still a lack of knowledge on the specific role of environmental factors on allelochemicals' bioavailability and effectiveness. Air and mainly soil are the media for the transport of allelochemicals, but pedoclimatic conditions are well-known to greatly affect their movement and retention [70]. Moreover, dosage, rate, time of application (in post- or pre-emergence), frequency of application, spectrum of target weeds (mono- or dicotyledons), persistence into the soil, etc., are issues needing to be addressed before producing a commercial formulation. For these reasons, the scientific community is called on to improve its efforts for the set-up of field experiments focused on the application of plant-based bioherbicides, also under an IWMS.

4. Biotechnologies in Crop Allelopathy

In addition to these agronomic techniques, allelopathic traits of crops can be managed to obtain weed-suppressive cultivars and improve their allelopathic potential, since the level of crop allelopathy is often insufficient to provide effective weed management in the field. The basic principle is to develop crops able to control weeds on their own through the synthesis and release of active allelochemicals. Table 4 summarizes the main agricultural biotechnologies, apart from the use of bioherbicides which were already discussed, that could be used for the enhancement of crop allelopathy.

4.1. Screening and Selection of Allelopathic Crop Cultivars

It is well known that the allelopathic potential of crops closely depends on the genotype [16]. Many studies have pointed out how cultivars differ from each other in their allelochemical concentrations and allelopathic activities. The most studied allelopathic crops showing significant allelochemicals variations (momilactones, benzoxazinoids and phenolic acids) in relation to the cultivar are rice, wheat, rye, barley and sorghum [8,9]. Considerable effort has been made by the research community in recent years on this topic. Recently, metabolomic and phytotoxic differences have been observed among six canola (*B. napus*) and two rye (*S. cereale*) cultivars [114,115]. Screening twelve barley accessions for the content of the alkaloids gramine, hordenine and its direct precursor *N*-methyltyramine, Maver et al. [116] found remarkable differences not only based on plant parts, but also between wild relatives and modern genotypes, thus providing important progress for the breeding of this crop. Similarly, Ladhari et al. [47] screened thirteen fig (*Ficus carica* L.) cultivars for their allelopathic activity and allelochemical concentration. The authors reported that the degree of inhibition was cultivar-dependent, as well as the phytochemical profiles, according to which fig cultivars were clustered into three groups. Scavo et al. [117] investigated the phytotoxicity and the quali-quantitative sesquiterpene lactone profile of six *C. cardunculus* genotypes belonging to its three botanical varieties, i.e., globe artichoke (var. *scolymus*), and cultivated (var. *altilis*) and wild cardoon (var. *sylvestris*). Ultra-high-performance liquid chromatography in tandem with mass spectrometry highlighted that wild cardoon showed the highest levels of sesquiterpene lactones, in accordance with similar research reporting higher amounts of allelochemicals in ancestor ecotypes, while the globe artichoke—i.e., the domesticated form—contained both the lowest concentrations and phytotoxic activity.

Table 4. Main biotechnologies involved in plant allelopathy.

Biotechnology	Main Effect	Description	Reference
Genotype selection	Screening allelopathic cultivars	Crop genotypes differ from each other in their allelochemicals' concentration and allelopathic activity. Screening and selecting genotypes allow obtaining a more allelopathic crop.	[117]
Stress induction	Increase in allelochemicals production	Induction of biotic and abiotic stress factors, or a combination of them, stimulates the synthesis of allelochemicals in donor plants.	[118]
Tissue culture	Increase in allelochemicals production Isolation from external factors during the study of allelopathic effects	Plant organ cultures such as hairy root cultures, both via normal callogenesis or using *Agrobacterium* spp. strains, may be applied to increase some competitive traits (e.g., rooting ability) and the production of allelochemicals, as well as to facilitate allelopathic studies.	[119]
Traditional breeding	Increase of crops' allelopathic potential or introduction of allelopathy de novo	Breeding programs can improve the allelopathic potential of crops just as they improved crop yields. However, poligeneticity and the low economic added value make this approach very difficult.	[120]
QTL analysis	Identification of genetic markers encoding allelopathic-related traits	The genetic analysis of quantitative trait loci (QTL) is very useful to identify the genes encoding the synthesis of allelochemicals.	[121]
Green chemistry	Increase in allelochemicals production	Improving allelochemicals' biotransformation by overexpressing the nitroreductase enzyme NfsB in *Escherichia coli* strains as a whole-cell biocatalyst.	[122]

4.2. Stress Induction

One of the main problems associated with allelopathic weed management is the low amount of allelochemicals' concentration in the donor plant and relative synthesis of these compounds for commercial use. A solution to this issue may derive from the exploitation of stress factors. In their 'stress hypothesis of allelopathy', Reigosa et al. [118] stated that plants' allelopathic potential is closely influenced by environmental changes, increasing when plants are under stress. Consequently, a stress condition generally enhances the synthesis of allelochemicals in the donor plant and the sensitivity of the target plant [3]. This is likely because when a plant recognizes a stress at cellular level, it usually starts a signal transduction leading to gene expression and to metabolic responses in terms of increased synthesis of secondary metabolites [118]. Different kinds of abiotic (light, drought, temperature, salinity, mineral availability) and biotic (pathogens, diseases, plant density) stress factors are known to increase the production of allelochemicals. For example, Oueslati et al. [123] demonstrated an increase of barley autotoxicity in drought conditions. In another study, 60% of plant shading was found to raise the concentration of sesquiterpene lactones in cultivated cardoon leaf extracts and their allelopathic activity [124]. Xuan et al. [125] reported that rice reacts to drought and salinity by enhancing the production of momilactones A and B, well-known rice allelochemicals, as a defensive mechanism. Under field conditions, generally different stress factors act in synergism, resulting in a further increase of allelochemicals' synthesis [3]. Although it is not certain if this behavior corresponds to a heightened release of allelochemicals into the environment by donor plants, stress induction can still be manipulated to obtain adequate amounts of allelochemicals and increase their concentration for the production of bioherbicides.

4.3. Genetic Engineering

In the past 20 years, biotechnology applications in weed management have focused on the development of transgenic allelopathy in crops through genetic engineering (GE) techniques. Before this approach, research attempted to use traditional breeding programs to enhance the natural allelopathic potential of crops or introduce allelopathy de novo, in the same way as breeding was used to improve crop production [126]. However, breeding methods have not succeeded for two main reasons: on one side the low economic added valued provided by allelopathy, compared to yield, and on the other side its polygeneticity [120]. Allelopathy, indeed, is a polygenetic characteristic weakly correlated to yield, thus needing the manipulation of more than one gene to encode the synthesis of allelochemicals. This aspect has been observed, for instance, in the case of benzoxazinoids such as DIMBOA and DIBOA in Poaceae members [127].

To overcome these difficulties, several GE tools (e.g., recombinant DNA, polymerase chain reaction, metabolic engineering, overexpression of genes, etc.) are currently under evaluation to better understand the metabolic pathways, enzymes and genes involved in the synthesis of allelochemicals [16,105]. Being a quantitative and polygenetic trait, one of the most promising GE approaches is provided by the analysis of quantitative trait loci (QTLs) based on restriction fragment length polymorphism (RFLP), amplified fragment length polymorphism (AFLP) and microsatellite (SSRs) markers to identify the genetic markers conferring crop allelopathic activity. QTL maps associated with allelopathic properties have already been developed in rice [128], wheat [129] and sorghum [121], but the knowledge of crop genomes can allow extending this approach to other crops. For example, despite its high heterozygosity, the whole genome sequence of *C. cardunculus* was published [130] and this was the first case for the Compositae family, one of the most important allelopathic families. Furthermore, Eljounaidi et al. [131] identified the P450 genes (CYP71AV9 and CYP71BL5) and the enzymes—the germacrene A synthase (GAS), the germacrene A oxidase (GAO) and the costunolide synthase (COS)—involved in the biosynthetic pathway of sesquiterpene lactones in *C. cardunculus*. Combining the genome sequence on one hand, and the knowledge of genes and enzymes encoding the synthesis of allelochemicals on the other hand, is it possible to develop a transgenic *C. cardunculus* genotype with improved allelopathy by genes' overexpression. Such a GE approach can also be applied to other allelopathic Compositae members by isolating the pools of mRNAs expressing an allelopathic trait, creation of an expression sequence tag (EST) library and transfer to the desirable crop. However, even though we know the biosynthetic pathways of some allelopathic phenolic compounds and terpenoids, as well as the enzymes involved in the biosynthesis of secondary metabolites, our actual knowledge on this topic is limited and what is more, both the enzymes and genes are species-specific, so that it is necessary to directly isolate them from the allelopathic plant [120]. Another recent and important advance in bioherbicide production by GE was achieved by de la Calle et al. [122], who improved the biosynthesis of D-DIBOA (2-deoxy-DIBOA) with 100% molar yield by *Escherichia coli* strains overexpressing the nitroreductase NfsB as biocatalyst.

Transgenic allelopathy on its own would unlikely provide a satisfactory weed management level in the field. For this reason, the latest GE future perspective is the creation of commercial cultivars with incorporated or introduced allelopathic traits together with competitive components (fast seedling emergence, high growth rate, early vigour, root development, wide leaf area).

5. Conclusions

In this review, we have pointed out the increasing importance of allelopathy as a new tool to make weed management more sustainable, both in conventional and organic agriculture. This field of research, which embraces different sciences, has gained in importance in recent years and, step by step, is becoming ever more common among farmers. The important advances in analytic chemistry, metabolomics, biotechnology and genetics have enabled the identification, isolation and purification of new allelochemicals, as well as the creation of transgenic allelopathic cultivars with marked allelopathic traits. Agronomic research has evaluated this broad and recent knowledge for its application as a weed control practice. To this end, promising results derive from the inclusion of allelopathic crops in rotational sequences, as living or dead mulches and by applying plant extracts as pre- or post-emergence bioherbicides. Despite these efforts, many allelopathic studies are still limited to laboratory conditions and most allelochemicals' modes of actions are unknown.

We recommend (1) more rigorously testing the agronomic performances of allelopathic crop rotation, cover cropping and bioherbicidal application; (2) a focus on the setup of field trials with involvement of biotic and abiotic factors, with the dual aim of considering both direct, indirect and synergistic allelopathic effects and acquiring a complete overview of allelopathy; (3) investigation of the different types of combination between allelopathic methods and traditional agricultural practices; (4) a focus on industrial processing for the development of commercial bioherbicides, given the high amounts of allelochemical-based candidates; (5) expanding the GE approach to the many well-known allelopathic crops and explore new GE tools for the biofortification of allelopathic crops. These recommendations will help to improve the efficiency of allelopathy as an environmentally friendly tool for weed management in agroecosystems, increase its diffusion among farmers and stakeholders, and reduce the use of synthetic herbicides and thus the development of weed-resistant ecotypes.

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