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Review Article

Stress Management

Environmental Effects and Management Strategies of the Herbicides

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Abstract

India has wide range of agro-climates and soil types and highly diverse agriculture farming systems with different types of weed problems. So, herbicides are the integrated part of the general cropping systems. In general, herbicides are formulated in such a way that they degrade from the environment after completion of their intended work, but a few of them persist in the environment and cause a serious hazard to the succeeding crop and also to the surrounding environments. Hence, a proper knowledge of herbicides is important to understand the management procedure, organization and hierarchy of the herbicides. It also provides an imminent idea to herbicide resistance, which continues to be a problem in sustainable agricultural management. In this review, the herbicides used in India, negative impact of herbicides on the environment, persistency of herbicides, their dissipation methods and different management practices to avoid/minimize herbicide carry-over effects were discussed. The combine effects of bioaugmentation and biostimulation along with organic matter addition might be a promising technology to accelerate the biodegradation. Apart from these, extensive field evaluation studies with other tools like crop rotation and increment of the organic matter content is definitely a promising technique for managing the herbicide persistence. Bioherbicides, a biological control agent for weeds, and transgenic approaches can be a good alternative for chemical herbicides in future. They provide high degree of specificity of target weed and have no effect on non-target, beneficial plants or man and do not form any residues in the environment.

Keywords: Herbicides, persistency, dissipation, management practices, bioherbicides

1. Introduction

Increasing global population and rising food demand has put our agricultural production to a challenge whether it has the capability to produce sufficient food in future through sustainable agricultural practices or not. However, interference of weeds, being one of the most important hindrances, declines crop yields and consequently overall food production (Soloneski, 2013). Weeds are the types of plants which are undesirable, persistent and interfere with growth of other crop plants. They can hold back crop yield annually by competing with crops for environmental resources like water, light and nutrients and lead to billions of dollars in global crop losses (Meena, 2015). They also affect in human activities, agricultural developments, natural processes and economy of the country. Therefore, weed management has been a major

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challenge for crop producers from the start of agriculture. It is important to have a long-range strategy to help predict and avoid potential weed problems in the future. Effective weed management is critical in maintaining agricultural productivity (Ahmed et al., 2010; Verma, 2014).

Herbicides have been used since long throughout the World. World War II started the 'chemical era' for the development of herbicides. The uses of herbicides are increasing day by day. Many developing countries like India, China, Bangladesh etc. are now experiencing the shortage of workers as millions of people move from rural to urban areas. In these countries, herbicides are far cheaper and more readily available alternative than hand weeding. For that reason, usage of herbicides occupies 44% of the total agrochemicals globally and 30% in India (Sondhia, 2014). They can remove weeds quickly in critical situations when manual weeding seems difficult or not possible. Herbicides destroy the weeds thereby helping the crops grow better and secure the crops from the harmful effects of weeds, i.e., competition for different environmental factors, releasing the toxins, modification of microbial population in soil and the air, harboring of pest etc. (Maheswari and Ramesh, 2019). But the efficacy and safety of herbicides are greatly influenced by soil and climate change (Robinson, 2019). Generally one-time application is enough but sometimes repeated application is also practiced. These plant poisons are not very toxic for animals, but indirectly affect animal and microbial habitat by changing the vegetation of treated site.

Herbicides vary greatly in their chemical composition. Most of the herbicides are highly persistent and non-biodegradable and remain harmful for a long period of time. Sometimes, Nitrogen fixation is greatly hampered or inhibited due to the application of certain herbicides. Improper use of herbicides also contaminates surface water such as ponds, streams, rivers and lakes as well as the ground water. The toxic herbicides slowly contaminate the food chain by increasing concentration each time. During the last decade these chemical residues have been increasing greatly in the environment (Mullison, 1970). This review describes about - the herbicides used in India, negative impact of herbicides on the environment, persistency of herbicides, their dissipation methods and different management practices to overcome herbicide carry-over effects. The complete information of these things will help to understand the substances well and enable their proper utilization by the agriculturists.

2. Herbicides Used in India

In the 1940s, farmers did not have much idea and choice for herbicides. To overcome the problem of broad leaf weeds, 2, 4-D was first used in crop fields. But in the 1970s, a significant number of herbicides of different chemical nature and with different modes of action were developed. It became vital to develop a method to maintain/keep these products organized, so that it would be easy for the proper herbicide selection, mode and time of applications, easy diagnosis of herbicide, resistance management strategies etc. Herbicides were classified depending upon needs, according to the time of application (pre-plant, pre-emergence, and post-emergence), method of application (soil applied and foliar applied), specificity (selective and non-selective), translocation (systematic/translocated and non-systematic/contact) etc. (Vats, 2015).

India has a wide range of agro-climates and soil types. The highly diverse agriculture and farming systems are beset with different types of weed problems. Because of their dynamic nature, they need continuous efforts and monitoring in different ecosystems (Rao, 2018). Traditionally, weed control in India is largely dependent on manual weeding. But scarcity and cost of agriculture labours gradually increased the adaptation of cost saving options, these include herbicides (Rao et al., 2018), more specifically chemical herbicides. According to Choudhury et al. (2016), herbicide usage has increased three times from 2006 to 2016 while land for cultivation did not change in that proportion. Consumption of traditional high dose molecules is also being replaced by low-dose newer generation herbicides. Choudhury et al. (2016) have also reported that Butachlor and Glyphosate were the highest used herbicides in India, and followed by Paraquat, Pretilachlor and Pendimethalin in 2007.

The Ministry of Agriculture, Government of India regulates the manufacture, sale, import, export and use of herbicides through the 'Insecticides Act, 1968'. According to the act presently 64 technical herbicides and 27 combination herbicides are registered (as on 15.5.2019) for use in our country (Table 1).

Table 1: Herbicides and their formulations registered in India under the Insecticides Act, 1968

Sl. No.	Name of herbicide	Formulation registered
1.	2 ,4-Dichlorophenoxy acetic acid (2,4-D sodium, amine and ester Salt)	a) 2,4-D sodium salt used as tech a.i. 80% w/w min. b) 2,4-D amine salt 58% SL 22.5% SL c) 2,4-D ethyl ester 38% EC, 4.5% Gr, 20% WP
2.	Alachlor	50% EC, 10% Gr
3.	Anilofos	30% EC, 18% EC
4.	Atrazine	50%WP
5.	Azimsulfuron	50% DF
6.	Bensulfuron Methyl	60% DF(FI)
7.	Bentazone	480 g/l SL
8.	Bispyribac sodium	10% SC (FI), 10% w/v SC (FIM)
9.	Butachlor	50% EC, 5% Gr, 50% EW
10.	Carfentrazone-ethyl	40% EC, 40% DF(FI), 53%MUP(FI)

Table 1: Continue...

Sl. No.	Name of herbicide	Formulation registered
11.	Chlorimuron ethyl	25% WP
12.	Cinmethylene	10% EC
13.	Clodinafop-propargyl (Pyroxofop-propinyl)	15%WP
14.	Clomazone	50% EC
15.	Cyhalofop-butyl	10% EC
16.	Dazomet	Dazomet technical (soil sterilant Gr) not permitted on tea
17.	Diclofop-methyl	28% EC
18.	Diclosulam	84%WDG
19.	Dinocap	48% EC
20.	Diuron	80% WP
21.	Ethoxysulfuron	10% EC, 15% WG (FI)
22.	Fenoxaprop-P-ethyl	10% EC, 9.3% EC one-time import, 6.7% EC
23.	Fluazifop-P-butyl	13.4% EC
24.	Flucetosulfuron	10% WG (FI)
25.	Fluchloralin	45% EC
26.	Flufenacet	60% WP
27.	Flumioxazin	50.0% w/w SC
28.	Glufosinate-ammonium	13.5% SL, 50.0% TK
29.	Glyphosate	41% SL, 20.2% SL, 5% SL
30.	Glyphosate-ammonium salt	71% SG, 5%SL (FI)
31.	Halosulfuron-methyl	75% WG (F1)
32.	Imazamox	In combination product
33.	Imazethapyr	10% EC, 70% WG (FI)
34.	Isoproturon	50%WP, 75%WP, 50% Flow
35.	Metamitron	70%SC
36.	Methabenzthiazuron	70%WP
37.	Methyl bromide	99% L, 98% L
38.	Methyl chlorophenoxy acetic acid	40% SL or 40% WSC (amine salt)
39.	Metolachlor	50% EC
40.	Metribuzin	70%WP
41.	Orthosulfamuron	50%WG
42.	Oxadiargyl	80%WP, 6% EC
43.	Oxadiazon	25% EC
44.	Oxyfluorfen	23.5% EC, 0.35% Gr
45.	Paraquat dichloride	24% SL
46.	Pendimethalin	30% EC, 5% Gr, 38.7% CS (FI)&FIM
47.	Penoxsulum	21.7% SC C(FI), 2.67% OD(FI), 50% w/w MUP, 21.7% SC (FIM v/s FIT),
48.	Pinoxaden	5.1% EC
49.	Pretilachlor	50% EC, 30.7% w/w EC, 37.0% EW
50.	Propanil	35% EC
52.	Propaquizafop	10% EC (F1)
53.	Pyrazosulfuron-ethyl	10% WP, 70% WDG (FI)
54.	Pyrithiobac-sodium	10% EC,
55.	Quizalofop-ethyl	10% EC, (FI), 5% EC (FI), 15.0% EC (FIM)
56.	Quizalofop-P-tefuryl	4.41% EC
57.	Sulfentrazone	39.6% SC
58.	Sulfosulfuron	75% WG
59.	Sulphur	85% DP, 80% WP, 40% SC, 80% WG/WDG , 55.16 SC (800 g l^{-1}) 40% WP, 52% SC
60.	Tembotrione	34.4% SC
61.	Thiobencarb (Benthiocarb)	50% EC, 10% Gr
62.	Triallate	50% EC
63.	Triasulfuron	20% WG
64.	Trifluralin	48% EC (All uses of this product shall be completely banned except use in wheat)

Source: Anonymous, 2019a; Gr: granules; EC: Emulsifiable concentrate; WP: Wettable powder; DF: Dry Flowable; SC: Suspension concentrate; EW: Emulsion; oil in water; HN: Hot fogging concentrate; WDG: Water dispersible granules; SL: Soluble concentrate; SG: Water soluble granule, WG: Water dispersible granules; CS: Capsule suspension

Combine application of herbicides either pre-plant incorporated or pre-emergence or post-emergence generally enhance the spectrum of weed control or the length of residual weed control. Tank-mixing of different herbicides may get better spectrum of weeds control in a single application and saves time and labour in a weed management program. Compatible herbicides mixing from different chemical families may develop control of specific weed populations and also provide control of several weed types at the same time, such as grassy and broadleaf weeds. For example, the combinations of mesosulfuron and iodosulfuron, clodinafop and metsulfuron, sulfosulfuron and metsulfuron control both grasses and broad leaf weeds in wheat (Sudha et al., 2016). Presently, in our country, 27 combination products of two active ingredients are available (Table 2). Some herbicides are also banned and restricted by the government and some are refused their registration (Table 3). Recently, Registration Committee, Central Insecticide Board has given approval for the combination pesticides having three active ingredients. New combination products containing three active ingredients will be very useful, cost effective and time saving application in controlling grassy weeds, broadleaf weeds, and sedges.

Table 2: Herbicides and Formulations Registered under section 9(3) of the Insecticides Act, 1968 for use in the Country

Sl. No.	Combination of Herbicides
1.	Anilofos 24%+2,4-D 32% EC
2.	Bensulfuron methyl 0.6% +Pretilachlor 6% Gr
3.	Carfentrazone ethyl 0.43%+Glyphosate 30.82% w/w EW
4.	Carfentrazone-ethyl 20%+Sulfosulfuron 25% WG
5.	Clodinafop-propargyl 15% +Metsulfuron-methyl 1%WP
6.	Clodinafop-propargyl 16.5%+Sodium acifluorfen 8%WP
7.	Clodinafop-propargyl 9% Metribuzin 20% WP
8.	Clomazone 20%+2,4-D ethylester 30% EC
9.	Fenoxaprop-P-ethyl 7.77% +Metribuzin 13.6% EC
10.	Fluxapyzoxad 62.5% g l^{-1} Epoxyconazole 62.5% g l^{-1} EC
11.	Fomesafen 11.1% w/w Fluazifop-p-butyl 11.1% w/w SL
12.	Hexazinone 13.2% Diuron 46.8% WP
13.	Imazamox 35% Imazethapyr 35% WG
14.	Imazethapyr 2% Pendimethalin 30% EC
15.	Indaziflam 1.65% GlyphosateIsopropyl ammonium 44.63% SC (FI)
16.	Mesosulfuron-methyl 3% Iodosulfuron-methyl sodium 0.6%WG (F1)
17.	Metribuzin 42% Clodinafoppropargyl 12% WG
18.	Metsulfuron-methyl 10% Chlorimuronethyl 10% WP
19.	Oxyfluorfen 2.5% Isopropyl amine salt of Glyphosate 41% SC
20.	Pendimethalin 30% Imazethapyr 2% EC
21.	Penoxsulam 0.97% w/w Butachlor 38.87% w/w SE
22.	Penoxsulam 1.02% Cyhalofop butyl 5.1 % OD
23.	Pretilachlor 6% Pyrazosulfuron-ethyl 0.15% Gr
24.	Propaquizafop 2.5% Imazethayper 3.75% w/w ME
25.	Propaquizafop 5% Oxyfluorofen 12% EC
26.	Sodium acefluorfen 16.5% Clodinafoppropargyl 8% EC
27.	Sulfosulfuran 75% Metsulfuron-methyl 5% WG

Source: Anonymous, 2019a

Table 3: list of herbicides which are banned, refused registration and restricted in use

A	Herbicides banned for manufacture, import and use	Diazinon, metoxuron, nitrofen, paraquat dimethyl sulphate, pentachlorophenol
B	Herbicides withdrawn	Dalapon, Simazine, Sirmate
C	Herbicides refused registration	2,4, 5-T, Ammonium sulphamate
D	Herbicides restricted for use	Dazomet

Source: Anonymous, 2019b

3. Negative Impact of Herbicides

Previously farmers did not have much choice for herbicides. They normally accustomed with the traditional methods. But increasing population pressure, urbanization, crisis of labour and increased cost of labour has forcibly changed their view to chemical weed management.

3.1. Effect of herbicides on the environment

Herbicides vary greatly in chemical composition and in the degree of threat they pose to the environment. Many of the herbicides are highly persistent. It is widely recognized that the main reason accounting for residues of certain herbicides like simazine and other triazines in ground and surface water was the widespread use of these herbicides at high doses on hard surfaces (Aslam et al., 2013). Heavy dose of herbicides affects microbial population of the soil. With herbicides targeting amino acid synthesis in both plants and microbes, there is a possibility that N_2 fixation may be inhibited by the application of certain herbicides. (Gonzalez et al., 1996) Indiscriminate use of chemicals might work for a few years but after some period, there will not be enough organisms to hold onto nutrients (Singh and Iyer, 2017). For example, landscape herbicides like triclopyr inhibits soil bacteria that transform NH_3 to NO_2. Overuse of glyphosate also reduces the growth and activity of free-living nitrogen fixing bacteria in soil and 2,4-D reduces nitrogen fixing capacity of the bacteria present on the roots of bean plant. It also reduces the growth and nitrogen-fixing capacity of blue-green algae, and inhibits the transformation of ammonia into nitrates by soil bacteria (Roberts and Hutson, 1999). Mycorrhizal fungi, which is present in roots of many plants, help in nutrient uptake. These fungi can also be damaged by herbicides in the soil. For example, oryzalin, trifluralin and triclopyr inhibit the growth of certain species of mycorrhizal fungi. Roundup shows toxicity to mycorrhizal fungi in laboratory studies. Triclopyr was found to be toxic to several species of mycorrhizal fungi (Aktar et al., 2009) and its oxadiazon reduces the number of mycorrhizal fungal spores (Roberts and Hutson, 1999; Moorman, 1989). On the other hand, the improper use of pesticides and herbicides may also cause the storm water infiltration into groundwater. According to USGS (United States Geological Survey), many herbicides were detected in urban streams than in agricultural streams. Commonly herbicides like 2,4-D, diuron and prometon are used by urban home owners and school districts. So, they are mostly found in surface and ground water. Trifluralin and 2,4-D were found in 19 collected sample out of 20 river basins studied (Kole et al., 2001).

3.2. Effect of herbicides on the animals

Most herbicides are specifically plant poisons, and are not very toxic to animals. However, by changing the vegetation of treated sites, herbicide use also changes the habitat of birds, mammals, insects, and other animals through changes in the nature of their habitat. Chlorpyrifos, is a common contaminant of urban streams, is highly toxic to fishes and kills them in waterways near treated fields or buildings (Anonymous, 2002). According to the EPA trifluralin is an active ingredient in the weed-killer and is extremely toxic to both cold and warm water fish. In a series of different tests, it was also shown to cause vertebral deformities in fish (Koyama, 1996). It is also stated that the weed-killers like Ronstar and Roundup are also acutely toxic to fish. In addition to direct acute toxicity, some herbicides may cause lethal effects on fish that reduce their chances for survival and threaten the population as a whole. Sometimes glyphosate or glyphosate-containing products can cause sub-lethal effects, such as erratic swimming and labored breathing, which raise the fish's probability of being eaten. 2, 4-D herbicides caused physiological stress responses in sockeye salmon and reduced the food-gathering abilities of rainbow trout (Ince et al., 2020). 2, 4-D or products containing 2,4-D are harmful to shellfish and other aquatic species. The weed-killer trifluralin is moderately to highly toxic to aquatic invertebrates, estuarine and marine organisms like shrimp and mussels (Anonymous, 1996).

Herbicides may hurt insects or spiders for example spider and carabid beetle populations decreased when 2,4-D applications destroyed their natural habitat. The herbicide oxidization is also toxic to bees, which acts as pollinators (Aktar et al., 2009). Herbicides can also be toxic to birds. Glyphosate treatment in clear cuts caused dramatic decreases in the populations of birds that lived there (Aktar et al., 2009). Negative effect of some organochlorines (OCs) on fish-eating water birds and marine mammals have been documented in North America and Europe (Kole et al., 2001).

Agricultural herbicide applicators are typically exposed to herbicide levels ranging from micrograms to milligrams per cubic meter of air through inhalation, but exposures through the skin are thought to be much greater (Spear, 1991). Spilling concentrated herbicide on exposed skin can be the toxic equivalent of working all day in a treated field (Libich et al., 1984). Dermal exposure can occur to the hands (directly or through permeable gloves), splashes onto clothing or exposed skin, and anywhere you wipe your hands (e.g., thighs, brow). Some tests have found relatively high levels of dermal exposure to the crotch and seat of workers who got herbicide on their hands, and then touched or wiped the seat of their vehicles (Marer, 1988), Herbicides can poison the body by blocking biochemical processes or dissolving or disrupting cell membranes. Small doses may not produce immediate visible effect, while large doses can cause severe illness or death. The effects may be localized, such as irritation to the eyes, nose, or throat, or generalized, which occurs when the compound is distributed through the body via the blood stream. Symptoms can occur immediately after exposure or develop gradually. Injuries are usually reversible, but in extreme cases can be permanently debilitating (Marer, 1988). A study showed that combined use of herbicides like glyphosate and paraquat caused a significant increase in urinary MDA levels in farmers (Intayoung et al., 2020).

Common symptoms of low-level exposure (such as occurs when mixing or applying herbicides in water) to many herbicides include skin and eye irritation, headache, and nausea. Higher doses (which can occur when handling herbicide concentrates) can cause blurred vision, dizziness, heavy sweating, weakness, stomach pain, vomiting, diarrhea, extreme thirst, and blistered skin, as well as behavioral alterations such as apprehension, restlessness, and anxiety (Marer, 1988). Extreme cases may result in convulsions, unconsciousness, paralysis, and death. Impurities produced during the manufacturing process and adjuvants added to the formulation may be more toxic than the herbicide compound itself. Consequently, LD50s determined for the technical grade of the herbicide may not be the same as that for the brand name formulation. Furthermore, combinations of herbicides can have additive and synergistic effects in which a formulation of two or more herbicides is 2 to 100 times as toxic as any one of the herbicides alone. Labels should be read carefully for manufacturer's warnings and safety precautions that may be required for a particular formulation (Thompson, 1996).

3.3. Effect of herbicides on plants

An important problem with broad applications is that they are non-selective. They are toxic to a wide variety of plant species, and not just the weeds. If herbicides are not used properly, damage may be caused to crop plants, especially if too large dose is used, or if spraying occurs during a time when the crop species is sensitive to the herbicide. Unintended but economically important damage to crop plants is sometimes a consequence of the inappropriate use of herbicides. Herbicide spray can directly hit non-target vegetation and contaminates air, soil, and non-target plants. As herbicides are intended to kill the plants, so definitely they can harm or kill desirable species if applied directly or drifted or volatilized on such plants. Vapors of many volatile esters of formulated herbicides are sufficient to cause severe damage to other plants. Sometimes drift or volatilization of phenoxy herbicides like 2,4-D, cause damage to nearby trees and shrubs (Dreistadt, 2016). Glyphosate exposure can also decrease seed quality and increase the susceptibility of certain plants to disease (Brammall and Higgins, 1998). The U.S. Fish and Wildlife Service have accepted that 74 endangered plants have become threatened by glyphosate alone. Whereas exposure to clopyralid can reduce yields in potato plants and EPA calculated that 1% volatilization is enough to damage non-target plants (Dreistadt, 2016). Carpenter et al. (2020) showed significant delay on peak flowering and/or reductions in flower production in wild plant species at the seedling or flower bud stage. In another study three years sublethal exposure to atrazine or tribenuron-methyl changed the species composition, reduced the number of plant species and the relative frequencies of some plants (Qi, 2020). Wagner and Nelson (2014) also concluded that herbicides can harm non-native and native plants at the seed stage. Rosculete et al., 2019 studied on the mitodepressive effect as well as the chromosomal aberrations (%) which is increased with a higher herbicide concentration in Allium cepa. Moreover, herbicides also affect the aquatic plants. In one study, oxadiazon was found to severely reduce algae growth (Ambrosi et al., 1978). Algae are a staple organism in the food chain of aquatic ecosystems. Studies looking at the impacts of the atrazine and alachlor herbicides on algae and diatoms in streams showed that even at fairly low levels, the chemicals damaged cells, blocked photosynthesis, and stunted growth in varying ways (Anonymus, 2000). A study showed that flurochloridone (FLC) caused serious oxidative and photosynthetic pigment damage when aquatic plants get exposed to different concentrations of FLC (Zhou et al., 2020).

3.4. Build-up of resistant biotypes

Apart from their effect on the environment, another major problem with herbicides has been the build-up of herbicide-resistant biotypes where the same herbicide has been used repeatedly for a number of years. This problem was not clearly foreseen at the start of the herbicide revolution but, since the early 1980s, triazine resistance has developed in most countries where these herbicides have been used. The usefulness of a number of other herbicides, including paraquat, dichlofopmethyl and sulfonylurea types has been affected by the development of resistant biotypes (Heap, 2014). Methods of dealing with this problem include prevention of weed seed shedding, crop rotation, herbicide rotation, control of weed escapes and tillage practices. This could be achieved if land managers were made more aware of the threat of resistant biotypes and made greater efforts in intensively managed areas to prevent weeds from shedding seeds by the use of a rotation of herbicides supplemented by physical means such as mulching, hand hoeing and hand weeding (Chhokar et al., 2018).

4. Persistency of Herbicides

A herbicide is said to be persistent if it is present in the soil in its original or closely related but phytotoxic forms even after its mission is accomplished and the quantity that exists is referred to as residue (Sankaran et al. 1993). Herbicides vary in their potential to persist in soil (Table 4). Herbicide families that have persistent members include the triazines, uracils, phenylureas, sulfonylureas, dinitroanilines, isoxazolidinones, imidazolinones and certain plant growth regulators belonging to the pyridine family (Sondhia, 2014; Devi et al., 2019). The persistence problem arises when the herbicides are applied scrupulously or continuously; the crop failure necessitates replanting; a susceptible crop follows a short-term crop which received a persistent herbicide; and the decomposition of the applied herbicide proceeds very slowly (Sondhia, 2014; Devi et al., 2019;). The longer persistence of herbicide poses a hazard to subsequent land use and is undesirable. The higher the persistence of herbicide, the higher is the chance of transportation to different distant compartments of environment, viz. surface water, ground water, etc., creating non-point source of contamination (Arora et al., 2019).

Table 4: Relative persistence of some herbicides in soil

< 1 months	1-3 months	3-6 months	> 6 months
MCPA	Alachlor, Acetochlor, Ametryn, Anilofos, Bispyribac-sodium, Butachlor, Carfentrazone-ethyl, Dalapon, Fluazifop-butyl, Halosulfuron, Metribuzin, Metamifop, Metsulfuron-methyl, Metolachlor, Oxyfluorfen, Propachlor, Pyrazosulfuron-ethyl, Thiobencarb	Clomazone, Chlorimuronethyl, Diallate, Dithiopyr, Ethofumesate, Fluchloralin, Imazethapyr, Isoproturon, Metamitron, Oxadiazon, Linuron, Pendimethalin, Pyrazon	Atrazine, Bromacil, Chlorsulfuron, Diuron, Diquat, Imazapyr, Picloram, Sulfentrazone, Sulfometuron, Simazine, Trifluralin, Paraquat

Source: Janaki et al. (2015)

5. Mechanisms of Herbicide Dissipation

Dissipation refers to the movement, degradation, or immobilization of an herbicide in the environment. Herbicides undergo biotic degradation by microbes or by plant enzymes and abiotic degradation including chemical degradation and degradation caused by the sunlight.

5.1. Natural degradation

Degradation occurs when a herbicide is decomposed to smaller component compounds, and eventually to CO_2, water, and salts through photochemical, chemical, or biological (microbial metabolism) reactions. Biodegradation accounts for the greatest percentage of degradation for most herbicides. When a single herbicide degrades, it usually yields several compounds (metabolites), each of which has its own chemical properties including toxicity, adsorption capacity, and resistance to degradation. Some metabolites are more toxic and/or persistent than the parent compound. In most cases, the natures of the metabolites are largely unknown (Mueller et al., 2015).

Photodegradation refers to decomposition by sunlight. Sunlight intensity varies with numerous factors including latitude, season, time of day, weather, pollution, and shading by plants, litter, etc. Studies of the photodegradation of herbicides are often conducted using UV light exclusively, but there is some debate as to whether most UV light actually reaches the surface of the earth. Therefore, photodegradation rates determined in the laboratory may overestimate the importance of this process in the field (Konstantinou *et al.,* 2001).

Microbial degradation is decomposition through microbial metabolism. Different microbes can degrade different herbicides, and consequently, the rate of microbial degradation depends on the microbial community present in a given situation. Soil conditions that maximize microbial degradation include warmth, moisture, and high organic content (Singh and Singh, 2016). Herbicides may be microbially degraded via one of two routes. They may be metabolized directly when they serve as a source of carbon and energy (i.e., food) for microorganisms, or they may be co-metabolized in conjunction with a naturally occurring food source that supports the microbes (Hutzinger, 1981). Herbicides that are co-metabolized do not provide enough energy and/or carbon to support the full rate of microbial metabolism on their own (Cork, 1991). Degradation rates of co-metabolized herbicides tend to remain constant over time.

Chemical decomposition is degradation driven by chemical reactions, including hydrolyzation (reaction with hydrogen, usually in the form of water), oxidation (reaction with oxygen), and disassociation (loss of an ammonium or other chemical group from the parent molecule). The importance of these chemical reactions for herbicide degradation in the field is not clear (Helling et al., 1971).

5.2. Immobilization/Adsorption

Herbicides may be immobilized by adsorption to soil particles or uptake by non-susceptible plants. These processes isolate the herbicide and prevent it from moving in the environment, but both adsorption and uptake are reversible (Lushchak et al., 2018). In addition, adsorption can slow or prevent degradation mechanisms that permanently degrade the herbicide. Adsorption refers to the binding of herbicide by soil particles, and rates are influenced by characteristics of the soil and of the herbicide. Adsorption is often dependent on the soil or water pH, which then determines the chemical structure of the herbicide in the environment (Helling et al., 1971). Adsorption generally increases with increasing soil organic content, clay content, and cation exchange capacity, and it decreases with increasing pH and temperature. Soil organic content is thought to be the best determinant of herbicide adsorption rates (Elgueta, 2016). Adsorption is also related to the water solubility of an herbicide, with less soluble herbicides being more strongly adsorbed to soil particles. Solubility of herbicides in water generally decreases from salt to acid to ester formulations, but there are some exceptions. For example, glyphosate is highly water-soluble and has a strong adsorption capacity. The availability of an herbicide for transport through the environment or for degradation is determined primarily by the adsorption/desorption process (Kanissery et al., 2019). Adsorption to soil particles can stop or slow the rate of microbial metabolism significantly. In other cases, adsorption can facilitate chemical or biological degradation. Adsorption can change with time and, in most cases, is reversible, i.e., the herbicide can desorb from the soil or sediments and return to the soil solution or water column (Stephane and Thierry*,* 2009).

5.3. Effect of Soil Factors on herbicide dissipation

Several soil factors are important in determining the persistence of herbicide, i.e., pH, organic matter, texture, moisture and temperature (Reinhardt and Nel, 1993). Soil pH may cause herbicide degradation directly by affecting the stability of the herbicide or indirectly by its effect on the soil microbes. The sulfonylureas (SU) herbicide breakdowns more quickly in acid soils, hence persisting longer in high pH soils, i.e., pH>7.0 (Paporisch et al., 2020). The Imadazolionones breakdown more readily in alkaline soils and therefore persistence is increased in low pH, i.e., pH<7.0 soils (Neina, 2019). Similarly, the organic matter binds the herbicide and releases them more slowly. Herbicides persist longer in high organic soils. In addition, soil rich in organic matter support microorganism, which play a critical role in the degradation of most herbicides (Gomez et al., 2014). Generally, the relative percentage of sand, silt and clay in a soil determines its texture. Clay particles provide extensive amounts of surface area that can adsorb significant amounts of herbicide. So, in soils with high clay content, a greater amount of the herbicide is required for adequate weed control as compared to sandy soils (Janaki et al., 2015). On the other hand, soil temperature and moisture play important factors in determining the rate of breakdown of herbicide in soil. Normally warm and moist soils favor herbicide breakdown. The lesser the rainfall after spraying, higher the carryover to the next season which increase the risk of damage to sensitive crops (Rana. 2018).

5.4. Plant uptake

Once absorption of herbicide occurs into the plants, it is metabolized. This effectively removes residues from the soil. The amount of herbicide absorbed by plants subsequently metabolized (degraded to) into inactive form. Corn can absorb and degrade significant amounts of atrazine. When plant stand densities are low, removal of herbicide residues is also low (Blanco et al., 2013).

5.5. Movement/volatilization

Movement through the environment occurs when herbicides are suspended in surface or subsurface runoff, volatilized during or after application, evaporated from soil and plant surfaces, or leached down into the soil. These processes actually occur simultaneously and continuously in the environment (Hutzinger, 1981). Volatilization occurs as the herbicide passes into the gaseous phase and moves about on the breeze. Volatilization most often occurs during application, but also can occur after the herbicide has been deposited on plants or the soil surface. The volatility of an herbicide is determined primarily by its molecular weight. Most highly volatile herbicides are no longer used. Volatility generally increases with increasing temperature and soil moisture, and with decreasing clay and organic matter content (Tabernero et al., 2020). The use of a surfactant can change the volatility of a herbicide. In extreme cases, losses due to volatilization can be up to 80 or 90% of the total herbicide applied (Helling et al., 1971).

6. Management Practices to Avoid/Minimize Herbicide Carry-Over Effects

It is important to plan a weed control strategy carefully so that herbicide carry-over can be avoided. Planning a weed control program should be based on the weed problem, herbicide options, including formulation and persistence, soil characteristics, weather conditions and crop rotation. Various management techniques such as seeding date, crop selection and fertilizer placement may be practiced to promote a vigorous competitive crop that has an advantage over weeds and helps to minimize the level of carry-over the following year. It is important to leave an untreated check area in the field for future comparison. A weed control plan to minimize or eliminate herbicide carry-over should include the following...

6.1. Selection of herbicides with minimum carry-over potential

Choosing a herbicide with little or no carry-over given your local soil and weather conditions will eliminate future crop injury problems. Some crops tolerate a particular herbicide residue and can be replaced soon after that herbicide is applied, while other crops remain sensitive to the herbicide for a longer time after application. Some herbicide can dissipate for many half-lives and still be injurious to certain crop species, while other herbicides persist longer but are less injurious to some crops. For example, in Figure 1, herbicides "A" (with a half-life of 38 weeks) persists longer in the soil than herbicides "B" (with a half-life of 5 weeks). However, potatoes are much more sensitive to injury from herbicide "B' than herbicide "A" even after 10 half-lives (Colquhoun, 2006).

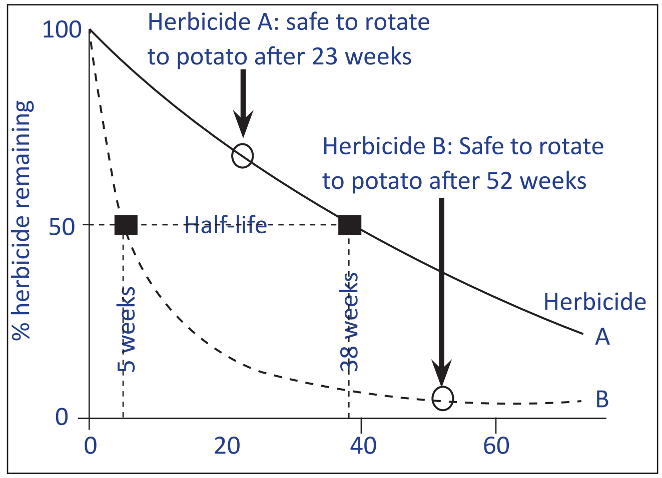

Figure 1: Comparison and persistence and carry-over of two herbicides (Colquhoun, 2006)

It has been shown that early season application of herbicide when the weeds are small reduces competition, improves crop yield and assists in reducing the carryover potential to succeeding crops. Minimum rates of herbicides should be applied to reduce the potential for carry-over. The higher the initial application rate, the longer it will take for the herbicide residue to dissipate. Careful, uniform and accurate application of herbicide is essential to reduce the potential for carry-over. Non-uniform application or incorporation can cause hot spots where higher than recommended concentrations of herbicide occur in patches. Damage usually occurs on headlands and corners or in strip throughout the field. In a conventional tillage system, tillage mixes the herbicide residues throughout the soil profile, accelerating rates of microbial degradation and diluting the herbicide residues (Huang et al., 2018). Keeping good field records, crop rotation and avoid back-to-back use of herbicides from the same herbicide group, this management strategy will assist in minimizing re-crop concerns. Combining a non-residual herbicide with the lowest recommended rate of a residual herbicide in a tank-mixture can reduce carry-over potential. When herbicide residue is detected or suspected a tolerant crop should be grown to either store or degrade the residue to non-toxic compounds. Soil also plays an important role in herbicide breakdown (Rana, 2018).

6.2. Enhancing the herbicide degradation by different methods

6.2.1. Biostimulation

The term "biostimulation" is often used to describe the addition of electron acceptors, electron donors, or nutrients to stimulate naturally occurring microbial populations (Scow and Hicks, 2005). Comprehensively, biostimulation could be perceived as including the introduction of adequate amounts of water, nutrients, and oxygen into the soil, in order to enhance the activity of indigenous microbial degraders (Couto et al., 2010) or to promote co-metabolism (De Lorenzo, 2008). The concept of biostimulation is to boost the intrinsic degradation potential of a polluted matrix through the accumulation of amendments, nutrients, or other limiting factors, and it has been used for a wide variety of xenobiotics. The addition of organic matter, bioprocessed materials or compost naturally initiates the microbial activity in the soil and could be utilized to treat contaminated soils. Fresh bioprocessed materials serve as rich source of nitrogen, carbon, and other nutrients and make excellent candidates for flourishing the microbial growth (Kadian et al., 2008). Devi et al. *(*2005) found that the continuous application of farm yard manure (FYM) to the rice crop enhanced the degradation of butachlor, pretilachlor and 2,4-D in the soil through enhanced microbial activity.

6.2.2. Nutrients addition

Mostly, nutrients in the soil stay below optimal concentration for microbial activity. Supplementing such soils with the necessary nutrients instigates the biodegradation of the pollutants and is a promising technique to enhance the bioremediation of contaminated sites. Nutrients like carbon, nitrogen, and phosphorus stimulate microbes to create the essential enzymes to break down the contaminants. Hance (1973) demonstrated the consequence of inorganic nutrient addition on the breakdown of atrazine in the soil. Thereafter, the concept of nutrient supplementation for enhanced degradation of contaminants was brought into the limelight by various researchers, and the prospects of microbial biostimulation through the manipulation of organic and inorganic nutrient status in the soil have since been investigated. In some cases, inorganic nitrogen starvation may be more effective in promoting degradation and has been reported for atrazine and other heterocyclic compounds (Sims, 2006). Qiu et al. (2009) confirmed that Dichlobenil was completely degraded in 60 hours in the P-supplemented soil extract, in comparison to less than 40% degradation without P supplement. The addition of fertilizer enhances the growth of tolerant plants, which increases the uptake of herbicide from the soil. It also promotes the growth of microflora, increasing biological breakdown of herbicide in the soil. For example, addition of phosphate enhances the microbial breakdown of the phenoxy herbicides 2,4-D and MCPA (Rana*,* 2018).

6.2.3. Bioaugmentation

The process of bioaugmentation is the introduction of specific microorganisms (indigenous or non-indigenous) aiming to enhance the biodegradation of target compound or serving as donors of the catabolic genes. Usually this goes in pair with the biostimulation (Kanissery and Sims, 2011). Increasing the population of particular herbicide degrading pure culture bacteria by artificial means may solve such type of problem. Mandelbaum et al. (1993) found that the instead of pure cultures, mixing pure cultures restored atrazine-mineralizing activity and also observed increased rates of atrazine metabolism with the repeated transfer of the mixed cultures even at the elevated concentrations. Radosevich et al. (1995) isolated an atrazine-degrading bacterial culture from an agricultural soil previously impacted by herbicide spills and used to enhance its degradation in soil and found that these organisms were capable of using atrazine under aerobic conditions as the sole source of C and N. Jaya et al. (2014) reported, *Rhizopus oryzea* is a potential fungal isolate and can be used for the bioremediation of alachlor from soil and the half-life values in sterile and non-sterile soil incubated with *Rhizopus oryzea* were found to be 7.2 and 8.6 days, respectively.

6.3. Deactivation of herbicides to reduce its persistent and harmful effects

6.3.1. Addition of organic matter

Herbicides are inactivated by plant residues or organic matter incorporated into soil. The organic matter acts in two ways. Primarily, the application of FYM adsorbs the herbicide molecules in their colloidal fraction and makes them unavailable for crops and weeds. After a lag phase, microbial population thriving on organic matter starts decomposing the herbicide residues at a faster rate due to high moisture holding capacity of organic matter in soils. Meena et al. (2007) reported that the FYM application at 12.5 t ha^{-1} reduced the atrazine residue significantly followed by compost (12.5 t ha^{-1}) and phosphoric acid (50 ppm) application. Residual toxicity of atrazine to the sensitive crop soybean was overcome by the application of FYM at 12.5 t ha^{-1} or compost 12.5 t ha^{-1} or charcoal 5.0 kg ha^{-1} along the seed line (Chinnusamy et al., 2008). Randhawa et al. (2005) found that the residues of isoproturon, 2,4-D and butachlor in the soil under rice-wheat cropping was not built up when the organic matter was continuously applied for five years. Janaki et al. (2014) reported the influence of clay and organic matter on the sorption and persistence of pyrazosulfuron-ethyl in rice growing soils and suggested that the persistence of the herbicide and its residue depended on the properties of the soil. Similarly, Arora (2014) also found that the leaching and persistence of oxyfluorfen depended on the organic matter addition through FYM in sandy clay loam soil. Sharma and Angiras (2004) observed that higher the organic matter content in soils, lesser was the persistence of atrazine and *vice versa*. Mukherjee (2009) used different organic amendments, *viz.* rice straw, FYM, saw dust, and charcoal and found FYM was the most effective for the degradation of atrazine to the extent of 89.5% within 60 days. Felsot and Dzantor (1997) observed that the use of organic amendments as an inexpensive option for the disposal of herbicide (alachlor, metolachlor, atrazine, and trifluralin) waste.

6.3.2. Use of non-phytotoxic oil, adjuvants and surfactants

Non-phytotoxic oil, adjuvants and surfactants reduce the residual hazard besides enhancing the weed killing potency. Adjuvants modify certain physical characteristics of the spray solution like surface tension and wetting ability, which may modify the spray solution's response to move in the soil (Dubovik et al., 2020). One of the beneficial effects of adjuvants, especially surfactants is a reduction in the amount of water available for evaporation from the soil surface (Janaki et al., 2015). Addition of olejan to the trifluralin applications caused a significant increase in of the herbicide degradation rate, both in laboratory and pot-field experiments (Swarcewicz et al., 1998). Application of cationic adjuvants may have led to the formation of neutral species by binding to certain anionic molecules in the soil system. The resultant complex may have dissolved the herbicide rendering it less mobile in soil. Surfactants are important small group of chemicals among adjuvants. They act as emulsifiers as well as wetters and spreaders. The addition of adjuvants could influence the speed of degradation and increase herbicide residues in soil and plant. Usually adjuvants are applied with herbicides in reduced doses (70–80% of recommended one) and herbicidal residues determined at harvest time are lower than those obtained from treatments, where recommended doses of herbicide (without adjuvant) were applied (Kucharski, 2003). Further the influence of adjuvants on herbicide residues in soil and plant, degradation rate and leaching depend on the kind of adjuvant (Kucharski and Sadowski 2009). Similarly, in a field experiment, Kucharski et al. (2011) observed a 43% increase in lenacil herbicide residues in the superficial soil layer, with the addition of adjuvants (oil and surfactant). Kucharski et al. (2012) found that the DT50 values for the mixture of chloridazon + oil and surfactant was about 8–14 days higher in comparison to the DT50 for chloridazon applied alone (43 days) and no significant differences were observed between degradation rates of chloridazon.

6.3.3. Use of adsorbents, protestants and antidotes

These are applied to the soil, crop seed or transplanted plant to protect the crop from herbicide injury. The mode of action may be due to either deactivation or adsorption of the herbicide, preventing its absorption and translocation by the crop. Activated charcoal has a high adsorptive capacity because of its extremely large surface area and may either be distributed or applied as narrow band over the seed at the time of planting (Ighalo et al., 2020). Janaki et al. (2015) reported that the application of activated carbon 8 and 18 kg ha^{-1} to the tobacco along with imazaquin and chlorimuron reduced the phytotoxicity besides increasing the yield from 2 to 4-fold.

Application of biochar is also a very good option to temporarily immobilize the herbicide residues in soil and allow the crop to escape from toxicity. The source of material used for biochar production also affects the sorption of herbicide residues. Biochar additions, even in small quantity, increased diuron sorption. Thus, the presence of carbonaceous material, even in small amounts, can dominate sorption of organic compounds in soils (Cabrera and Spokas, 2011). Similar results were obtained by Yu et al. (2010) for the sorption of pyrimethanil under similar conditions. The influence of biochar and its sources on herbicide dissipation is presented in Table 5.

Adsorption of herbicide residue can be increased by the addition of adsorbent material such as activated charcoal. The use of activated charcoal on a large scale is not economic. However, on small areas as a spot treatment for chemical spills or where high value crops are produced its use might be economically justified (Ed Peachey. 2020).

6.3.4. Use of safeners

Herbicide safeners are group of structurally diverse synthetic chemicals with the unique ability to protect crop plants from injury by certain herbicides (Farago et al., 1994). They are used commercially to improve herbicide selectivity between crops and weed species and can be either as a mixture with the herbicide (Table 6) or as a seed treatment to the crop seed prior to sowing. They act as *“bioregulators”* controlling the amount of a given herbicide that reaches its target site in an active form (Rosinger, 2014). A safener-induced enhancement of the metabolic detoxification of herbicides in protected plants is the most apparent mechanism for the action of all commercialized safeners. Herbicide-detoxifying enzymes such as glutathione transferases (GST), cytochrome P-450 monooxygenases (Cyt P450), esterases, and UDP-glucosyltransferases are induced by herbicide safeners. At the molecular level, safeners appear to act by activating or amplifying genes coding for these enzymes like GST (Hatzios and Wu, 1996).

6.4. Use of Natural herbicides can be good alternatives

Allelopathy is a natural biological phenomenon of interference among organisms in such a way that an organism produces one or more biochemicals that influence the growth, survival, and reproduction of other organisms (Cheng and Cheng, 2015). Allelochemicals may have beneficial (positive allelopathy) or detrimental (negative allelopathy) effects on the target organisms. Allelochemicals could be recruited in weed management as alternatives to chemical herbicides. Allelochemicals are listed as six classes (Putnam, 1988) that possess actual or potential phytotoxicity. These classes are, namely, alkaloids, benzoxazinones, cinnamic acid derivatives, cyanogenic compounds, ethylene and other seed germination stimulants, and flavonoids which have been isolated from over 30 families of terrestrial and aquatic plants. Like synthetic herbicides, there is no common mode of action or physiological target site for all allelochemicals (Maria et al., 2013).

Allelochemicals are present in different parts of the plant, i.e., leaves, flowers, fruits, stems, bark, roots, rhizomes, seeds and pollen. They may be released from plants into the environment through volatilization, leaching, root exudation, and decomposition of plant residues. Rainfall causes the leaching of allelopathic substances from leaves which fall to the ground during period of stress, leading to inhibition of growth and germination of crop plants (Mann, 1987). The allelochemical interference implies their interference with each other as well the interference with other surrounding plants. Several chemicals can be released together and may

Table 5: Biochar and herbicide dissipation in soil

Herbicide	Finding
Atrazine	A lag phase of 11 days in the dissipation of atrazine in the nonamended and biochar amended silt loam soil. Later, dissipation was greater in the unamended soil (Mesa et al., 2011).
Atrazine	Increase in the degradation in a clay soil adapted to atrazine, and amended with biochar and attributed to the stimulation of the soil microflora by the nutrients provided by biochar (Jablonowski et al., 2012).
Acetochlor	Amending soil with biochar resulted in a DT50 of 34.5 days (Janaki et al., 2015).
Isoproturon	Biochar amendment increased the isoproturon persistence in soil with the DT50 of 2.2 days in the unamended soil to 5.6 days in the 2% (w/w) biochar amended soil (Si et al., 2010).
Atrazine and trifluralin	Decreased bioavailability of the chemicals by the wheat straw biochar. Hence, choosing the appropriate application rates for biochar amended soils is essential (El-Naggar et al., 2019).
Pyrazosulfuron-ethyl	Biochar (0.5%) amendment did not have significant effect on herbicide degradation. Half-life values in the control, 0.5% biochar amended and rice planted soils were 7, 8.6, and 10.4 days, respectively (Manna and Singh. 2015).
Fluometuron and MCPA	Not all biochar amendments will increase sorption and decrease leaching of fluometuron and MCPA. The amount and composition of the organic carbon (OC) content of the amendment, especially the soluble part (DOC), can play an important role in the sorption and leaching of these herbicides. Biochar and surface area are other important parameters to be considered for sorbent election (Cabrera et al., 2011).
MCPA	Enhanced MCPA persistence and soil toxicity in sandy soil amended with straw biochar. Also, significantly more MCPA remained after 100 days if amended with straw-derived biochar in comparison to wood-derived biochar (Muter et al., 2014).

Table 6: Commonly used herbicide safeners

Safeners	Crop	Herbicide	AM
Naphthalic anhydride	Maize	Thiocarbamate	
Naphthalic anhydride	Maize	Phenylcarbamates, Dithiocarbamates, Chloroacetanilides, Sulfonylureas, Imidazolinones, Cy-clohexenones, Arylophenoxyalkanoic acids	ST
Naphthalic anhydride	Maize, Oats	Chlorsulfuron, Diclofop-methyl	ST
Dichlormid	Maize	Tthiocarbamate herbicides	SD
Dichlormid	Maize	Chloroacetanilide herbicides, Sethoxydim, Clomazone	SD
Dichlormid	Wheat	Diallate	SD
Substituted NDichloro-acety 1-1,3 oxazolidines	Maize	Thiocarbamate herbicides	SD
Oxime ether	Grain Sorghum	Chloroacetanilide herbicides	
Benoxacor	Maize	Metolachlor with herbicide	
Cloquintocet-mexyl	Wheat	Clodinafop-progaryl	SMWH
Cyometrinil	Sorghum	Metolachlor	ST
Fenclorim	Rice	Pretilachlor	
Flurazole	Sorghum	Alachlor, Acetochlor, Thiocarbamate	ST
Fluxofenim	Sorghum	Metolachlor	ST
Flurazole	Cereals	Halosulfuron-methyl	SMWH
Mefenpyrdi-ethyl	Wheat, Rye, Triticale, Barley	Fenoxaprop-ethyl	SMWH

AM: Application method; ST: Seed treatment: SD: Seed dressings; SM: Spray as mixture; SMWH: Spray as mixture with herbicide; Source: Janaki et al,. 2015

exert toxicities in an additive or synergistic manner. Different crops such as beet (*Beta vulgaris* L.), lupin (*Lupinus lutens* L.), maize (*Zea mays* L.), wheat (*Triticum aestivum* L.), oats (*Avena sativa* L.) and barley (*Hordeum vulgare* L.) are known to have an allelopathic effect on other crops (Hamid, 2011). For instance, some wheat cultivars were found to significantly inhibit both germination and radicle growth of annual ryegrass (Wu et al., 2003). The allelopathic potential of wheat cultivars was positively correlated with their allelochemical (total phenolics) content. Different allelopathic compounds of some crops, that are important in weed management are presented in Table 7 (Bhadoria, 2011).

Table 7: Allelochemicals of some important crops

Crops	Allelochemicals
Rice	Phenolic acids
Wheat	Hydroxamic acids
Cucumber	Benzoic and cinnamic acids
Black mustard	Allyl isothiocyanate
Buck wheat	Fatty acids
Clovers and	Isoflavonoids and phenolics
Sweet clover	Phenolics
Oats	Phenolic acids and scopoletin
Cereals	Hydroxamic acids
Sudangrass	Phenolic acids and dhurrin
Sorghum	Sorgoleone

Source: Bhadoria, 2011

Allelopathic interferences often result from the combined action of several different compounds. Allelopathic plant extracts can effectively control weeds, since mixtures of allelopathic water extracts are more effective than the application of single-plant extract (Naeem et al., 2018). Combined application of allelopathic extracts and reduced herbicide dose (up to half the standard dose) give as much weed control as the standard herbicide dose in several field crops. Lower doses of herbicides may help to reduce the development of herbicide resistance in weed ecotypes (Farooq et al., 2011). Allelopathy thus offers an attractive and environmental friendly alternative to pesticides in agricultural pest management (Farooq et al., 2011). Generally, low concentrations of allelochemicals are stimulatory while it is inhibitory with higher concentrations (Lovett, 1989). Allelochemical concentrations in the producer plant may vary over time, and also vary in different type of plant tissue. Foliar and leaf litter leachates of *Eucalyptus* species, for example, are more toxic than bark leachates to some food crops (Iqbal et al., 2017). Biodegradable natural plant products rarely contain halogenated atoms and possess structural diversity and complexity, and these can act directly as herbicides or may provide lead structures for herbicidal discovery (Duke *et al.,* 2000). Selection of allelopathic plants is a good and commonly used approach for identification of plants with biologically active natural products (Table 8).

The role of biotechnology in allelopathy has received much

Table 8: Examples of allelopathy

Allelopathic plant	Impact
Rows of black walnut interplanted with corn in an alley cropping system	Reduced corn yield attributed to production of juglone, an allelopathic compound from black walnut, found 4.25 meters from trees (Jose and Gillespie, 1998).
Rows of Leucaena interplanted with crops in an alley cropping system	Reduced the yield of wheat and turmeric but increased the yield of maize and rice (Moura et al., 2014).
Lantana, a perennial woody weed pest in Florida citrus	Lantana roots and shoots incorporated into soil reduced germination and growth of milkweed vine, another weed (Negi et al., 2019).
Sour orange	Leaf extracts and volatile compounds inhibited seed germination and root growth of pigweed, bermudagrass, and lambsquarters (Ghaderi et al., 2018).
Red maple, swamp chestnut oak, sweet bay, and red cedar	Preliminary reports indicate that wood extracts inhibit lettuce seed as much as or more than black walnut extracts (Rathinasabapathi et al., 2005).
Eucalyptus and neem trees	A spatial allelopathic relationship if wheat was grown within 5 m (Kumbhar and Patel, 2016).
Chaste tree or box elder	Leachates retarded the growth of pangolagrass, a pasture grass but stimulated the growth of bluestem, another grass species (Mushtaq et al., 2020).
Mango	Dried mango leaf powder completely inhibited sprouting of purple nutsedge tubers (Kowthar et al., 2016).
Tree of Heaven	Ailanthone, isolated from the Tree of Heaven, has been reported to possess non-selecitve post-emergence herbicial activity similar to glyphosate and paraquat (Heisey, 1996).

Table 8: Continue...

Allelopathic plant	Impact
Rye and wheat	Allelopathic suppression of weeds when used as cover crops or when crop residues are retained as mulch (Kunz et al., 2016).
Broccoli	Broccoli residue interferes with growth of other cruciferous crops that follow (Hao et al., 2003).

Source: El-Hadary and Chung, 2013

attention nowadays. Different crop species possess different allelochemicals and each of them has special potentialities in weed control (Duke et al., 2015). Through biotechnological process, genes controlling the production of allelochemicals are improved which in turn results in increased quantity of these allelochemicals production. Extensive work has been carried out for mapping allelopathic QTLs or the quantitative trait loci in chromosomes (Chauhan et al., 2014). Some researchers also suggested transgenic approaches as successful tools. This can be utilized to introduce genes from high allopathic genotypes to low or non-allelopathic genotypes. The quantity and quality of secondary metabolites of allelopathic plants are also changed by antisense knockout techniques and overexpression of genes (Chung et al., 2018).

7. Conclusion

Indiscriminate use of herbicides affects environment and human health. To tackle this, there is a necessity of various management practices like choosing suitable herbicide, its dose, time of application, crop rotation and use of organic matter. Bio-augmentation and bio-stimulation along with organic matter might be a promising technology to accelerate biodegradation. Bio-herbicides can also be a good alternative. Similarly, natural herbicides with zero persistency, provide high degree of specificity. Moreover, modern biotechnological techniques might be helpful to improve the allelopathic potentiality of plants.

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