



Herbicide residues and their management strategies

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ABSTRACT

Herbicides have become obligatory for increasing the agricultural production and to maintain the non-cropped area free from weeds and pests. 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 pose a serious hazard to the succeeding crop and also to the surroundings. Mostly the triazines, isoxazolidinones, imidazolinones and a few of sulfonyleureas are persistent herbicides. Hence, it is essential to compile the available literature on the management of herbicide residues in the soil environment. In this review, the management aspects were covered under five broad categories, *viz.* cultural and mechanical, enhanced degradation, deactivation, reducing the availability in soil, and removing from the site of contamination. From the review, it was found that the integration of mechanical and cultural management practices with herbicides for managing weeds is a viable protecting option since the safeners exhibit varying behaviour in soil on influencing the herbicide persistence. Further, the combination of bioaugmentation and biostimulation along with the organic matter addition might be a promising technology to accelerate the biodegradation. Although it requires extensive field evaluation studies, biostimulation in conjunction with other tools like crop rotation and increasing the organic matter content is definitely a promising technique for managing the herbicide persistence minimizing its residue in the soil.

Key words: Biostimulation, Deactivation, Enhanced Degradation, Herbicide, Management

Herbicide usage becomes inevitable in the present day intensive agricultural system to obtain large harvests and minimize the yield loss due to weeds. The herbicide demand in India is rising sharply and could double in the next three years as an acute labour shortage makes them a cheaper option and a rally in farm goods prices prompts farmers to grow crops with extra care (Mukherjee 2011). Usage of herbicides occupy 44% of the total agrochemicals globally and 30% in India (Sondhia 2014).

Herbicides are a group of organic compounds that possess far-reaching environmental consequences when persistent in the soil. A 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 (Sankaran *et al.* 1993). The longer persistence of a herbicide poses a hazard to subsequent land use and is undesirable. Recent concerns of ground and surface water

contamination by some of the herbicides has led to renewed interest on persistence and dissipation behavior of herbicides in the environment. Several monitoring programmes have also been implemented by different countries to check the environmental contamination and for ecological risk assessment of herbicides. However, the information on managing herbicide persistence in the soil saving the crop from those situations are limited. Though the studies are conducted around the world and a few places in India, there is a lack in the published information. This article aims to hoard the information on herbicide persistence and its management across the world.

Persistence and residue 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 (Sankaran *et al.* 1993, Sondhia 2014) and the quantity that exists is referred to as residue. Herbicides vary in their potential to persist in soil. Herbicide families that have persistent members include the triazines, uracils, phenylureas, sulfonyleureas, dinitroanilines, isoxazolidinones, imidazolinones, and certain plant growth regulators belonging to the pyridine family (Curran 2001). The

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relative persistence of some common herbicides in soil when applied at recommended rates for weed control are given in the table 1.

The chemical properties of the herbicide affect its persistence in soil and the important factors include water solubility, vapor pressure, and susceptibility to chemical and microbial alteration or degradation (WSSA 2002). Besides the climatic conditions prevailing in the locations, the physicochemical properties of the soil have influences on the persistence of an herbicide (Sharma and Angiras 2004, Janaki *et al.* 2013, Sondhia 2014) in soil and its carry over potential. Detailed review on the degradation and residue of different herbicides in soil and health concerns are already published by Sondhia (2014).

Management of herbicide residues in soil

There are several ways to avoid herbicide persistence and carryover problems. Literatures available on various management techniques to minimize the persistence and residue hazards in soil and carryover problems are reviewed under five different categories for the ease of understanding.

Cultural and mechanical management practices

Integrated weed management: Integrated weed management (IWM) involves the application of a variety of management practices to control weeds. Herbicides are used only when weed populations exceed an economic threshold level that justifies their application. Field scouting is required to monitor weed populations. Nonchemical weed control methods, such as crop rotation, cultivation, competitive hybrids, rotary hoeing and altered planting dates, are emphasized as management practices that can reduce the need for herbicides. The effectiveness of the integrated weed management using chemical and mechanical means in different crops has been studied vastly in India and also at

world level. Vaishya *et al.* (2003) found that the pre-emergence application of pendimethalin 1.0 kg/ha or pre-plant incorporation of fluchloralin 1.0 kg without phytotoxicity on crop. Sathiyavani and Prabhakaran (2014) reported that the pre-emergence application of metribuzin 0.7 kg/ha on 3 day after planting (DAP) of turmeric plus hand weeding on 45 and 75 DAP for effective weed management and higher yield without phytotoxicity to crop and carryover problems. Similarly, Sharma *et al.* (2013) found that the application of 2,4-D at three levels of 0.5, 1.0 and 2.0 kg/ha in wheat crop at 35 days after sowing persisted in soil up to 15, 45 and 75 days, respectively, however, residues of 2,4-D were found below detectable level (0.02 ppm) in wheat grain and wheat straw. Nalini *et al.* (2010) found that the pre-emergence application of pendimethalin (38.7%) at 2.0 kg/ha 3 day after sowing (DAS) + hand weeding (HW) on 45 DAS showed effective weed control in cotton without leaving any residues in the soil at the time of harvest and carryover problems to the succeeding crops, *viz.* pearl millet, cowpea and sunflower grown in sequence. Sharma *et al.* (2014) reported that pre-emergence application of pendimethalin did not leave any residues in soil beyond harvest of the garlic at any of the applied dose. Sharma and Angiras (1996) found that the residue of pendimethalin 1.5 kg/ha applied in wheat + sarson intercropping system was only 0.001 ppm in soil after harvest of these crops.

Ploughing or cultivating the land: Tillage operations help in bringing deep present herbicide residues to soil surface which would aid in decontamination by volatilization. Ploughing with disc plough or intercultivators reduce the herbicide toxicology, as the applied herbicide is mixed to a large volume of soil and get diluted. Olson *et al.* (1998) stated that the atrazine loss was low in the chisel-disk system with incorporation compared to no till and ridge till systems. Zablotowicz *et al.* (2007) observed

Table 1. Relative persistence of some herbicides in soil

| < 1 month | 1-3 months | 3-6 months | > 6 months |
|-------------------------------|--|---|---|
| 2,4-D, Glyphosate, MCPA | Alachlor, acetochlor, ametryn, anilofos, bispyribac-sodium, butachlor, carfentrazone-ethyl, dalapon, fluzifop-butyl, halosulfuron, metribuzin, metamifop, metsulfuron-methyl, metolachlor, oxyfluorfen, propachlor, pyrazosulfuron-ethyl, thiobencarb | Clomazone, chlorimuron-ethyl, diallate, dithiopyr, ethofumesate, fluchloralin, imazethapyr, isoproturon, metamitron, oxadiazon, linuron, pendimethalin, pyrazon | Atrazine, bromacil, chlorsulfuron, diuron, diquat, imazapyr, methazde, picloram, simazine, sulfometuron, sulfentrazone, trifluralin, paraquat |

Source: Loss (1975); Sankaran *et al.* (1993); Hager *et al.* (2000); Sharma and Angiras (2003); Sharma *et al.* (2006); Chinnusamy *et al.* (2008); Sharma *et al.* (2013); Sharma *et al.* (2014); Ramprakash *et al.* (2014); Sondhia (2014); Tandon (2014)

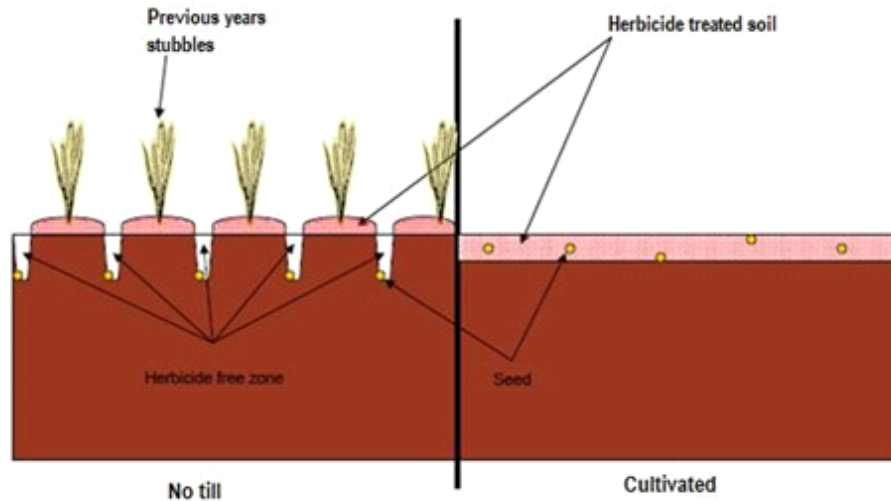


Fig. 1. Difference between the distribution of herbicides in soil under no-till and cultivated conditions (Source: Barry 2012)

the rapid degradation of fluometuron in conventional tillage (CT) compared to no-tillage (NT) soils in the 2 to 10 cm depth and found that the ryegrass cover crop systems, under NT or incorporated under CT, stimulated microbiological soil properties and promoted the herbicide degradation in surface soils. Since, most herbicide transformations in soil are mediated by microbial metabolism, modification of the soil environment and microbial populations by reduced tillage and/or cover crops can affect herbicide fate (Levanon *et al.* 1994, Locke and Zablotowicz 2003).

According to Gaston and Locke (2000) the herbicides degradation was faster in the surface layers than deeper layers of soil and is faster at CT than NT. In compliance with a study on the behavior of atrazine in the soil at no-till by Hang *et al.* (2010), only in a few isolated cases the faster herbicide degradation was in deeper soil layers than in the surface layers. Dao (1991) found unbalanced degradation of metribuzin and S-ethylmetribuzin due to slow herbicide release fixated in the crop residues. Straw affinity is able to reduce efficiency of herbicides that were activated in the soil, if they were applied into soil surface at no-till. Alletto *et al.* (2009) reviewed in detail the impact of tillage practices on the sorption, degradation and movement of herbicides and found that depending on the nature of crop residues, the degradation of molecules can be affected by the presence of mulch, but in contrasted ways. In no-tillage, vetch residues accelerated the degradation of metolachlor by from 1.5 to 3 times, but had no effect on the degradation of atrazine (Teasdale *et al.* 2003). On the contrary, according to

laboratory studies, vetch residues seemed to slow down fluometuron degradation compared with soil samples without vetch residues (Brown *et al.* 1994, Zablotowicz *et al.* 1998) or other types of residues such as wheat residues (Gaston *et al.* 2001), rye residues (Zablotowicz *et al.* 1998), etc. This slowdown could be due to the abundance of nitrogen in legumes.

Incorporation of herbicides: Mechanical incorporation of a herbicide by placing it below the mixing zone (eg., atrazine) helps to reduce runoff loss, which takes place through the solution or water phase and not much with soil particles. Some herbicides are sensitive to sunlight and need to be mixed into the soil to minimize losses. Some herbicides are volatile and can be lost through evaporation, especially from wet soil. Application of pre-emergent herbicides as pre-sowing and then incorporating them into the seed bed during the sowing process will often increase safety to crops because the sowing operation removes a certain amount of herbicide away from the seed row (Fig. 1). This can conversely reduce weed control for the very same reason, as chemical is moved out of the seed row. Hence, it is wise to include a water soluble herbicide into the mix aiming to have a portion of it into the seed furrow (Barry 2012).

Use of crop residue from the previous year and mulch can reduce sediment concentrations and losses. With the development of special tools, subsurface herbicide application can provide incorporation with minimal disturbance of surface residue. Mickelson *et al.* (2001) found that the soil incorporation and subsurface herbicide application

with the Mulch Master can reduce herbicide losses through surface runoff when compared to surface application with no-till (Table 2).

Crop rotation: Soil can be decontaminated of herbicide residues by deliberately including crop plants that are resistant to the particular herbicide. Crop rotation spreads the planting and herbicide application season, reducing the risk of encountering widespread herbicide runoff during a single runoff event. Suzer and Byuk (2010) found that the rape seed and sugar beet are highly sensitive to the imidazolinones (imazamox + imazethapyr) and should be avoided in the rotation as a succeeding crop when the previous crop was applied with these herbicides. While they also reported that the maize, winter wheat and barley were unaffected and can be used in rotation. Bresnahan *et al.* (2000) also reported that the recropping with canola and sugar beet should be avoided in the growing season if the previous crop sunflower received mixture of imazamox and imazethapyr to avoid carryover problems.

Cobucci *et al.* (1998) reported that the sensitivity of rotational crops to fomesafen and imazamox residues was in decreasing order from sorghum to corn, millet, and then rice and to acifluorfen from sorghum to corn, rice, and then millet. For corn, rice, and millet injury is possible under certain environmental conditions (i.e., low soil moisture content and high clay and organic matter soil) but appears to be low with high precipitation conditions. Verma *et al.* (2014) reported that the maintenance of appropriate crop rotation with legume and non-legume crops, and growing of cover crops during fallow period helps to suppress the weed population by smothering without applying the herbicides.

Growing herbicide tolerant crops: Certain herbicide tolerant crops can reduce herbicide residues in a soil by absorbing and deactivating these in their

tissues. Maize and millets, for instance, are very good consumers of triazine herbicides. Vetiver was not affected by exposure to the herbicides, atrazine and diuron, at concentrations as high as 2,000 mg/L which are likely to be encountered in the environment only in situations of accidental spillage, or direct application to waterways (Cull *et al.* 2000). Singh and Walia (2005) reported that the crops like methi, turnip, berseem and gobhi-sarson were not affected by the carryover effect of sulfosulfuron and hence can be grown in soil have sulfosulfuron residue. Sathiyavani (2014) found that the spraying of glyphosate from 1.04 to 1.56 kg/ha as post-emergence on 25 days after planting in the turmeric field did not affect the main crop and provided a broad spectrum of control of all weeds and also does not show any phytotoxicity symptoms on turmeric at 30 days after application. Bandana *et al.* (2015) reported that in soil, the glyphosate persisted up to 30, 45 and 60 days at application doses of 0.5, 1.0 and 2.0 kg/ha, respectively and in tea leaves, residues were detected for up to 15 days at all doses, however, concentration was found to be below the maximum residue limit (1 mg/kg).

Light irrigation after application: Continuous moist soils often result in a more rapid breakdown of herbicides due to creation of favorable conditions for microbial activity. While controlled irrigations enhance all modes of deactivation, heavy irrigations leach herbicides out of the root zone of the crop. Rice *et al.* (2002) stated that the saturated soil favored the dissipation of metolachlor and the formation of soil-bound residues. Significantly greater quantities of a dechlorinated metabolite were measured in the saturated surface soil compared to the unsaturated soil. Lovell *et al.* (2002) found that the degradation of isoxaflutole was faster in soil maintained at -100 or -1500 kPa compared to that in air-dry soil. At 25°C, the half-lives for isoxaflutole were 9.6, 2.4, and 1.5 days

Table 2. Herbicide losses with water and sediment as influenced by the method of incorporation

| Treatment | Chemical losses with water (g/ha) | | | Chemical losses with sediment (g/ha) | | |
|--|-----------------------------------|-------------|-----------|--------------------------------------|-------------|-----------|
| | Atrazine | Metolachlor | Cyanazine | Atrazine | Metolachlor | Cyanazine |
| Surface application and incorporation using mulch master | 0.94b | 1.32b | 1.43b | 0.09b | 0.06c | 0.07b |
| Sub surface application and incorporation using mulch master | 7.61b | 10.1b | 9.05b | 0.35b | 1.13b | 0.48b |
| Surface application and no incorporation (no-till) | 148a | 112a | 231a | 1.70a | 1.93a | 2.64a |
| Surface application and incorporation using dines | 1.87b | 1.30b | 2.25b | 0.20b | 0.31c | 0.20b |

[a] Means with the same letters are not significantly different at 10% confidence level

in air-dry, -1500 kPa and -100 kPa moisture regimes, respectively.

Site specific application using variable rate applicator: The interaction between herbicide chemistry and soil properties greatly affects its weed control efficacy and the potential for crop injury. Because of this, fields with significant variability in soil properties are good candidates for variable rate of application of soil-applied herbicides. The combination of automatic tractor steering and variable rate technology is well suited for site-specific application of pre-emergence herbicides. With tractor guidance control and variable rate controllers, growers can increase the efficiency of chemical application by applying optimum rates based on soil texture. These technologies have primarily been adopted by growers of major crops such as corn, wheat and soybeans (Koch and Khosla 2007). Bauer and Schefcik (1994) found that recommended application rates of pre-emergence soil applied herbicides can vary as much as 50% in a given field due to varying soil textures. Kurt *et al.* (2011) studied the effectiveness of benefin herbicides in controlling weeds on vegetable crops using the variable rate technology in different textured soils and found that the use of this technology resulted in significantly less crop injury and significantly more marketable yield as compared to uniform application. In the portions of the lettuce field with loamy sand textured soils, 35% less herbicide was applied and up to 40% more heads were harvested. Furthermore, there was no significant difference in weed control efficacy found between the two application methods examined (Table 3).

In soils with high clay content, a greater amount of the herbicide is required for adequate weed control as compared to sandy soils. If higher rates necessary for good weed control in high clay content soils are used on sandy soils, excessive herbicide concentrations in soil solution can cause injury to lettuce seedling roots (Tickes and Kerns 1996).

Enhancing the herbicide degradation

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 cometabolism (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 has been used for a wide variety of xenobiotics (Kadian *et al.* 2008).

The dearth of adequate decomposable organic matter in the soil gives insufficient substrate to stimulate microorganisms in the decomposition of herbicides (Felsot and Dzantor 1990) and thus leaves herbicides recalcitrant in the soil for years without degradation. 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 Buyuksonmez *et al.* (1999). 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). The general conclusion from the studies involving organic amendments in the soil was that the herbicide concentrations in the soil were reduced to significantly lower levels within short spans of time when compared to the unamended treatments (Kanissery and Sims 2011). Durga Devi *et al.* (2005) found that the continuous application of FYM to the rice crop enhanced the degradation of butachlor, pretilachlor and 2,4-D in the soil through enhanced microbial activity.

Table 3. Influence of standard and variable-rate application treatments of benefin on cumulative weed emergence per plot at two and four weeks post-germination

| Soil texture | Rate technology application (lb/acre) | | Total weeds (no./plot) on 14 days after germination | | Total weeds (no./plot) 28 days after germination | |
|-----------------|---------------------------------------|----------|---|-------------------|--|-------------------|
| | Standard | Variable | Standard | Variable | Standard | Variable |
| Sandy clay | 2.0 | 2.5 | 3.63 ^a | 4.21 ^a | 2.43 ^a | 2.62 ^a |
| Sandy clay loam | 2.0 | 2.0 | 4.35 ^a | 3.52 ^a | 3.06 ^a | 2.83 ^a |
| Loamy sand | 2.0 | 1.5 | 4.73 ^a | 4.13 ^a | 2.45 ^a | 6.05 ^a |

^aMeans followed by the same letter in each column are not significantly different at P=0.05 according to the analysis of variance and the Fisher's LSD means separation test. (Source: Kurt *et al.* 2011)

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 (1976) 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 (Table 4). In some cases, inorganic nitrogen starvation may be more effective in promoting degradation and has been reported for atrazine and other heterocyclic compounds (Bichat *et al.* 1999, Sims 2006). This can potentially be accomplished by supplying excess carbon to make nitrogen limiting.

Recently, Qiu *et al.* (2009) confirmed that P was a limiting nutrient during the degradation of coexisting dichlobenil and atrazine by bacterial degraders in soil. Dichlobenil was completely degraded in 60 hours in the P-supplemented soil extract, in comparison to less than 40% degradation without P supplement. It is noteworthy that the degree of enhancement of

atrazine degradation was even greater, in that it was completely degraded in P-supplemented extract within 40 hours, compared to less than 10% degradation without the P supplement.

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). Microorganisms are capable of degrading the herbicide compounds in the soil by utilizing them as a supply of nutrients and energy. 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 the 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 oryzae* 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 oryzae* were found to be 7.2 and 8.6 days, respectively. Mukherjee *et al.* (2005) found that the

Table 4. Stimulating the biodegradation of herbicides in soil through nutrient supplements

| Herbicides targeted | atrazine | Nutrients and influence | References |
|---------------------------------|----------|--|--|
| | | Ammonium nitrate, potassium nitrate and ammonium phosphate | Hance (1973) |
| Dichlobenil, Atrazine | | Phosphorus | Qiu <i>et al.</i> (2009) |
| 2,4-D, Mecoprop | | Glucose, phosphate | De Liphay <i>et al.</i> (2007) |
| Isoproturon | | Nitrate and phosphorous | Perrin-Ganier <i>et al.</i> (2001) |
| Atrazine | | Mannitol | Assaf and Turco (1994) |
| Atrazine | | Glucose | Abdelhafid <i>et al.</i> (2000) |
| Pretilachlor, 2,4-D ethyl ester | | Enhanced 2,4-D degradation due to the combined application of organic and inorganic source of N in transplanted rice-rice system. However, the pretilachlor degradation was stimulated and enhanced by the 100% organic sources of nitrogen. | Shanmugasundaram <i>et al.</i> (2005) Janaki <i>et al.</i> (2009 and 2010a, b) |
| Butachlor | | Dissipation was rapid due to the combined application of organic and inorganic sources of N in the rice soil continuously for ten years and has been attributed to the enhanced population of microbes in soil as influenced by the organic matter addition. | Chinnusamy <i>et al.</i> (2012) |
| 2,4-D, MCPA | | Application of combined NPK fertilizers enhanced their degradation from soil | McGhee and Burns (1995) |
| MCPA | | Nitrate is not suitable as an alternative electron acceptor for MCPA degradation and, in certain circumstances, inhibits aerobic catabolism of the herbicide in the soil | McBain <i>et al.</i> (1997) |

dissipation of lactofen was faster in soil solarization technique and was enhanced by the straw amendment to the tune of 90% and suggested that this technique is promising one remediating the herbicide residues from the site of persistence.

Deactivation of herbicides

Addition of organic matter: Pesticides 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 and 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 reduced the atrazine residue significantly followed by compost (12.5 t/ha) and phosphoric acid (50 ppm) application. Residual toxicity of atrazine to the sensitive crop soybean was overcome by the application of farm yard manure at 12.5 t/ha or compost 12.5 t/ha or charcoal 5.0 kg/ha 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 above 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*.

The effectiveness of FYM was evaluated and reported by Rathod *et al.* (2010) in reducing persistence of three dinitroaniline herbicides, *viz.* pendimethalin, trifluralin and fluchloralin from a field, cropped with Indian mustard (*Brassica juncea* L.) in sandy loam soil of middle-west Indian agro-climatic conditions. They found that the persistence of all three dinitroaniline herbicides was decreased with addition of FYM and observed a reduction of the half-life of all three herbicides when FYM incorporated. Decreased residues of dinitroaniline herbicides with an incorporation of FYM and faster degradation of herbicides in soil with organic matter have also been reported by Jacques and Harvey (1979) and Patel *et*

al. (1996). Senesi and Testini (1984) stated that the H-bonding, London-Van der Waals forces and cation exchange are responsible for the adsorption of herbicides by organic materials. Pritchard and Stobbe (1980) revealed that phytotoxicities of dinitroanilines decreased with increased organic matter but persistence of fluchloralin and trifluralin was increased with increased organic matter, which may cause crop injury a year later. The effectiveness of different organic amendments on enhancing the herbicides degradation in soil has been reviewed by Kanissery and Sims (2011). While Topp *et al.* (1996) observed a significantly shortened lag period in dairy manure-treated plot prior to atrazine herbicide degradation. Gan *et al.* (1996) identified dairy manuring as a successful technique to enhance the remediation of atrazine-contaminated soil. Though the addition of organic matter reduces the residues on herbicides in soil, the type of organic sources plays a role in influencing the herbicide degradation in soil especially under low moisture conditions and also under conservation practices (Zablotowicz *et al.* 1998). 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. However, 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.

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 (Walker 1980, Singh and Tan 1996). One of the beneficial effects of adjuvants, especially surfactants is a reduction in the amount of water available for evaporation from the soil surface (Bayer 1967). 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 (Hall *et al.* 1993). The addition of adjuvants could influence the speed of degradation and increase herbicide residues in soil and plant, but

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 2009a).

Kucharski and Sadowski (2009b) found that the addition of oil adjuvant slowed down degradation and increased the level of ethofumesate residue in soil. Reddy and Singh (1993) evaluated bromacil and diuron herbicides lixiviation in soil columns and found the significantly lower vertical movements of bromacil, while there was no such effect on diuron. These two herbicides present distinct physicochemical characteristics that explain their differential movement abilities in the soil. From the environmental point of view, the adjuvant effect was positive in the case of bromacil, but the agronomic efficacy was restricted. Cabrera *et al.* (2010), in laboratory studies affirmed that metazachlor herbicide added to oil and surfactant showed reduced

degradation rates and increased residues in the soil. 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.

Use of adsorbents, protectants and antidotes:

They are applied to the soil, crop seed or transplanted plant to protect the crop from herbicide injury. The mode of action may be due either to 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 broadcasted or applied as narrow band over the seed at the time of planting. Yelverton *et al.* (1992) reported that the application of activated carbon 8 and 18 kg/ha to the tobacco along with imazaquin and chlorimuron reduced the phytotoxicity besides increasing the yield from two to four fold.

Table 6. Biochars and herbicide dissipation in soil

| Herbicide | Finding | Reference |
|--------------------------|---|----------------------------------|
| Atrazine | A lag phase of 11 days in the dissipation of atrazine in the non-amended and biochar amended silt loam soil. Later, dissipation was greater in the unamended soil. | Spokas <i>et al.</i> (2009) |
| 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 <i>et al.</i> (2010) |
| Acetochlor | Amending soil with biochar resulted in a DT ₅₀ of 34.5 days | Spokas <i>et al.</i> (2009) |
| Isoproturon | Biochar amendment increased the isoproturon persistence in soil with the DT ₅₀ of 2.2 days in the unamended soil to 5.6 days in the 2% (w/w) biochar amended soil. | Soperia <i>et al.</i> (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. | Nag <i>et al.</i> (2011) |
| 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 <i>et al.</i> (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 <i>et al.</i> (2014) |

Biochar addition: 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 on the same soil and using the same amendments at similar rates. The influence of biochar and its sources on herbicide dissipation is presented in table 6.

Use of safeners: Herbicide safeners are a 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 7) 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. 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).

Reducing the availability of herbicides in soil

Use of optimum and reduced dose of herbicide: The indiscriminate use of herbicides leaves behind residues in food and produce. Hence, the hazards of herbicide residues can be minimized by the application of chemicals at the least possible dosage by which the desired weed control is achieved. Applying herbicides in bands rather as broadcast will reduce the total amount of herbicide to be applied. This will be practicable in line sown crops or crops raised along ridges, such as cotton, sugarcane, sorghum, maize etc. Several workers have been reported that the optimum dose of herbicides did not leave any residues in soil grown with different crops. Jayakumar and Mohammed Ali (1984) reported that the recommended dose of atrazine and 2,4-D did not persist in soil and confirmed through growing the sensitive crops like finger millet, sunflower etc.

Shanmugasundram *et al.* (2005a) observed that more than 90% of the applied atrazine degraded from the sugarcane grown soil on 90th day at 2.0 kg/ha while it took 180 days at 5.0 kg/ha. The influence of quantity of application on the persistence and dissipation of herbicides like metsulfuron, imazethapyr, metamifop, oxyfluorfen, metamiltron, atrazine, pendimethalin, metribuzin, metolachlor, pretilachlor, alachlor etc in different soils under various situations were reported by many researchers (Janaki *et al.* 2009, 2010b, 2012a, 2012b, 2013a, 2013b, 2015; Sondhia 2009, 2013). They found that the increase in quantity of application increased the residue and persistence of herbicides in soil irrespective of locations and soil types.

Use of herbicides in combination and split doses:

The use of herbicides in combinations can reduce the rates of application of highly persistence molecules in soil and in turn reduced their concentration. Similarly, applying herbicide in splits will reduce the amount of herbicide available to runoff at any one given time. Kalaichelvi *et al.* (2010) reported that the tankmix application of chlorimuron-ethyl (Kloben 25% WP) + quizalofop-P-tefuryl (Pantera 4.41% EC) + 0.2% surfactant at 9 + 40 g a.i./ha had a satisfactory weed control and did not have severe phytotoxicity symptom on soybean crop. Further, this combination did not have any residual effect on succeeding crops. Janaki *et al.* (2010c) reported that the split application of metamiltron for sugarbeet weeds, reduced the persistence time of that herbicide in soil when compared to single application. Similarly, the split application of ethofumesate for weed control in sugar beet increased the dissipation of it with the DT₅₀ values to 5.2 days as against 7.5 days under single application (Janaki *et al.* 2014). Punia and Yadav (2014) reported that the use of 1% ammonium sulphate as surfactant with the post-emergence application of pinoxaden 40 g/ha at 35 DAS and carfentrazone 25g/ha at 42 DAS enhances the weed control efficiency and yield of wheat without any phytotoxic injury.

Method and time of application: Band application is the process by which herbicide is applied in a narrow band varying in width. In the area in-between the treated bands, weed control is maintained through mechanical cultivation (Hansen *et al.* 2000). Applying atrazine in a narrow band in crop rows is an effective method of reducing the total amount of atrazine applied. One or more well-timed cultivations are necessary to prevent inter-row weeds from establishing and competing with the crop. Both the pre-emergence and post-emergence herbicides may be applied in the band.

Alternative use of herbicides: Avoid repeated use of herbicides with similar modes of action to reduce the potential development of herbicide resistance. Shanmugasundaram *et al.* (2005b) found that the rotational use of butachlor with pretilachlor along with 2,4-D as a POE for rice-rice cropping system for four years did not leave the residue of any herbicides in soil at the time of harvest.

Match rates to weed infestation levels and using suitable formulations: In many fields, most weeds are clustered, with as much as 70-90% of the land having very few weeds. At harvest it is possible to map these areas, so herbicide can be applied only where needed. Rate and site specific technology, although in the developmental stages, will enable adjustment of herbicide rates according to soil organic matter, soil pH, soil texture, and weed type and location within a field. Cuevas *et al.* (2007) found a high persistence and low mobility of lenacil in a

clayey soil in southwest Spain, where lenacil residues in top layer were detected even after 60 days of herbicide application. Grey and Webster (2013) compared the EC to microencapsulated (ME) pendimethalin formulation in controlling the weeds in cotton crop and found that the ME formulation consistently reduced cotton injury, either as spray or fertilizer impregnated application. Hence, by utilizing the ME formulation, supplementing, or even delaying pendimethalin application to in-season timings impregnated on fertilizer, growers could extend residual weed control until cotton can develop canopy and suppress weed growth. While pendimethalin has lower volatilization than other dinitroaniline herbicides such as trifluralin (Savage and Jordan 1980), the ME formulation decreases volatilization and provides extended activity. This has been observed with another ME formulated herbicide, alachlor (Vasilakoglou and Eleftherohorinos 1997).

Table 7. Commonly used herbicide safeners

| Safners | Crop | Herbicide | Application method | References |
|---|-------------------------------|---|---------------------------------|---|
| Naphthalic anhydride | Maize | Thiocarbamate | Seed treatment | Hatzios (1983), Parker (1983), Stephenson and Ezra (1983) |
| Naphthalic anhydride | Maize | Phenylcarbamates, Dithiocarbamates, Chloroacetanilides, Sulfonylureas, Imidazolinones, Cyclohexenones, Arylophenoxyalkanoic acids | Seed treatment | Hatzios (1983), Parker (1985) |
| Naphthalic anhydride | Maize, Oats | Chlorsulfuron, Diclofop-methyl | Seed treatment | Parker (1983) |
| Dichlormid | Maize | Tthiocarbamate herbicides | Seed dressing | Pallos <i>et al.</i> (1977), Stephenson and Chang (1978) |
| Dichlormid | Maize | Chloroacetanilide herbicides, Sethoxydim, Clomazone | Seed dressing | Leavitt and Penner (1978), Hatzios (1984), Devlin and Koszanski (1987a,b) |
| Dichlormid | Wheat | Diallate | Seed dressing | Mullison (1979) |
| Substituted N-Dichloroacetyl-1,3 oxazolines | Maize | Thiocarbamate herbicides | Seed dressing | Dutka and Komives (1987), Gorog <i>et al.</i> (1982), Hatzios (1983) |
| Oxime ether | Grain Sorghum | Chloroacetanilide herbicides | Seed dressings | Chang and Merkle (1982, 1983) |
| Benoxacor | Maize | Metolachlor | Spray as mixture with herbicide | Sankaran <i>et al.</i> (1993) |
| Cloquintocet-mexyl | Wheat | Clodinafop-progaryl | Spray as mixture with herbicide | Sankaran <i>et al.</i> (1984) |
| Cyometrinil | Sorghum | Metolachlor | Seed treatment | Turner <i>et al.</i> (1982) |
| Fenclorim | Rice | Pretilachlor | Spray as mixture with herbicide | Pyon (1986), Quadranti and Ebner (1984) |
| Flurazole | Sorghum | Alachlor, Acetochlor, Thiocarbamate | Seed treatment | Schafer <i>et al.</i> (1981), Ketchersid and Merkle (1985) |
| Fluxofenim | Sorghum | Metolachlor | Seed treatment | Rao (2000) |
| Flurazole | Cereals | Halosulfuron-methyl | Spray as mixture with herbicide | Hatzios and Hoagland (1989) |
| Mefenpyr-diethyl | Wheat, Rye, Triticale, Barley | Fenoxaprop-ethyl | Spray as mixture with herbicide | Hatzios and Hoagland (1989) |
| Oxabetrinil | Sorghum | Metolachlor | Seed treatment | Hatzios and Hoagland (1989) |

Based on the history of weed flora and soil type, the herbicide application rate may be increased or decreased. Many times, if field preparation is done well, the weed flora competition at initial period won't be there, hence the pre-emergence herbicides and dose must be chosen in such a way that it can control the late emerging weeds also. Kanagam *et al.* (2005) reported that later emerging weeds in ground nut can be managed with the application of either metolachlor or fluchloralin 1.0 kg/ha.

Removal from site of contamination

Phytoremediation: The *in situ* use of vegetation in bioremediation schemes is termed as phytoremediation which is an emerging technology for the cleanup of contaminated environments such as soil, water and sediments. Different tolerant plants are planted at the contaminated sites which uptake the main pollutant along with other nutrients and thus changing the soil chemistry and increases microbial activity. Success of phytoremediation technique mainly depends upon the selection of proper tolerant plant and suitable soil (Arthur and Coats 1998). Rice and Sikka (1973) observed atrazine (¹⁴C) removal of about 59% by submerged aquatic plant. Poplar trees seemed to be effective in the rapid assimilation of ring leveled atrazine (90%) from sandy soil in less than 9 days (Burken and Schnoor 1996) whereas, in clayey soil the assimilation was very poor. Similarly, transgenic poplars, over expressing α -glutamylcysteine synthetase (α ECS), could be used for phytoremediation of herbicides due to the increased GSH levels. The suitability of poplars for phytoremediation of soils artificially contaminated with the chloroacetanilide herbicides, acetochlor or metolachlor was studied by Gullner *et al.* (2001) and found that the transgenic plants showed increased herbicide tolerance, due to elevated endogenous α -ECS and GSH levels, resulting in rapid herbicide degradation.

Future research needs

In India, most of the research has been done pertinent to cultural and mechanical management of herbicide residues in soil and to some extent on the split application or rotational use of herbicides. However, the research works on the deactivation of herbicides utilizing the various organic sources; enhancing the degradation by biostimulation and removal of contaminants from the site using the phytoremediation techniques are scanty or nil. Similarly, the effect of crop residues on the behavior of herbicide residues in soil and environment is also

very little. Hence, extensive site specific field studies will be essential to develop holistic measures for the management of herbicide residue in soil environment.

Conclusions

Herbicides have been identified as an indispensable part of the crop production programme. However, to sustain the soil environment, the indiscriminate use of them should be avoided. While using herbicides, all the prevention and management aspects should be kept in mind for huge harvest as well as for quality food production without deteriorating the environment. Hence, integrating the mechanical and cultural management practices with herbicides for managing weeds is a viable option. The combination of bioaugmentation and biostimulation along with organic matter addition might be a promising technology to accelerate the biodegradation. Although it requires extensive field evaluation studies, biostimulation in conjunction with other tools like crop rotation and increasing the organic matter content is definitely a promising technique for managing the herbicide persistence and residue in the soil.

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