ROLE OF PROTECTANTS IN CHEMICAL WEED MANAGEMENT - A REVIEW

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ABSTRACT

Safeners are chemical compounds that protect crop plants from herbicide injury. They are also referred as antidotes or protectants. Naphthalic anhydride (NA) is the first commercial herbicide antidote developed by USA. Marketed safeners are members of diverse chemical groups. Herbicide safeners act either at a common target site or influence the amount of herbicide that reaches its target site in an active form. Safener reduces the phytotoxicity on crop. The other organic amendments the protect from herbicidal injury are FYM, activated carbon, and activated charcoal. This paper reviews role of protectants in chemical weed management in crop production.

Many of the currently available herbicides that are useful in managing difficult to control weeds are not sufficiently selective. In addition, the selective control of weeds that are botanically related to crops has always been a problem. To overcome these problems several approaches have been tried with varying degree of success. Safeners are used to improve crop tolerance to herbicide. These are chemical compounds that protect crop plants from herbicide injury with effective weed control. Herbicide safeners are also referred as antidotes or protectants or antagonists.

Development of herbicide antidotes

1962 : Introduction of chemical antidote S-449 as an effective antidote of barban injury to wheat
1969 : 1, 8 - naphthalic anhydride as an antidote against EPTC injury to corn.
1970 : R·25788 as effective antidotes against thiocarbamate injury to corn.
1971 : 1, 8 - naphthalic anhydride was patented as the first commercial herbicide antidote.
1972 : R·25708 was patented as the second commercial herbicide antidote.
1974 : Martil - Oxime ethers against chloro - acetanilide herbicide injury to grain sorghum
1978 : CGA - 43089 was patented as third commercial herbicide antidote.
1980 : 2,4-disubstituted 5-thiazolecarboxylic acids as effective antidotes against chloroacetanilide herbicide injury to grain sorghum.
1982 : CGA-92194 as an effective antidote against metolachlor injury to grain sorghum (Hatzios, 1983).

Types of protectant

a) Naphthopyranone derivatives: 1,8-naphthalic anhydride is effective only as seed dressing (at about 0.5% by weight of seed). It was introduced under the trade name of ‘protect’ for the treatment of maize which could then safely withstand greatly increased doses of EPTC or other thiocarbamate herbicides.

b) N,N - Diallyl -2,2-dichloroacetamide (R-25788): R-25788 was introduced as a combined formulation with EPTC under the trade name ‘Eradicane’. It can be used as a seed dressing like naphthalic anhydride. It is also effective as a soil treatment at modest doses of 0.5 - 1 kg ha⁻¹. It is more specific and can be used as an overall spray in combination with the herbicide to protect maize.

c) Cyometrinil (CGA-43089): [(Z) - cyanomethoxyimino (phenyl) acetonitrile] It
is introduced as a seed dressing to protect sorghum against metolachlor and acetanilide herbicide such as alachlor.

d) Mon-4606 (Flurazole): [2,4 -Disubstituted 5-thiazole carboxylates]: It is used as a seed treatment to protect sorghum against alachlor and related acetanilide herbicides. It is commercially available as “Screen”.

e) Fenchlorim (CGA-123407): [4,6-dichloro 2-phenyl-pyrimidine]: It is mixed with pretilachlor and the new mixture to called “Sofit” (Mixture of pretilachlor + CGA - 123407) which is selective to wet seeded rice. It protects rice crop germination and development against adverse effect of herbicide. The full herbicide activity obtained in saturated soil under permanent flooding. Sofit is not suitable for upland rice.

Use of herbicide safeners

Most of the developed safeners are used for the protecting grain crop viz.: maize, grain sorghum and wet-sown rice as pre-emergence applications of carbamothioate and chloroacetanilide herbicides (Hatzios and Hoagland, 1989). In recent years, safeners developed are useful to protect winter cereal crops against post-emergence applications of the aryloxophenoxypro- pionate herbicides (Kreuz, 1993). The safening of maize and rice against with safener sulfonylurea, imidazolinone, cyclohexanidione and isozanolidinone herbicides are used in controlling weeds in maize and rice (Hatzios and Hoagland, 1989).

Marketed safeners are members of diverse chemical groups including naphthopyranones (e.g. naphthalic anhydride or NA); dichloroacetamide (e.g. dichlorimid, benoxacor, BAS-145138, R-29148, furilazole); dichloromethyldioxolans (e.g. MG-191); oxime ether derivatives (e.g. oxabetrinil, fluxofenim); substituted thiazoles (e.g. flurazole); phenylpyrimidines (e.g. fenclorim); triazole carboxylates (e.g. fenchlorazole-ethyl) and quinolinoloxacates (e.g., chloquintocet-mexyl).

Safeners applied as prepackaged mixtures with the herbicide improves crop tolerance to herbicides (Hatzios and Hoagland, 1989). But their selective placement is some times desirable for achieving the best results under field conditions. Thus, safeners used with grain sorghum and the safener in maize or other crops are applied mainly as seed treatments (seed safeners) to avoid the safening of weeds that are botanically related to the crop (Kreuz, 1993).

Mechanisms of action

Safeners may act either as “antagonists” of herbicidal effects at a common target site or as “bioregulators” influencing the amount of a herbicide that reaches its target site in an active form. The chemically diverse groups of herbicides that are antidoted by safeners on grass’ crops exert their action by a variety of biochemical mechanisms, which are well-defined for sulfonylureas, imidazolinones, isoxazolinones, isoxazolidinones, aryloxyphenoxypionate and cyclohexanediones, but still speculative for carbamothioates and chloroacetanilides (Devine et al., 1993). Safeners may reduce the amount of a herbicide reaching its site of action by either reducing the rate of its uptake and/or translocation or by enhancing the rate of its metabolic detoxification. Omokawa et al. (1995) showed that the protective action of the rice safeners daimuron against injury from bensulfuron-methyl was due to significant reduction in the uptake of this herbicide by safened rice seedlings.

A safener enhances herbicide detoxification in protected plants is currently accepted as the most likely mechanism explaining the protective action of all
commercialized safeners. Besides, safeners have been found to enhance the conjugation of acetanilide and sulfoxidized carbamothioate herbicides with glutathione either by elevating the levels of reduced glutathione (GSH) or by inducing the activity of glutathione transferase (GST) enzymes. These also enhance the activity of other detoxifying enzymes such as cytochrome P450-dependent monooxygenases (Cyt P450s), UDP-glucosyl-transferases (Gts) and carboxylesterases which appear to be involved in the protection of grass crops against sulfonylureas, imidazolinones and aryloxyphenoxypropionates. Glutathione, found primarily in its reduced form (GSH), is a very important non-protein thiol participating in key metabolic processes of plants such as protein synthesis, adaptation to environmental stresses (e.g. peroxidative damage, drought etc.) and detoxification of selected herbicides (Farago et al., 1994). Safeners may elevate GSH levels in protected plants either directly or indirectly. The conjugation of the thiol group of GSH to a variety of electrophilic substrates is catalyzed by a superfamily of ubiquitous enzymes known as glutathione-S-transferases (Pickett and Lu, 1989; Timmerman, 1989).

Treatment with selected herbicide safeners enhances the conjugation of chloroacetanilide and sulfoxidized carbamothioate herbicides to GSH in protected grass crops (Farago et al., 1994). The efficacy of safeners in protecting sorghum against acetanilide herbicides is dependent on their ability to increase GST activity (Grondwalf et al., 1987). The exact mechanism of the safener-induced enhancement of GST activity is not clearly established. It has been suggested that safeners act by an enzyme induction rather than activation process since dichlormid and oxabetrinil did not alter in vitro GST activity (Jepson et al., 1994; Wiegand et al., 1986). Safeners may act also by inducing the activity of cytochrome P450-dependent monooxygenases, which are involved in the metabolic detoxification of carbamothioate, aryloxophenoxypropionate, sulfonylurea and imidazolinone herbicides in protected crops (Hatzios, 1991; Kreuz, 1993). Hydroxylated metabolites of selected herbicides, produced as a result of oxidative metabolism, are known to conjugate rapidly with glucose or other plant sugars (Devine et al., 1993; Sandermann, 1992). The glycosylation of hydroxylated herbicides is mediated by UDP-glucosyltransferases. As per the recent report, the safener NA may protect maize against injury from the sulfonylurea herbicide thifensulfuron-methyl by inducing the activity of hydrolytic enzymes such as carboxylesterases. Naphthalic anhydride enhanced the de-esterification of thifensulfuron-methyl causing a 30-50% increase in the formation of the parent acid, thifensulfuron, in maize coleoptiles (Hatzios, 1983). Glutathione conjugates of herbicides in plants are catabolized to their cysteine and thiolatic acids derivatives, which are further acylated with malonic acid (Sandermann, 1992). Similarly, the glucose conjugates of several herbicides are known to form secondary metabolites with malonic acid (Devine et al., 1993). These terminal metabolites may be stored as soluble metabolites in the vacuoles of plant cells or deposited as "bound residues" into cell wall components.

Factors affecting field performance

Several environmental factors such as temperature, light, soil moisture and soil type have been reported to influence the efficacy of herbicide antidotes in the field. The activities of the antidotes Naphthalic anhydride and CGA 43089 against herbicide injury on crops were higher at higher temperatures than at low temperatures (Leek and Penner, 1981). CGA 43089 was not effective in counteraction metalachlor injury to grain sorghum under extremely wet conditions in the field (Ketchersid et al., 1981). NA was highly effective as a barban antidote in oats grown in light sandy
soils but much less effective in silty clay soils. Likewise, R-25788 was able to prevent EPTC injury to corn when applied as a soil drench at any time prior to coleoptile emergence. If the antidote was applied to EPTC-treated corn after emergence, various degrees of corn injury were evident (Thiessen et al., 1980).

Adverse effects

Studies established that treatment of crop seeds with the optimum rates of herbicide antidotes did not result in any adverse phytotoxic effects on crop growth. NA as safener provides some protection to yield bears against injury from EPTC when applied as seed dressing at 0.5% but it causes marked chlorosis to the bean foliage. Chlorotic on bean foliage is also caused by R-25788 in the absence of EPTC when it is applied as seed treatment at 2% by seed weight. The application of CGA-43089 as a seed dressing at rates higher than 1.88 g/kg of sorghum seeds was found to be phytotoxic to grain sorghum (Blair, 1979).

Use of organic amendments to reduce herbicide injury

a) Application of farmyard manure: Farm yard manure application is an effective method to mitigate the residual toxicity of herbicides. FYM absorbs the herbicide molecules in their colloidal fraction and make them unavailable for crops and weeds. Besides, FYM enhances the microbial activity which in turn degrade the herbicide at a faster rate. Selvaraj (1985) found that the residues of atrazine (0.5 kg/ha) applied to pearl millet crop affected the subsequent greengram and cowpea. However, the FYM application at 12.5 t/ha to pearl millet found to mitigate the residual toxicity of atrazine in soybean crop.

b) Activated carbon: It offers an excellent opportunity for stretching the selectivity of herbicides to a wide variety of crops. Activated carbon was first used as an absorbent of 2,4-D in the form of a uniform, 2.5 cm wide band over partially covered crop seed rows (Gupta, 1976). Its effective rate was 130 kg/ha on clay loam soils and 390 kg/ha or more on sandy soils. In dibbled vegetables, activated carbon can be placed over crop seeds in the seed holes. Pre-emergence herbicides sprayed later are retained by carbon, thus avoiding their absorption by the germinating crops seeds. Robinson (1965) reported success with dipping roots of horticultural seedlings in activated carbon before transplanting them in the herbicide treated soils. It has proven successful in improving selectivity of EPTC to maize and cowpea and of chloramben, butachlor and EPTC to rice (Gupta and Niranwal, 1976).

Toth et al. (1987) reported use of activated carbon to protect tomato seedlings against metribuzin. Seed pelleting with activated carbon has been developed as yet another way of using gum or PVA (polyvinyl acetate).

c) Activated charcoal: Activated charcoal has been found a strong absorbent of herbicides like 2,4-D, EPTC, 2,4,5-T, propham, propachlor, trifluralin, nitralin, chloramben, diuron, simazine and butachlor. Therefore, if the germinating crop seeds and seedlings are surrounded by a layer of activated charcoal with in the soil, they can be made to escape absorption of many soil applied herbicides (Pilshchikova et al., 1991). Activated charcoal adsorbs most of the herbicides. In transplanted vegetables like tomato and brinjal, it is applied by adhering it on the seedling roots. It can also be applied by coating it on the crop seeds with the help of thick gum. Rice has been protected against butachlor, chloramben and oxadiazon (Nagiu, 1973). Application of activated charcoal can be done to the soil either at the time of sowing or before sowing. Doses required in the range of 10-40 kg/ha (Henne and Guest, 1974).

Protectant on wet seeded rice

Application of pretillachlor and safener on 4 and 8 DAS did not cause any toxicity to
rice seedlings. Thiobencarb applied on 8 DAS was slightly toxic to seedling with toxicity rating of 1.17. Pendimethalin application on 8 DAS showed slight stunting, discolouration and stand loss of seedlings. Butachlor caused stand loss, stunting and more pronounced injury to rice seedlings (2.17). A visual rating of weed control on 21 DAS indicated that there was good to excellent control with pretilachlor + safener, good control with thiobencarb and moderate to satisfactory weed control with butachlor and pendimethalin (Balasubramanian, 1996). Phytotoxicity problems were not observed in treatments with the new herbicide formulation (herbicides with safener). Pretilachlor + safener at 0.6 kg a.i. ha\(^{-1}\) applied 3 DAS was found most effective in controlling weeds. Yield was statistically at par with that of weed free check and that of the crop the received two hand weedicings. Compared with butachlor and thiobencarb treated plots, higher plant density with one manual weeding at 30 days was found to suppress weeds significantly (Bishat et al., 1996). Application of pretilachlor + Fenclorim supported with hand weeding recorded higher WCE (85.9%) followed by hand weeding twice (83.3%) and butachlor supported with hand weeding (82.9%) at 60 DAS. Among the two pre-emergence herbicides, Pretilachlor + Fenclorim was found more efficient than butachlor. Butachlor followed by hand weeding dominated Pretilachlor + Fenclorim followed by hand weeding in controlling broad leaved weeds (Udhayakumar, 1997). Pretilachlor + Safener at 0.45 kg ha\(^{-1}\) on 4 DAS recorded consistently higher weed control efficiency (89.6 to 97.6%) in both seasons as compared with hand weeding twice (83.2 to 91.1%). Crop growth characters and yield attributes recorded higher values with Pretilachlor + safener application. Higher grain yield was recorded with the application of Pretilachlor + safener at 0.45 kg ha\(^{-1}\) on 4 DAS followed by one hand weeding at 25 DAS. Even in comparison with hand weeding twice, weed management through the application of Pretilachlor + safener at 0.45 kg ha\(^{-1}\) registered on yield increase of 164 to 359 kg ha\(^{-1}\). This was made possible through a consistently high degree of weed control throughout the crop growth stage (Ramesh and Veerabadran, 1997). Pretilachlor + Fenclorim applied at 3 DBS recorded the highest weed control efficiency followed by butachlor applied at 3 DBS (70.4%) and Pretilachlor + Fenclorim applied 3 DAS (69.9%). Among the four herbicides, the weed control efficiency was in the order of Pretilachlor + Fenclorim (71.7%), butachlor (64.3%), oxyfluorfen (63.6%) and pendimethalin (58.3%) (Udhayakumar et al., 1996).

At 25 DAS, the weed density and biomass were minimum with Pretilachlor (+safener). Higher yield and economic could be obtained by pre-emergence application of thiobencarb or pretilachlor (+safener) on 6 or 8 DAS with follow up hand weeding (Premsekhar, 1996). In general, single herbicide applied at 6 or 8 DAS limited the weed growth, maximum grain yield of 50.6 q ha\(^{-1}\) was recorded at 8 DAS application. Application of Pretilachlor (+safener) enhanced the yield to 54.5 q ha\(^{-1}\) and thiobencarb yielding at par (53.1 q ha\(^{-1}\)) the higher B:C ratio was obtained in wet seed rice by applying pretilachlor (+safener) (2.75) or benthiocarb at 8 DAS each followed by a hand weeding (Kandasamy and Chandrababu, 1994). Butachlor without safener applied at 2 or 7 DAS caused toxicity to rice seedlings, but this was significantly less when applied at 7 DAS than at 2 DAS. Other butachlor safener combinations also caused acute toxicity symptoms, but rice plants were able to recover. Butachlor at 2 kg ha\(^{-1}\) + safener at 0.188 kg ha\(^{-1}\) (7 DAS) was the most effective combination for yield and weed control. Rice yield of the butachlor at 1.5 kg ha\(^{-1}\) + safener at 0.188 kg ha\(^{-1}\) (2 and 7 DAS) treatments
was equal to that received two hand weedings. At each time of application (i.e. 2 or 7 DAS) butachlor with safener at 0.094 or 0.188 kg ha\(^{-1}\) controlled weeds effectively and increased rice grain yield significantly over its application without safener (Angiras and Rana, 1998). Application of softi 1.0 kg and butachlor safener 1.5 kg/ha on 3 DAS was found to be effective in weed control and resulted in higher grain yield and net returns (Jayadeva et al., 1997). When no herbicide was applied, plant height at 2 weeks after seeding was not affected by the depth of the flooding and the use of NA (protectant). However, when butachlor was applied the rice plants were significantly taller in the NA(-) protected plots than in the plots without NA regardless of the depth of flooding. Flooding to 50% of the plant height (4cm deep) resulted in a reduction in plant height. Application of NA to the seed reduced herbicide injury at all flooding depths. Even though NA protected the rice seedlings from crop injury, farmers are unlikely to use it because it is expensive and they are not familiar with seed coating (Pablico et al., 1988). The seeds treated with charcoal (1%) and lignite (1%) were least affected when the butachlor was applied at the time of sowing or four days after sowing compared to other seed treatments. Butachlor inhibited or reduced the seed germination by interfering with analyse activity when applied as pre-emergence herbicide to rice. Seeds treated with charcoal registered the highest yield and yield attributes followed by lignite and other seed coating materials (Venkataraman and Kempuchetty, 1996). Among the metolachlor doses, metolachlor 0.35 kg a.i./ha + safener recorded lesser weed DMP of 132 and 124 kg ha\(^{-1}\) and grain yield of 710 and 1296 kg ha\(^{-1}\) respectively in both seasons which was on par with Farmer's methods of hoeing (Ramamoorthy et al., 1995).

Protectant on Wheat

Herbicide resistant bacteria were isolated from the rhizosphere and multiplied and applied as seed dressing which were sown in earthen pots along with weed seeds (P.\textit{minori}). Various concentrations of herbicide below and above standard doses were applied as pre-emergence. It was noticed that the bacteria could differently protect the crop against herbicide injury in lower doses upto 30 days with reduced toxicity as compared to control. \textit{P.\textit{minori}} however remained relatively highly affected in this doses (Anonymous, 1996).

Protectant in fibre crop

Two field trials were conducted at Bangalore and Guntur during kharif season to determine the response of hybrid cotton variety DCH 32 and MESH 138 to clomazone (Command 50EC) with phorate as a safener, phorate was placed in furrow near the seed and command applied as pre-emergence. At Bangalore, clomazone @ 0.375, 0.5, 0.75 and 1.0 kg a.i./ha was compared with clomazone alone and phorate alone. The crop plant density was 12 seed/ m\(^2\), cotton germination was not affected by the clomazone + phorate. Only 13% of plant survived in clomazone alone plots. First 2 leaves of 69-76% of plants had phytotoxic symptom till 30 DAS. However at Guntur the treatments were clomazone @ 0.4, 0.6 and 0.8 kg a.i./ha. The crop density was 12 seeds m\(^2\). Cotton germination was normal with no detected phytotoxicity. Command was effective in controlling \textit{Digitaria \textit{sangunalis}}, \textit{Echinochloa \textit{crusgalli}}, \textit{Amaranthus \textit{viridis}}, \textit{Portulac \textit{oleracea}} and \textit{Parthenium \textit{sp}}. Phorate @ 1.0 kg a.i./ha is able to safer cotton satisfactorily (Jha et al., 1994).

Protectant in vegetable crop

In tomato, when the herbicide was applied 6 hours before the application of herbicide protectants (HPs) like \textit{Physalis \textit{minima}} root extract (2.5%), jaggery (3%), glutamic acid (100 ppm) and glutathione (100
ppm) the 2,4-D toxicity to the tomato plant was maximum and was at par with sole 2,4-D treatment which otherwise meant that, once the herbicide injury is caused, the HPs can not protect the plant. However, when the HPs were applied in advance i.e. 3 days before the application of 2,4-D, the herbicide injury was the minimum in all treatments except Jaggery and at par with the control. The weed dry matter was lowest with 2,4-D treatment and other treatments are at par with it except in control where a higher weed dry matter was noted. Jaggery treatment could not protect tomato against 2,4-D injury (Anonymous, 1996).

**CONCLUSION**

The protection is more successful with maize, sorghum and rice. There was been only limited success in protecting broad leaved crops. Safeners proved successful only against herbicide that affect cell division not against photosynthetic inhibiting herbicides. The amendments such as FYM, compost, activated charcoal, activated carbon and antidotes may be utilized as herbicide protectants.

**FUTURE RESEARCH**

- Future potential for antidotes in respect of the control of weed species in closely related crops, the increased options for herbicide use in minor crops and the possibility of reduced costs for broad spectrum weed control in major crops.
- The dose, time and method of application of such amendments and antidotes have to be standardised.
- The precise knowledge of the mode of action of safeners have to be studied clearly.

**REFERENCES**


