

Herbicide residue in food chain and environment:

impact on society and management

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The enormous benefits and widespread application of herbicides has undoubtedly increased crop production but has also resulted in unintentional exposure to the ecosystem. As herbicides are chemical in nature and judicious use of herbicide provide selective and economical weed control but excessive, repeated and indiscriminate use may results in residue, phytotoxicity and adverse effect on succeeding crops, non-targets organisms, environment and ultimately hazard to human beings.

Key words: Environment, Food Chain, Herbicide residue, Impact, Management

According to World health organization (WHO) ‘any substance or mixture of substances in food for man or animals resulting from the use of a pesticide and includes any specified derivatives, such as degradation and conversion products, metabolites, reaction products, and impurities that are considered to be of toxicological significance’ are defined as herbicide/pesticide residues. In India, herbicide use has increased to 30 % during the last decade in managing weeds in the country. It was found that only less than 20 % of applied pesticides actually reach the target, the rest is distributed into the ecosystem thereby posing a threat to environment, human beings and aquatic life.

When herbicides are not used properly, they cause adverse impact on the environment. Herbicides vary in their potential to persist in soil. The longer the persistence of the herbicide, the greater is the threat to the environment and human health used by it. They may interfere with the ecological functioning leading to

serious imbalance in the environment which ultimately affects our life.

Herbicide residue in food chain and environment

For effective weed control herbicide must remain in the soil long enough to provide satisfactory weed control and degrade to non-toxic products when their purpose is accomplished. Longer persistence poses a hazard to subsequent land use which is undesirable. Herbicide enters in the environment through application to plant/or soil, drifts and vapours and are subjected to various reactions under different soil and environment conditions.

The contamination of the environment by herbicides depends upon some of the factors like nature of herbicide, its persistence in the soil, bioaccumulation (biomagnification), amount used, and method of application. No doubt, herbicides kill weeds but it was seen that it also affect the crop plants. Slow degradation and persistence of herbicide for several weeks in soil lead to herbicide

residues in soil. These residues in soil sometimes interfere with rotation of crops sensitive to herbicides. It was been observed that the residues of sulfosulfuron were significantly higher in surface soil at higher dose compared to sub-surface soil at lower dose up to 150 day at 25-100 g/ha in wheat under field condition. Terminal residues of pendimethalin were detected in the green field peas, chickpea, tomato, cauliflower, and radishes applied as pre-emergence herbicide at 750 to 185 g/ha rates. A pre-harvest interval of 118 days for onion crop after the oxyfluorfen application was suggested. Herbicide application resulted in the disappearance of certain plant species including weed species. Besides, plants sprayed at the seedling stage or at later reproductive periods delayed flowering and reduced seed production. Studies in Britain suggested that since the 1950s, there were large changes in the populations of some birds that bred on agricultural land. These changes may be partly caused by the extensive use of herbicides, a practice that has

changed the species and abundance of non-crop plants in agro-ecosystems. Herbicide residues in water occur as a result of direct application, runoff from land and aerial drift from application. Herbicide residues in air are mainly found to be either from spray and dust storms at the time of application or from volatilization from treated areas.

Herbicides persistence in the soil is expressed as half life or time required to degrade 50% of the original molecule. However, the half life is not absolute because it depends on the soil properties, temperature, herbicide doses and application methods and climatic conditions, influence the fate of the herbicides in the soil. Varied persistence of herbicides in soil was reported in diverse soil. The persistence of pyrazosulfuron-ethyl in soils is mainly influenced by soil organic matter and moisture. Chlorsulfuron degraded faster in low pH soil than in high pH soil. Metsulfuron-methyl dissipated more rapidly in acidic silty loam soil as compared to high pH soil and light did not play any role in altering the persistence. Residues of metsulfuron-methyl in rice soil was found 8 to 16 ng/g at 2-8 g/ha application rates at 30 days. Atrazine in soil showed a gradual degradation with advancement in maize crop growth and residue were not found at harvest whereas 56 ng/g of residue in the post-harvest soil were found at double the recommended dose. Bromacil and diuron at 3 kg/ha persisted on top 2.5 cm of the soil profile even after 8 months. The persistence of fluazifop-p-butyl at two application levels and three temperature level revealed fast degradation in soil.

Butachlor degradation in soils is mainly influenced by soil organic matter and moisture and rapid disappearance was noticed at field capacity followed by submergence and air dry conditions in all soils.

The 2, 4-D at 0.4 kg/ha alone or in combination with anilofos persisted up to harvest. Clodinafop-propargyl ester generally converted to acid, a major metabolites and also responsible for herbicidal action. Its

dissipation was not affected by soil pH and soil type. Residues of clodinafop in soil were found 93 to 81 ng/g in alluvial, red and black soil, respectively. Sorghum and cucumber plants were found sensitive plants to detect metribuzin residues in soil. Pendimethalin applied at 1 to 4 kg/ha rates in wheat crop showed persistence up to 200 days in sandy loam soil and caused phytotoxicity to the succeeding sensitive sorghum crop at higher dose. Harvest time samples of paddy grains, rice-bran and-straw, treated with butachlor showed residues 2, 9 and 6 ng/g in bran, straw and rice grains, respectively at 1.0 kg/ha, however, @ 2 kg/ha application, the residue were 1, 5, 10 and 25 µg/g in rice-bran-straw and paddy grains, respectively. Residues of metsulfuron-methyl and pretilachlor in rice grains and straw at harvest were found below 0.1 ng/g. In a field experiment, isoproturon residues were found 6, 41 and 22 ng/g in the post-harvest soil, wheat grain and straw, respectively. Metribuzin residues were not found in the soil, grains and straw following an application @ 210 to 420 g/ha in wheat crop. Fenoxaprop residue in the soil of wheat field was found 0.4 to 11 ng/g at 70-400 g/ha application rates.

Impact of herbicides on the society

Improving crop productivity: Remarkable benefits were derived from the use of herbicides in agriculture, forestry and non-crop lands which the Indian economy is largely dependent. The primary benefits of herbicides use are the direct gains expected from their use through improving productivity. Herbicides provided both an economic and labour benefit. Increased and judicious use of herbicides in agriculture increased the productivity dramatically in most countries. These also greatly reduced drudgery in weed management in various crops and improve the quality of agricultural products. This in turn also controlled wide range of human and livestock disease vectors which acts as a host to these weeds thus reducing the number of infected individuals by prevention of spread of

disease. Herbicides are relatively safe on lands which may erode when applied judiciously. Non-selective herbicides can effectively clear fields, where houses and roads can be built.

Effects on non-targeted plants: Declining plant diversity and abundance widely reported in agro-ecosystems due to repeated herbicide use. Intensive use of herbicides within crop fields and the associated drift in adjacent habitats are partly responsible for this change. Work to quantify the phenological stages of non-target plants in *in-situ* field situations during herbicide spray and to compare plant susceptibility at different phenological stages demonstrated that a large number of non-target plants had reached reproductive stages during herbicide spray events in woodlots and hedgerows. Besides, delays in flowering and reduced seed production occurred widely on plants sprayed at the seedling stage or at later reproductive periods, with plants sprayed at reproductive stages often exhibiting more sensitivity. Unintended but economically important damage to crop plants is sometimes a consequence of the inappropriate use of herbicides. Build-up of resistant biotypes Apart from their effect on the environment, another major problem with herbicides was the build-up of herbicide-resistant biotypes where the same herbicide was 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 were used.

Effect water system and fishes: Many herbicides are routinely detected from the surface and ground water sources in developed countries. Herbicides like, butachlor, atrazine, pendimethalin, paraquat are strictly banned or restricted in the USA, and European countries owing to their high concentration in the ground and surface water and potential health hazards to aquatic, animal and human lives. In India, reports on monitoring and detection of herbicide residues in water are limited as compared to developed

countries. Pyrazosulfuron-ethyl residue levels of 15 µg/g on 21st day and of 2.3 µg/g on 35th day were detected in the underground water. The water samples collected from Singoor reservoir, Hyderabad were found contaminated with residues of atrazine (NO-1.056 µg/litre). The concentration of atrazine residues in Osmansagar water was 56 ng/litre during post-monsoon November 2005 and total pesticide residues together 3.369 µg/litre. Residues of paraquat were not detected after 20 days at 0.80 kg/ha application rate to control *Eichornia* but application of 1.8 kg/ha showed 69 and 28 µg/litre residues in pond and canal water, respectively. Sulfosulfuron residues were not detected after 200 days in surface and sub-surface soils in all the doses. High mobility of metsulfuron-methyl under continuous saturated moisture condition was found. More fish mortality observed with 2, 4-DEE and paraquat than with glyphosate. Accumulation of sulfosulfuron in fish was found in the range of 9 to 496 ng/g. One of the metabolite of sulfosulfuron, aminopyrimidine was identified at higher concentration levels (10-100 ng/mL) than other metabolites.

Effects on non-target organisms: High doses or long exposure might lead to deleterious effects on non-target organisms and limit their survival rate. Fenoxaprop and metolachlor were conjugated to earthworm (*Eisenia fetida*) at low rates. The metabolism of the Gram-negative bacteria *Stenotrophomonas maltophilia*, sometimes present in rice field irrigation channels, could be negatively affected by some rice field herbicides. A mixture of quinclorac and bensulfuron-methyl induced the activity of the antioxidant enzymes superoxide dismutase and catalase of a *S. maltophilia* strain (WZ2), and demonstrating the induced oxidative stress caused by the herbicides. Bensulfuron-methyl did not affect bacterial numbers remarkably, either in the overlying water or in the surface paddy soil, but the nitrification potential was significantly suppressed. The nitrogen-fixing ability was suppressed shortly after

butachlor application but was augmented after 37 days both in upper and lower soil layers. N-fixing cyanobacteria were mostly relatively tolerant to 2, 4-D under field conditions.

Effects of herbicides on humans: Higher level of herbicide residues can cause serious threat to the society. Human being can be poisoned by herbicide residues. Increasing incidences of acute herbicide self-poisoning by butachlor, fluchloralin, paraquat, 2, 4-D, pendimethalin, glyphosate etc. are a significant problem in parts of Asia. Herbicides can enter the body through inhalation of dust and vapour that contain herbicide or orally by consuming food and water contaminated with herbicide residues or through direct contact with skin. The World Health Organisation in 2015 has categorized herbicide glyphosate being used extensively as carcinogenic to humans. Mainly herbicides are petroleum-based. It was found that humans exposed to herbicide residues in the womb are at a high risk of developing deformed reproductive anatomies, defects or alteration in metabolism and brain development. The exposure effect may result in mild skin irritation to birth defects, genetic disorders, tumours etc.

Herbicide residue management

Presence of herbicide residues in the environment led to serious problems like contamination of water, air and soil. When applied at recommended rates most herbicides breakdown within a few days or weeks after application and impose no restrictions on cropping options to the next year. Some herbicides however, do not degrade quickly and can persist in the soil for weeks, months or years following application. The use of residual herbicides can be beneficial as the residues prevent growth of sensitive weed species throughout the season. These residues however, can restrict the crops that can be grown in rotation. Various management techniques were developed which can be adopted to minimize the residue hazards in soil.

Cultural and mechanical management practices: Integrated weed management practices involved different practices to control weeds. When the level of weeds in field crosses a threshold value then herbicides are used. Research show that early removal when the weeds were small reduces competition and improves crop yield. Early season application also assists in reducing the carry over potential to succeeding crops. The longer the herbicide is exposed to breakdown factors such as, moisture and temperature the lower the risk of carry over. Practices like crop rotation, competitive hybrids, rotary hoeing and altered planting dates are done under non-chemical weed control. The herbicide toxicity can be reduced by ploughing with disc plough or inter-cultivators because the applied herbicide is mixed to a large volume of soil and get diluted. To reduce runoff loss, herbicide can be placed below the mixing zone i.e. mechanical incorporation. Mulch and crop residue from previous year can help in reducing sedimentation concentration and losses to some extent.

Deactivation of herbicides: Herbicides are inactivated by plant residues or organic matter incorporated into soil. Farmyard manure application is an effective method to mitigate the residual toxicity of herbicides. Application of farmyard manure adsorb the herbicide molecules in their colloidal fraction and make 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 moisture holding capacity of high organic matter soils. Higher quantity of atrazine, sulfosulfuron and dinitroaniline herbicides residues applied to wheat and mustard crop affect the subsequent field crop. The farmyard manure application at 10 t/ha or green manuring with *Sesbania* to the soil found to mitigate the residual toxicity of atrazine, sulfosulfuron and dinitroanilines, pendimethalin, trifluralin fluchloralin and in sandy loam soil. Organic matter adsorbs the herbicide particles

making them unavailable for the crop and weeds. After a lag period, herbicide particles are decomposed faster by micro-organisms as organic has moisture content. The farmyard manure application at 12.5 tonne/ha reduced the atrazine residue significantly followed by compost (12.5 tonne/ha) and phosphoric acid (50 ppm) application.

Use of non-phytotoxic oil, adjuvants and surfactants also decrease the residual hazards. Atrazine residual hazard could be reduced by mixing in non phytotoxic oil which would also enhance the weed killing potency. The use of non-phytotoxic oil with atrazine in maize crop reduced the weed dry matter and enhanced the yield of maize and subsequent wheat with considerable reduction in the area affected in wheat. Adsorbents, protectants and antidotes are applied to protect the plant from injury caused by herbicide. Addition of biochar allows the crop to escape from toxicity by immobilizing the herbicide residues in soil. Safeners are synthetic chemicals which help in preventing herbicide injuries.

Activated charcoal (carbon) can reduce herbicide contamination in specific areas and can also be used as a root dip to protect transplants (tomatoes, peppers, strawberries, ornamentals etc.) from triazine or substituted urea herbicides. Activated charcoal has a high adsorptive capacity because of its extremely large surface area which vary from 600-1,200 m²/g. Activated charcoal may either be broadcasted or applied as narrow band over the seed at the planting. Herbicides that carbon can deactivate include trifluralin, 2, 4-D, chloroacetamide, and sulfonylureas herbicides. The incorporation of 50 kg/ha of activated charcoal inactivated completely chlorsulfuron applied @ 1.25 and 2.50 kg/ha and did not affect the yield of maize untreated control. Antidotes or plant protectants are applied to the soil, crop seed or transplants to protect the crop from herbicide injury. The mode of action of antidotes may be due to deactivation or adsorption of

the herbicide, preventing its absorption and translocation by the crop. e.g., 1, 3-naphthalic anhydride (NA) and 2, 2-dichloro-N, N-diallyl acetamide can be used to minimize injury from EPTC.

Reducing the availability of herbicides in soil: One of the main reasons for increasing herbicide residues in the environment is that herbicides are used above the threshold level. Excess use leads to processes like accumulation, leaching, drifts etc. So, application of herbicides in least dosage can help managing the herbicide residue problem. Herbicides when applied in combinations reduce application rate of persistent molecules and ultimately leading to their reduction. When herbicides with same mode of action are used time and again, the soil and the crop may become resistant to such herbicides. Use of alternate herbicides can prove a way out to reduce herbicide residue. Herbicides such as carbamates, thiocarbamates and dinitroaniline are lost in the environment by surface volatilization. Tillage operations help in bringing deep present herbicide residues to soil surface which would aid in decontamination by volatilization. Ploughing with disc plough or inter-cultivations reduce the herbicide toxicity, as the applied herbicide is mixed to a large volume of soil and get diluted. In deep ploughing the herbicide layer is inverted and buried in deeper layers and thereby the residual toxicity reduced.

Enhancing the herbicide degradation: Nutrient addition helps in increasing the herbicide degradation e.g. carbon, (C) nitrogen (N) and phosphorus (P) enhance the enzyme production by microbes. Introduction of specific micro-organisms to fasten the degradation process i.e. bioaugmentation can also be used. Some soil microbes such as bacteria and fungi play an important role in deactivating residues. *Aspergillus flavus* and *Aspergillus terricola* rapidly degraded metolachlor applied @ 10 kg/ha up to 92 % and 87 % after 20 days in sterile and non-sterile soils,

respectively. *Penicillium chrysogenum* and *Aspergillus* spp. were found as potent pyrazosulfuron-ethyl and penoxsulam degrading fungi.

SUMMARY

Herbicides are an indispensable component of agricultural sector. However, their indiscriminate use led to the herbicide residues in soil, air, water. Herbicides in most instances when applied at recommended doses did not result in residues in food chain or in soil at level that should cause concern. Notwithstanding, to guarantee minimal negative side-effects on crop ecosystems other than the soil-plant systems, herbicides should have no or low toxicity, except for the target weeds. Even though the switch to low-dose herbicides has significantly reduced herbicide consumption, most surface water and groundwater samples still contain herbicides, sometimes at levels harmful for human health and for environment. Herbicide use should be done in recommended dosage so that least possible deterioration of the environment is done.

Integrating practices like bio-augmentation, use of organic matter can help in residue management. Phyto-remediation is an emerging technology for the removal of herbicide residues from the contaminated site. Therefore, mitigation strategies of herbicide residue hazard need to be developed to lessen their effect on environment by reducing adverse impacts to less than significant levels. To avoid potential ill effects, strict and stringent regulatory mechanism is to be developed. A critical aspect to mitigation is the implementation of best management practices which is facilitated by effective education and training programs.

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