Technical Bulletin No.19

Safe use of herbicides and mitigation modalities







Shobha Sondhia
P.K. Singh



ICAR - Directorate of Weed Research
Jabalpur (Madhya Pradesh)
ISO 9001 : 2015 Certified

Technical Bulletin No. 19

Safe use of herbicides and mitigation modalities

Shobha Sondhia
P.K. Singh

ICAR - Directorate of Weed Research
Jabalpur (Madhya Pradesh)
ISO 9001 : 2015 Certified

Correct citation: Sondhia S. and Singh P.K. 2020. Safe use of herbicides and mitigation modalities, published by ICAR-Directorate of Weed Research, Jabalpur. p-50.

Published by: ICAR-Directorate of Weed Research , Jabalpur

© **Authors** 2020. All right reserved, no part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronics, mechanical photocopying, recording or otherwise without the prior permission of the author.

DISCLAIMER

This bulletin is developed with the basic objective of understanding on herbicide residues in the environment and agricultural products and mitigation modalities. Compliance with the specifications and disclosure of information do not constitute an endorsement or a warranty of a particular herbicide safety for a particular purpose, including its suitability for the control of any given weeds, or its suitability for use in a particular area for a crop. The suitability of herbicide for a particular purpose and the content of the labeling instructions must be read by the user based on the recommendations. Furthermore, herbicides which are manufactured to comply with these specifications are not exempted from any safety regulation or other legal or administrative provision applicable to their manufacture, sale, transportation, storage, handling, preparation and/or use. Therefore, authors disclaim any and all liability for any injury, damage, death, loss, or other prejudice of any kind that may arise as a result of, or in connection with use of herbicides for weed management.

Preface

Almost all herbicides have toxicological significance and may pose potential risk when present on soil, foodstuff, feed and other components of environment above the safety limits. The amount of herbicide in an agricultural product or harvest is determined by its analysis using various sophisticated instruments by the specially trained persons because these are invariably present in micro-quantities and generally estimated at ppm or ppb level using sensitive methods. After the herbicide application in the field, many chemical transformations processes takes place under natural conditions and varying metabolites are formed with varying degree of toxicity, hence, these are also consider under the broad head of residues.

Herbicides are generally applied at a recommended dose(s) with single application or sometimes followed by another herbicide/ and or in combinations, generally do not results in toxic level of residues; However, sometimes even small quantity of herbicide residues may damage sensitive or succeeding crops. In this bulletin the information is provided on herbicide residues and ways to manage/mitigate them in the soil by various techniques.

Technical bulletin entitled, '**Safe use of herbicides and mitigation modalities**' is prepared with the objectives to provide science-based information for the general public about safe use of herbicides, herbicide residues, various safety aspects during preparation of herbicide solution and spray, etc. Some remedial measures are also given and suggested to avoid any possible phytotoxicity of herbicides that may happened with the sensitive crop or following a cropping sequence or choosing a succeeding crop in the same field having sprayed with a particular herbicides. We hope that this informative bulletin shall empower general people, farmers and other users to make the right decisions.

September, 2020

Shobha Sondhia
P.K. Singh
ICAR-Directorate of Weed Research,
Jabalpur

CONTENTS

1.	Application of herbicides	03
2.	Herbicide application and residue risk	07
3.	Basis of herbicide persistence in the soil	08
4.	Herbicide leaching	10
5.	Herbicide drift and environmental risk	10
6.	Degradation of herbicides in plant and soil and subsequent residues	11
7.	Non targeted effect of herbicides	20
8.	Mitigation methods to minimize herbicide residue risk	23
9.	Use of bio-indicator for detection of residues	31
10.	Precautionary measure to minimize herbicide risk	33
11.	Do's and don'ts of herbicides	36
12.	Guidelines for safely mixing and loading of herbicides	37
13.	Cleaning equipment and containers	38

Safe use of herbicides and mitigation modalities

Herbicides play an important role in enhancing crop yield through effective and timely weed management and helped farmers and food producers. Herbicides are commonly used for weed management, however it also means to be any substance intended for controlling for use as a plant growth regulator, defoliant, desiccant, or sprouting inhibitor and substances applied to the crops either before or after harvest. In India, herbicides are increasingly used for control of weeds in field and plantation crops than ever before.

When we discuss various concern on residues after the spraying of herbicide in agricultural field, it has to be understood that risk associated with herbicides residues in crop produce and food are supposed to be less. Specific recommendations have been developed on the dose, time and methods of application for control of weeds for each crop or cropping sequence. However, in some instances, herbicide use caused moderate to severe phytotoxicity to standing crop or even the succeeding crop.

Herbicide driven technology provided effective control of weeds and since 1990 onward herbicide use has increased mainly due to continuous increases in labour cost and timely management of weeds. The consumption of technical grade herbicides was 15 MT in 70's, and increased to an astonishing quantity of 3211.52 MT (technical grade) in 2017-18. Punjab and Haryana lead in herbicide usage in wheat and rice in the country.

As herbicides are synthetic chemicals and designed to kill weeds, hence pose toxicity at varying level that can be categorized according to World health Organization (WHO) guidelines. According to WHO, pesticides are classified into four toxicity categories (I, II, III and IV). The categories are based on oral LD_{50}, inhalation LC_{50}, dermal LD_{50}, eye effects and skin irritation. The LD_{50} value is a statistical estimate of the number of mg of toxicant per kg of bodyweight required to kill 50% of a large population of test animals. The **Table 1** below shows example of LD_{50} value of herbicides and related examples.

Table 1: LD_{50} value of herbicides with examples

LD_{50} of active ingredient (mg/kg)	Estimated lethal amount of pure active ingredient for a 70 kg adult male	Examples
<5	A few drops	-
5-50	1 teaspoon	Dinoseb
50-500	30 g or 2 tablespoons	Diquat
500-5000	500 g or 500 ml	Atrazine, alachlor
>5000	>1000 g or 1000 ml	DCPA, chlortoluron

The LD_{50} values of other pesticides especially insecticides is very low if compared with the herbicides LD_{50} values which, indicates less toxicity and less harm to the environment and public health. In a regulatory decision, few herbicides are withdrawn since 2006 such as dalapon and simazine. However, alachlor is to be phase out from 31st December, 2020, whereas, trifluralin (The registration, import, manufacture, formulation, transport, sell and its all uses except use in wheat shall prohibited from 2020). Use of herbicide in India in agricultural commodities is also continuously increasing. An example of consumption of major herbicides in India in metric tons based on Directorate of Plant Protection, Quarantine & Storage for 2019-20 is presented in **Table 2**.

Table 2: Consumption of major herbicide in India (Source: Directorate of Plant Protection, Quarantine & Storage 2020).

Herbicides	**2019-20** (MT, Technical grade)
2,4-D-Amine Salt	1067
Atrazine	346
Chlodinafop-propargyl	147
Glyphosate	571
Paraquat dichloride	113
Pendimethalin	198
Pretilachlor	621

To control weed and achieve higher crop yield, large quantity of herbicides are being applied annually to the agricultural crops. As herbicide application is now become a common practice among the farmers, many people are very much concerned on possible side effects as well as presence of herbicide residues in the crop plants particularly at the time of harvest or in agricultural products. This worry is also genuine as these herbicides are also synthetic chemicals and come under the broad class of pesticides and designed to kill weed plants. If, these chemicals are not used properly, they may affect human health as the risk of close contact with the person is higher who spray these herbicides. The risk of herbicide residues may also be high if they persist in the soil longer than the crop growth periods or as a result of persisting residues in the crop plants at the harvest. Therefore determination of herbicide residues in the soil, water, crops and crop products is considered to an effective method to know the degradation and resulting residues in the agricultural commodities.

Herbicide residue analysis requires several instrumentation facilities, management, personnel, quality assurance and quality control, documentation of results and raw data, which are considered as prerequisites for obtaining reliable and traceable results and described in general in the ISO/IEC 17025 standard (1999) and in a series of guidance documents of many international agencies such as OECD, GLP, IUPAC, EPA, FAO, etc. Pesticide use in India is regulated by the Central Insecticides Board and Registration Committee (CIBRC) and the Food Safety and Standards Authority of India (FSSAI). The CIBRC registers pesticides for crops while the FSSAI sets the maximum residue limits of pesticides for the crops it has been registered for. These herbicide residues should not exceed a Maximum Residue Limits (MRLs) above which they may pose risks to human health.

1. Applications of herbicides

Herbicides can be applied for weed management in a variety of ways to the crop at various growth stages. They can be applied as single component products or as combination products, using the different properties and weed spectrum of the components of the mixtures. Application of herbicide is largely decided by their mode of action and selectivity. Following an improper method of application of a herbicide may results in poor weed control and /or severe crop injury. Important methods of application of herbicides to crop and non-crop areas are given as below;

1.1 Soil application of herbicides

1.1.1 Surface application

Soil active herbicides are commonly applied to the surface of the soil where they may be either left undisturbed or incorporated into the soil. Even when left on the soil surface, the applied herbicide should be able to move into upper 3-4 cm of soil under the influence of rain or irrigation to kill the germinating weeds. Sometimes a surface applied herbicide may have to be physically incorporated into the soil for varied reasons. For example, the triazine performed well in dry weather when these are mixed gently with the treated soil. Volatile herbicides must be incorporated into the soil to prevent their rapid volatilization or photodecomposition. The optimum depth of incorporation of different herbicides for achieving selective control of weeds varies considerably.

1.1.2 Subsurface layering

It is a method of the application of a herbicide in a concentrated band about 7-10 cm below the soil surface. This technique has proved effective in controlling certain perennial

weeds with conventionally, soil incorporated herbicides, usually employed to control only annual weeds. The concentrated layer of the herbicide inhibits the growth of new shoots of specific perennial weeds such as *Cyperus rotundous, Convolvulus arvensis,* etc. The subsurface layering of herbicides is achieved with special nozzles introduced below the soil under the cover of sweep hoods.

1.1.3 Broadcast and band application

Broadcast application of herbicides is characterized with the application over the full surface area, without leaving any intentional gaps. Whereas, band application usually means treating a narrow strip directly over or on the crop row. The band application of herbicide is primarily a cost saving device since it reduces the quantity of herbicide in the ratio of the treated band width to the crop width such as a 30 cm wide band of a herbicide applied over crop rows that were spaced 90 cm apart, will require one third of the quantity of herbicides needed for its application by the broadcast method. The herbicide band width usually 30-35 cm in the band application method, the inter rows must be cultivated later to remove weeds from the unsprayed areas. This will also help in the control of perennial and some other weeds, which may be resistant to the herbicide.

1.1.4 Soil fumigation

Depending upon the nature of soil fumigant it can be applied either 1) by soil injection, 2) by releasing it under sealed plastic covers or 3) by direct soil surface application example metham.

1.2 Foliage application of herbicides

1.2.1 Foliage applied herbicide

Foliar herbicides may be selective or non-selective and are classified as those that kill on contact or those that are translocated through plant tissue into the root system and kill the whole plant. Examples of non-selective foliar applied herbicides are glyphosate, (translocated), and paraquat, diquat (contact herbicides). Selective translocated herbicides include 2, 4-D; contact selective herbicides include propanil. Contact herbicides usually act quickly and are useful in controlling annual weeds or perennial weed seedlings. They are less effective in established perennial weeds because regrowth can occur from roots or underground stems. All of the contact herbicides and some of the translocated herbicides are only effective when applied to leaves because they are rapidly inactivated in the soil. Foliar uptake depends on a number of factors:

1.2.2 Blanket application

Blanket application or over to top application of herbicides stands for their uniform application to standing crops disregard to the location of the crop plants. Only highly selective herbicides are applied by this method, example, 2, 4-D in wheat, 2, 4-DB in lucerne.

1.2.3 Directed spraying

In tall growing crops which are grown in widely spaced row, it is possible to apply herbicides to the weeds or soil without treating the foliage or shot of the crop. Example, application of paraquat in sugarcane crop. Directed application is done by covering the spray nozzle under a hood or shield or by carefully directing the nozzles to the inter-row space. This saves the crop plants from herbicide injury and improves weed kill. Orchards and plantation are good venues of directed herbicide sprays.

1.2.4 Protected spraying

Non-selective herbicides can be used to obtain selective weed control in distantly planted vegetables and ornamentals by covering the non-target plants before application of the herbicide with plastic or metallic covers. This can be done in 3-4 rows at a time and shifting the covers to the untreated rows each time. Protected spraying is somewhat laborious but it pays itself when weeding of high value vegetables crops and ornamentals in involved.

1.2.5 Spot treatment

Spot treatment is usually done on small areas of serious weed infestation to kill it and to prevent its spread. Herbicides are applied either to soil or foliage. When applied to the soil, they are known as soil applied herbicides and when applied to the foliage of the weed, referred as foliage applied herbicides.

1.3 Types of herbicide treatments

1.3.1 Pre-plant incorporated

Pre-plant incorporated herbicides such as diuron, oryzalin, tebuthiuron are applied before the crop is sown and are incorporated into the soil (**Figure 1**). Hence, they are also applied before weeds emerge. The herbicides are incorporated in the soil because of being their volatile nature. They would be lost if they were not incorporated. They would be degraded if they remained on the soil surface. Volatility is a useful characteristic as it allows the redistribution of the compound throughout the soil following incorporation. For example pre plant incorporation of fluchloralin at 1.0 kg/ha is recommended for groundnut.



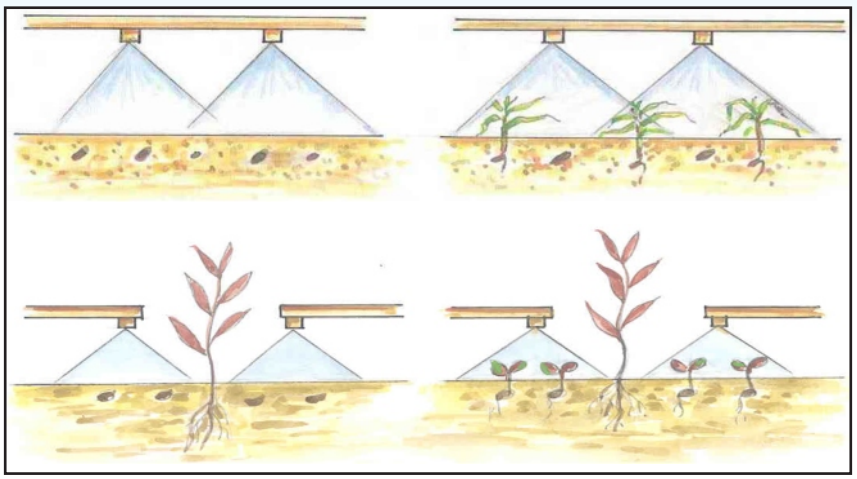
Figure 1: Incorporation of herbicides in the soil

1.3.2 Pre-emergence

Pre-emergence herbicides are applied pre-weed emergence and this will usually mean as pre-crop emergence as well (**Figure 2**). Herbicides which have greater toxicity on the emerging crop seedlings are applied before the crop is planted. Such compounds are taken up underground by the roots or hypocotyls of the weed. It is important for such compounds to possess some water solubility, in order that they become available to the germinating weed, but not so much that they are leached away from the weed germination zone and they must also be relatively persistent in the soil so that weeds that germinate over a period of time are all controlled.

1.3.3 Post-emergence

Post-emergence herbicides are applied after the emergence of the weed (and usually, but not necessarily, the crop as well). The auxin- herbicides, are taken up by the weed and translocated throughout the target plant they are systemic and, consequently, it is not so important to ensure that the whole of the weed is covered. Some post-applied herbicides are only active through the foliage, for example the auxin-herbicides, whilst others are taken up through the roots following application, e.g. isoproturon (**Figure 2).** The sulfonylureas can be taken up through the foliage and the roots. Hence the fact that a herbicide is applied post-weed emergence does not indicate that the compound is taken up by the foliage only, it is merely a convenient description of the use of the compound. For examples of foliage-absorbed herbicides include 2, 4-D, diquat, glyphosate.



Pre-emergence **Post-emergence**

Figure 2: Pre and post emergence application of herbicides

1.3.4 Lay by application

In lay by application, spraying of herbicides is done after the last cultivation in crops, such as after ridging in sugarcane and cotton.

2. Herbicide application and residue risk

Small quantities of herbicides in the form of active ingredients or breakdown products on or in the treated crop/soil at the time of harvest are generally known as residues. These small amount is expressed as µg/g equal to parts per million (ppm) or µg/kg or ppb (part per billion) or even at low level, ng/kg. Maximum rsidue limits (MRL) are generally described for each herbicide. Maximum residue limits are based on good agricultural practice (GAP) and will never, under any circumstances, be higher than can be justified on toxicological grounds. MRLs are legal limits that are used for enforcement purposes to monitor misuse of a chemical.

For effective weed control, herbicide must remain in the soil long enough to provide satisfactory weed control and degrade to innocuous 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. Herbicides have the capacity to move in the environment away from the target area, and may cause damage to non-target plants and animals. Some herbicide formulations are sufficiently volatile to cause plant injury from drift of vapour. For example, 2, 4-D esters volatilize off with vapours sufficient to cause severe damage to other plants, while 2, 4-D amines are essentially non-volatile and can drift only as droplets or dry particles. Herbicide drift can largely eliminated by use of proper nozzle and spraying technique and by using granular, foam, gel and encapsulated materials.

When a herbicide applied to control weeds in a crop at various crop stage, it may result in residues in the soil (through adsorption), weed and crop plants (through translocation and uptake), water (through the process of leaching that include vertical and horizontal), air (through the process of vaporization depending on the volatility of the herbicides and weather conditions), etc. In our studies it was found that imazethapyr dissipated at higher rate under higher temperature and brighter sunshine condition. Sulfosulfuron residues were not detected in the soil at harvest under wheat cropping system at 25 -50 g/ha application rates. Isoproturon and flufenacet degraded to non-detectable level within 60-75 days, whereas metribuzin applied in potato crop at 0.85 and 1.20 kg/ha persisted up to harvest in black soil.

Herbicides enter in the body of human and animal through skin, swallowing or breathing. Exposure can occur both during and following a herbicide application in a field. Most herbicides in the atmosphere get there as a result of fine spray droplets not settling but drifting and finally evaporated from the plant and soil surface. All herbicides have the potential to do this. Some herbicides also sufficiently volatile to enter the atmosphere by evaporating (volatilizing) from the surface of sprayed plants or from the soil eg., trifluralin and the volatile ester formulations of 2,4-D. The potential danger pose by these herbicides in the atmosphere and nearby plants is supposed to be short term. Photosensitive herbicides are susceptible to photodegaradtion by the Ultraviolet light. Ultraviolet light striking a herbicide molecule has sufficient energy to disrupt some of the bonds between its constituent atoms and destroying the molecule. Rates of photodegaradtion for any herbicide will depend upon the intensity of sunlight and volatility of the herbicide molecules.

3. Basis of herbicide persistence in the soil

Most of the soil-applied herbicides are absorbed by plant roots and underground absorptive sites, besides they undergo several degradation processes. During spray, foliar applied herbicides are also fell in the soil surface apart from plant surface and result in the residues in the soil. When herbicides are applied at recommended dose the persistence of herbicides in the soil may not arise after the crop growth period. Longer persistence in the soil arises when the application rate is more than the recommended rate, which occur due to indiscriminative uses and improper methods of herbicides application. The duration of activity of herbicides in the soil is the net effect of absorption, volatilization, leaching and degradation whether biological or non-biological. Residues remaining on or in a crop commodity from a given method, timing and rate of herbicide application may vary with site and climate. The best guideline to use is that the herbicide should persist throughout the critical period of competition for the crop and weeds. A higher temperature will cause greater volatilization of volatile herbicides and at the same time hasten microbial action. Heavy rainfall will cause greater leaching and runoff. Higher humidity enhances the soil microflora proliferation. Under average conditions, triazines herbicide persists in the soil for up to 90 days after application. For substituted ureas, like isoproturon, 60 to 100 days are required for complete degradation; depending upon the application rate. The persistence

of phenoxy carboxylic acid, amide and dinitroaniline groups of herbicides in the soil is found to be 20 to 60 days. Field experiments under direct seeded puddled conditions conducted at Coimbatore showed that application of 0.4 kg/ha anilofos and 2, 4-D resulted in anilofos persistence in the soil up to 56 days after application and residues after two successive rice crops were below the level of detection. At higher doses, both anilofos and 2, 4-D residues were recorded in rice grain and straw, but the residue levels were far below the maximum residue limit (Radhamani *et al*. 1997).

Herbicides are quite different from other pesticides as far as their application is concerned. For example, a similar insecticide may be used to control same pest in different crop, however, different herbicides have to be used in different crop often to control the same weed. This aspect of crop specificity is to be understood properly, otherwise there will be problems of crop injury. Herbicides are normally applied in the range of g/ha to kg/ha as pre-emergence, early post or post emergence to control variety of weeds in the cropped and non-cropped situations. The herbicides dissipate quickly in the soil by biochemical processes and half-life is generally reported to be less than 10-60 days under tropical conditions under prevalence of high rainfall and high temperature. In general, the residues of herbicides in the soil and crop produce were not detected at the time of harvesting, however in some instances they were detected in the food grain either in low quantity or below the maximum residue limits.

Selectivity can also be understood with the dose response curve for many plants for herbicides. The dose response curve is a logistic curve as shown below. At very low doses there is no significant effect on the plant. As the dose of herbicide increases the amount of damage increases until at high doses the plant dies and increasing the dose will have no further effect.

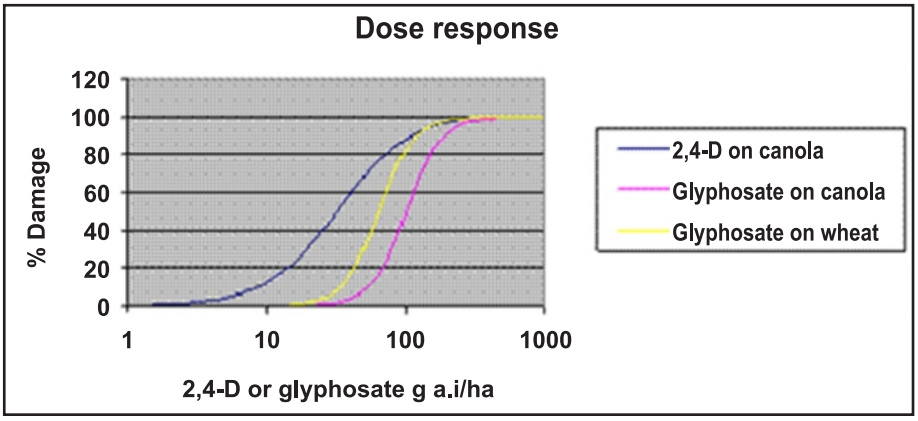


Figure 3: Dose response curve of the herbicide for the affected species

(Adopted from Department of Primary Industries and Regional Development, Government of Western Australia, https://www.agric.wa.gov.au/herbicides/herbicides?page=0%2C5)

In the **Figure 3,** example of 2,4-D and glyphosate spray on canola and wheat shows that wheat is damaged more than canola by low doses of glyphosate and the no-effect-level (NOEL) is around 10 grams of active ingredient per hectare (g/ha) for wheat and 25 g/ha for canola. For canola, the dose required to kill it, is similar for glyphosate and 2, 4-D. However, because the slope of the dose response curve for 2, 4-D is less than that for glyphosate, the NOEL for 2, 4-D on canola is much less that the NOEL for glyphosate. This means that canola crops are more tolerant to glyphosate drift than they are to 2, 4-D drift. This drift can be reduced by increasing the droplet size, followed by reducing boom height, followed by application at reduced wind speeds.

4. Herbicide leaching

As rain water moves down the soil profile from the surface, herbicides in the soil will move with it to some extent, this is known as leaching. This leaching is a dynamic process, whereby the herbicide alternates between being dissolved in the water and therefore moving with it, and being adsorbed onto soil particles and therefore become immobile to some extent. The rate of movement of any herbicide down the profile therefore depends on its solubility in water and the strength with which it absorbs onto soil particles. Therefore, after sometimes or in the next crop season, when net water movement is back toward the drying surface soil, it is possible that due to reverse water flow previously leached herbicide may move up from sub-soil to the surface soil. However, response of triazine residues will vary in the damage they cause according to the seasonal conditions. Residue effects will be much less when the season start is uniform and rainy compared to dry. Sulfonylurea and imidazolinone residues are less affected by soil moisture as they are more soluble in water. One has to be careful in those soils that have sand over alkaline clay. The sulfonylureas can leach down to the clay where they will be more persistent due to the high pH of the soil.

5. Herbicide drift and environmental risk

While using herbicide for weed control one should also properly understands the herbicide drift. Drift is the movement of herbicide away from the target area in the atmosphere. The three main forms of drift are droplet drift, vapour drift and particulate drift. Among these three forms, droplet drift is the main cause of off-target damage. Spray emerging from a boom breaks up into droplets of varying size. Larger droplets fall onto the target area, while the smallest droplets may remain in the air. Because droplet drift usually disperses as it moves away from the sprayed area, the type of crop damage it causes in adjoining areas is easily recognized. That part of the sensitive crop which is closest to the sprayed area is severely damaged but this damage decreases away from the severe zone. The vapour is produced by evaporation from the droplets when they leave the boom and from the target surface after spraying. Like droplets, vapour disperses rapidly as it is carried away from the target area. The vapour will remain suspended in the air unless the contaminated air is forced back to ground level where it may damage growing plants.

Vapour can drift for long distances, and the characteristic feature of vapour drift damage is that no clear damage gradients can be seen. Damage, which is generally mild but widespread, is usually caused by a large body of contaminated air several square kilometres in size.

The smaller droplets provide better coverage which is important when the target plant is small; when the herbicide is poorly translocated or when low carrier volumes are used. The larger droplets result in greater interception or less drift, but the poorer coverage may need to be compensated by using translocated herbicides or higher carrier volumes. Most commercially available nozzles produce a range of droplet sizes so there is usually a proportion of a very fine droplet that may drift. For aqueous sprays the addition of a drift reducing agent may increase the production of droplets that are less than 100 µm diameter and cause greater drift. Large droplets fall faster than small droplets. It is to be understood that about 2-10% of spray volume of aqueous formulations will be in drift-prone droplets - less than 100 µm diameter - with normal flat fan or cone nozzles and less on boom sprays. Emulsifiable formulations of herbicides will produce about twice as many droplets in this size range with the same equipment.

Herbicide drift can cause significant damage to the crops. Most agricultural herbicides are applied as fine droplets produced by hydraulic nozzles on boom sprays, mostly set up to deliver droplets in the 150-300 µm range. Droplets from 100-200 µm in diameter usually stick to the first surface they encounter but droplets larger than 500 µm are likely to bounce off leaves and end up on the soil or lower canopy and droplets smaller than 50 µm are likely to float around the target plant and drift off.

6. Degradation of herbicides in plant and soil and subsequent residues

A certain proportion of any selective/non-selective herbicide applied to a crop will be absorbed by crop plants and by weeds and some portion fell down on the soil surface. Susceptible weeds are not able to metabolize applied herbicide effectively and quickly and this lead the weed plant to die. During this process, cells of weed plants rupture and release a range of oxidizing enzymes. These enzymes destroy much of the weed plant tissues, and the herbicide as well. Thus this fraction of the herbicide also degraded from the weed plants after some time. Crop plants are able to tolerate applied herbicides due to various enzymes within them which metabolize the herbicide before it can cause permanent damage. Herbicide is degraded within the plants and from the soil by several bio-chemical processes and destroyed. Very small quantity of herbicides may found in the soil or agricultural products at harvest and referred as herbicide residues.

Due to presence of residues many herbicides that are used in cropping rotation have the potential to damage crops grown in other season /years of that rotation. Generally, herbicides are degraded into non-toxic compounds by a combination of biological and chemical processes such as volatilization, leaching, runoff and degradation by microbes, and photodecomposition and do not cause any problems for the crops. However,

sometimes, even susceptible crop in the crop rotation in the same field is affected by the residues of herbicides applied in the previous crop.

Herbicide degradation in the soil is occurred due to availability of adequate moisture and soil temperature and the action of microscopic living organisms **(Figure 4)**. When a herbicide is added to their environment, it also becomes a potential food supply. These organisms break down the organic material in the soil to provide the energy they need to live as it is their food supply. Some herbicides are also susceptible to chemical reactions which alter their structure and render them into non-phytotoxic form. These degradation processes depend upon soil physico-chemical properties as well as temperature and moisture level. Generally, degradation of herbicide increase in direct proportion to the soil temperature, and begin when the moisture level rises above the wilting point. Extra moisture in the soil increases the rate of degradation but less than higher temperatures. Some herbicides are broken down quickly, while other herbicides take longer time to dissipate, hence persist for longer duration where they were applied. These can injure sensitive crops that are sown in the following seasons. Herbicides may affect fauna and flora adversely through improper use, and enter in to the, soil/water system through effluents or the direct input of herbicide contained by sewage sludge into aquatic environments.

In an instance injury to cotton (*Gossypium hirsutum* L.) (Main *et al.* 2004; Pekarek *et al.* 2010), sugar beet and sorghum (*Sorghum bicolor* L.) (FMC Corporation 1999) has been reported one year after sulfentrazone, metsulfuron, sulfosulfuron, chlorimuron application, and consequently extended recropping intervals were advised for these crops (Sondhia and Singhai 2008; Sondhia 2014). Lentil shown to exhibit sensitivity to sulfentrazone and sulfosulfuron residues (Johnson 2011; Sondhia and Singhai 2008) and a higher re-cropping interval of 36 months are recommended after sulfentrazone application.

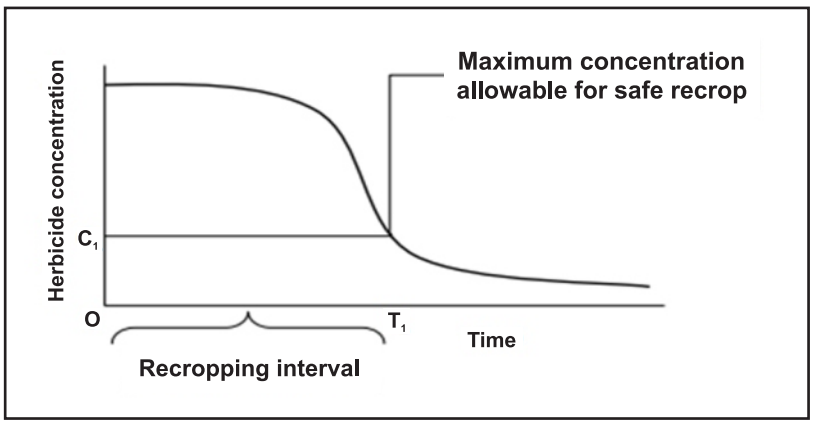


Figure 4: Depiction of dissipation of herbicides over time

Triazines (for example, atrazine and simazine), sulfonyl ureas (chlorsulfuron, triasulfuron), imidazolinones (imazethapyr, imazamox) are possible candidates for carryover. It has been found that imidazolinones group of herbicide are more persistent on acid soils and sulphonyl ureas on alkaline soils. Triazines are also persistent on alkaline soils. Less rainfall and dry spell after any herbicide application may result in higher level of residues on the soil surface. Herbicides persistence in the soil is expressed as half life or time required to degrade fifty percent of the original molecule. However the half life is not absolute because it depends on many factors, such as, the soil properties, temperature, herbicide doses, application methods and climatic conditions etc. and influence the fate of the herbicides in the soil.

The persistence of pyrazosulfuron-ethyl in the soil is mainly influenced by soil organic matter and moisture. Chlorsulfuron and metsulfuron-methyl degraded faster in low pH soil than in high pH soil. Residues of metsulfuron-methyl in rice soil were found 8 - 16 ng/g at 2-8 g/ha application rates at 30 days. Atrazine in the soil showed a gradual degradation with advancement in maize crop growth and residue were not found at harvest whereas 56 ng/g of residues 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 even after eight months. The persistence of fluazifop-p-butyl at two application levels and three temperature level revealed fast degradation in the soil.

Adsorption of herbicide in the soil also plays a significant role in deciding degradation of herbicides. For example, adsorption of alachlor increased with increase in concentration, time of incubation, rise in activation temperature, lowering of pH and increase in the organic matter content. High adsorption in soil, limit the herbicide efficacy. Butachlor degradation in soil 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 the soils.

In a study, 2, 4-D at 0.4 kg/ha alone or in combination with anilofos persisted up to harvest. Clodinafop-propargyl ester generally convert 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 the soil were found to be 93 to 81 ng/g in alluvial, red and black soil, respectively. In a monitoring study of four herbicides, butachlor residues were 61% followed by pendimethalin (36%), and fluchloralin (3%) and alachlor was not detected in all the locations. Herbicides were found in the range of <0.01 to 1.46 ng/g with a mean of 0.21 ng/g. Herbicide with high water solubility and low volatility are prone to leaching. Imazethapyr was found to leach in the clay loam soil up to the depth of 70 cm at 100 and 200 g/ha applied doses (Sondhia 2013). Pendimethalin could leach in the clay loam soil up to the depth of 55 cm in 200 mm rainfall condition (Sondhia 2007 b). High mobility of metsulfuron-methyl under continuous saturated moisture condition was found (Sondhia

2009 b). In one of our studies, residues of sulfosulfuron were significantly higher in surface soil as compared to sub-surface soil and found up to 150 days at lower soil depths at 25-100 g/ha applied doses in wheat grown field (Sondhia 2009 b) and residues in the surface soil (0-15 cm) were in the range of 0.003- 0.005 µg/g at 25- 100 g/ha doses by 100 days. Sulfosulfuron residues were not detected after 200 days in surface and sub-surface soils in all the doses.

Pendimethalin applied at 1.0 to 4.0 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. Persistence of some herbicides in the soil can be understood in Indian conditions by **Table 3**.

Table 3: Persistence of some herbicides in the soil under Indian tropical conditions

Herbicide	Persistence in soil (days)	Reference
Atrazine	45-90	Sondhia 2001, 2002; Nag and Das 2009
Alachlor	60-80	Sharma 2002; Sondhia 2014
2, 4-D	45-90	Sushilkumar *et al.* 2003; Kumari *et al.* 2004
Butachlor	100	Sondhia *et al.* 2006, Sondhia 2008
Dithiopyr	90-150	Gupta and Gajbhiye 2002
Fluzifop p-butyl	30-90	Leela 1993 ; Sondhia 2007
Isoproturon	90-120	Sondhia and Singh 2006
Imazosulfuron	60	Sondhia 2007, 2008
Metoxuron	80	Randhawa and Sandhu 1997
Metribuzin	20-100	Sondhia 2002
Oxadiazon	56-125	Raj *et al.* 1999; Sondhia and Varshney 2010
Pyrazosulfuron-ethyl	35-60	Mukherjee *et al.* 2010; Naveen *et al.* 2012; Sondhia et al 2013
Pretilachlor	30-60	Kumar 2011; Sondhia 2012
Pendimethalin	60-200	Rai *et al.* 2000; Sondhia 2012, 2013
Thiobencarb (benthiocarb)	28-60	Jayakumar and Ramulu, 1993; Aktar *et al.* 2007
Oxyfluorfen	60-80	Devi *et al.*1998, Sondhia and Dixit 2005, 2007, Sondhia 2009
Imazethapyr	90-240	Sondhia 2008, 2012
Metolachlor	40-190	Devi *et al.* 2000

6.1 Herbicide residues in crops produce at harvest

Now-a-days, many herbicides are being routinely applied for effective weed control in the crops. Some of the results are being described here for better understanding on fate of herbicide residues in cereals. In a study, herbicide residues were determined in the rice and wheat plants that were collected at harvest that contained grains and straw. For

instance, at harvest, application of butachlor at 1.0 kg/ha resulted in residues i.e. 2, 9 and 6 ng/g in rice bran, straw and rice grains, respectively, however at 2.0 kg /ha application rate, the residues were found to be 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 to be 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 at 210-420 g/ha in wheat crop. Fenoxaprop residues in the soil of wheat field was found to be in the range of 0.4-11 ng/g at 70-400 g/ha application rates.

Atrazine applied at 1.0 kg/ha rate in maize crop degraded by harvest and residues were not detected in maize grains but at 2.0 kg/ha rate, 0.088 mg/kg of residues were detected (Sondhia and Saraswat 2000). Atrazine was degraded to undetectable levels at applied doses (1.0- 2.0 kg/ha) by the time the maize crop was harvested (90 days) and half-life of atrazine varied from 23 to 31 days in the soil. In chickpea and Indian mustard, low levels of fluchloralin residues were detected in the soil at 150 days that corresponds to 64-85% and 69-82% degradation, respectively. However, the flucloralin persistence was not affected by preceding atrazine treatments applied to maize. The maize yield declined with an increase in atrazine dose and was lowest at 2.0 kg/ha (24.8 and 16.3 q/ha, respectively, compared to 32 and 25.2 q/ha in the hand-weeded treatment).

Terminal residues of pendimethalin were monitored in the green field peas and chickpea applied as pre-emergence herbicide at 750-185 g/ha rates. Low pendimethalin residue level was found in mature pea grain (0.004-BDL µg/g) and straw (0.007-0.001 µg/g) at 750-185 g/ha applied doses, respectively (Sondhia 2012, 2013). In another study, pendimethalin residues were 0.025, 0.015, <0.001 µg/g in chickpea grains at 750 to 185 g/ha treatments. Much lower concentration of pendimethalin residues viz. 0.015 to <0.001 µg/g were found in the straw at 750, 350 and 185 g/ha treatments, respectively (Sondhia 2012). Similarly, Mandal *et al.* (2014) and Mukhopadhyay *et al.* (2012) reported that quizalofop-ethyl application at 50-100 g/ha on blackgram did not result in residues in seed, foliage and soil at harvest. Dissipation of trifluralin in the soil of black gram at 90 days was found approximately 97% with the half life values 23.3 to 26.2 days. Irrespective of any dose, residues of trifluralin were not detected in black gram crop soil and plant samples at harvest (Aktar *et al.* 2009). Imazethapyr residues in soil, soybean grains and straw were found 0.008, 0.102 and 0.301 µg/g, respectively at 100 g/ha application rate (Sondhia 2008). Fluazifop-p-butyl can leach up to 15 cm soil and at harvest 0.012-0.036 mg/kg residues were found in the soil of soybean crop with 0.250-0.500 kg/ha rates, respectively and

fluazifop-p-butyl at 0.5 kg/ha rate resulted in translocation of 0.005 and 0.001 mg/kg residues in soybean grains and cake, respectively (Kulshrestha *et al.* 1995).

Terminal residues of pendimethalin applied as pre-emergence at 1.0 kg/ha in tomato, cauliflower, and radishes were detrmined under field conditions. At harvest, 0.008, 0.001 and 0.014 µg/g residues of pendimethalin were found in tomato, cauliflower, and radishes, respectively (Sondhia 2013). Residues of oxyfluorfen applied in mature onion were below the maximum residue limit (0.05 µg/g) (Sondhia and Dixit 2007; Sondhia 2008) and a pre-harvest interval of 118 days for onion crop after the oxyfluorfen application was suggested (Sondhia 2010). At harvest, 0.009 and 0.006 mg/kg terminal residues of fluchloralin were found in stover and grains when applied at 0.75 and 1.50 kg/ha, respectively (Saikia and Pandey, 1999). Sondhia and Dubey (2006) did not found pendimethalin residues of pendimethalin in onion collected at mature stage, however 0.007 µg/g pendimethalin residues were detected in green onion at 1.0 kg/ha application rate.

Similarly 0.005 and 0.003 µg/g haloxyfop residues were detected in the green and mature onion bulbs collected at 50 days and at harvest, respectively (Sondhia 2014). It was found that 2, 4-D residues at 0.06 mg/kg level caused malformation in leaves (Kathpal *et al.* 1980). Metamitron persisted in sugar beet crop plant up to 15 days while up to 30 days in soil. On day 90, metamitron was detected in the soil at 7.0 kg/ha treated plots (Janaki *et al.* 2013). Application of pendimethalin, and trifluralin resulted in below detectable limit residues (0.02 mg/kg) in celery seeds (Kaur and Gill 2012). In cucumber, anilophos residues (ND–0.042 mg/kg) were detected.

6.2 Herbicide residues in other plantation crops, vineries, and non-cropped area

In a study napropamide dissipation in soil and residues in tea was evaluated. Napropamide rapidly dissipated in the soil with half-lives in the range of 12.54–27.87 days. The initial deposit of napropamide in tea cropped soil was found in the range of 1.18–1.49 and 2.08–2.90 µg/g at recommended dose (1.125 kg/ha) and double the recommended dose (2.25 kg/ha), respectively. At 30 days after application of the herbicide, more than 50% of the residue was dissipated (Biswas *et al.* 2013). In a study conducted at Ludhiana, glufosinate ammonium applied as post-emergence to cotton at 0.45- 0.90 kg/ha degraded to safe level by 20 day. Sushilkumar *et al.* (2003) evaluated persistence of glyphosate in non-crop area and found that residues were not detected after 45 days at 2.0-2.5 kg/ha application rates, however, at 3.0 kg/ha glyphosate persisted up to 60 days in black soil of Jabalpur.

Norflurazon, oxyfluorfen, oxadiazon or trifluralin-persistent herbicides commonly

used for weed control in vineyards. Norflurazon was found as the most persisting herbicide although there were detectable residues of all the herbicides on both red and white grapes. The penetration of herbicides into the flesh of the grapes was found to be significantly greater for white grapes than for red grapes. Small-lot winemaking experiments showed that norflurazon persisted at levels close to the initial concentration through vinification and into the finished wine (Ying and Williams 2004). Alachlor residues were found at trace level in cotton plant, cotton lint and oil, water and fish at 2.5 and 5.0 kg/ha application rates under field condition at Chennai (Ramesh and Maheshwari 2004). At Anand, pendimethalin applied at 0.6-0.9 % to tobacco resulted in 0.198 to 0.376 mg/kg residues in tobacco leaves and 0.72 mg/kg residues in leaves treated with 0.5 % pendimethalin, and 0.04-0.079 mg/kg residues were found when treated with 0.25% pendimethalin (Parmar *et al.* 1998).

A comprehensive summary of herbicide residues in crop plants at harvest are given in **Table 5.**

Table 5. Herbicide spray on crops and resulting residues in the soil, food grain and straw

Herbicides	Crop	Dose (g/ha)	Residues (µg/g)			References
			Soil	Grains	Straw	
Ethoxysulfuron	Rice	15-20	<0.001	<0.001	<0.001	Sondhia and Dixit 2012, Sondhia 2014
Butachlor	Rice	1000	0.005	0.025-0.002	0.029-0.006	Reddy *et al.* 1998; Sondhia *et al.* 2006
Sulfosulfuron	Wheat	25	BDL	0.010-BDL	0.004-BDL	Ramesh and Maheshwari 2004, Sondhia, Sondhia and Singhai 2008, 2009, Sondhia 2014
Metsulfuron-methyl	Rice	4-4	BDL	BDL	0.002	
	Wheat	4-8	BDL	BDL	BDL	
Isoproturon	Wheat	1000	0.006-0.032	0.035-0.041	0.065-0.022	Sondhia and Singh 2008; Arora *et al.* 2013,
Oxyfluorfen	Rice	150-250	BDL	0.018	0.106	Sondhia 2009,
Imazosulfuron	Rice	30-40	BDL	BDL	BDL	Sondhia 2007
		50-60	BDL	0.006-0.009	0.009-0.039	
Fentazamide	Rice	240-420	BDL	BDL	BDL	Mukherjee and Gopal 2005,
Anilofos	Rice		<MRL	<MRL	<MRL	Jayakumar and Sankaran, 1995
Fluazifop-p-butyl	Soybean	0.5	0.012-0.036	0.005	0.001	Kulshrestha *et al.* 1995
Clodinafop	Wheat	240	0.021-BDL	0.096-BDL	BDL	Sondhia and Mishra 2006, Arora *et al.* 2013, Sondhia 2014
Topramezone	Maize	25	BDL	BDL	BDL	Sondhia 2019
Tembotrione	Maize	120	BDL	BDL	BDL	Sondhia 2019

**Source: (Sondhia 2010, 2014, 2016, 2018)* **BDL-Below detection limit

These results showed that if herbicide are applied at recommended dose, time using recommended nozzle and spray volume in a given crop, risk of resulting herbicide residues above the maximum residue limit (also referred as maximum permissible limit) is minimal or very less.

6.3 Herbicide residues in sea grasses and coral reef

The widespread expansion of the industry on the great barrier reef catchment area have resulted in a 3–7 fold increase in herbicide use (e.g. atrazine, 2,4-D and diuron). Mixture of herbicide residues following river discharge events has the capacity to produce cumulative chronic effects on sensitive species of marine plants and corals. These effects may cause a change in the community structure of mangrove, seagrass and coral reef ecosystems. Most of the herbicide residues detected in the GBR lagoon (diuron, atrazine, hexazinone and ametryn) can be attributed to application in sugar cane cultivation and exceeded the permissible limits. Tebuthiuron, on the other hand, is found to be linked to beef grazing management practices (Lewis et al. 2011).

6.4 Herbicide in aquatic bodies, fishes and other non targeted organisms

With the increasing use of herbicides for weed control, the herbicide may enters into streams and underground water sources by runoff, drift and leaching mechanism. Many herbicides are routinely detected from the surface and ground water sources in developed countries like, USA, New Zealand, Australia, Canada, Japan and European countries. The most often detected herbicides are 2, 4-D, atrazine, cyanazine, carbaryl, simazine, bromacil, diuron, diazinon, prometon, metolachlor, dinoseb, picloram, metribuzin, metsulfuron, glyphosate, metolachlor, propanil, butachlor, pendimethalin, oxyfluorfen, etc. (Sondhia 2014). Some herbicides such as, butachlor, atrazine, pendimethalin, paraquat are strictly banned or restricted in USA, and European countries due 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.

In a study, pyrazosulfuron-ethyl residues were found to be 0.0154 mg/kg and 0.0023 mg/kg at 21st and 35th day, respectively in the underground water (Naveen *et al.* 2012). Water samples collected from Singoor reservoir, Hyderabad were found to be contaminated with atrazine residues (NO-1.056 µg/L). The concentration of atrazine residues in Osmansagar water was 0.056 µg/L during postmonsoon November, 2005 and total pesticide residues load was 3.369 µg/L (Reddy and Reddy 2010). Residues of alachlor were detected up to 60 days in acidic, neutral and basic buffer solution fortified with 0.5 and 1 µg /g and residue were below the detection limit after 140 days in water and no residues were detected after 80 days. Residues of paraquat were not detected after 20 days at 0.80

kg/ha application rate when applied to control *Eichornia crassipes* but application at 1.8 kg/ha showed 0.069 and 0.028 mg/L residues in pond and canal water, respectively. Paraquat residues in the fish samples were also detected below the acceptable daily intake of 0.002 mg per kg body weight. It is reported that only 0.80 to 1.11 % of the applied paraquat remained in the sediment fraction however paraquat at 0.8- 3.2 kg/ha application rates increased the pH and electrical conductivity of water.

A laboratory experiment was conducted to study the persistence of pretilachlor in water having acidic, neutral and alkaline pH for 60 days. Irrespective of pH, pretilachlor residues were detected up to 15 days after application and were below detectable limit on 30th day. The half-life of pretitachlor in different pH water varied from 3.05 to 3.30 days and there was not much difference in half- life due to increase or decrease in pH of irrigation water (Deepa and Jayakumar 2006). The total mean concentration of atrazine ranged from 0.72 to 17.3 µg/L whereas 0.91 to 40.9 µg/L residues were defecated as the mean concentration of simazine in groundwater samples collected from Delhi (Aslam *et al.* 2013). However in one study more fish mortality observed with 2, 4-DEE and paraquat than with glyphosate.



Figure 6: Toxicity of herbicides to fishes

In a study Yadav *et al.* (2013) revealed genotoxic potential of butachlor even at low dose level (1.0 mg/kg) in fishes and suggested that butachlor interferes with cellular activities in fishes at genetic level inducing chromosomal aberrations and suggested a serious concern towards the potential danger of butachlor for aquatic organisms. In another study fish mortality was more with 2, 4-DEE and paraquat than with glyphosate (Muniappa *et al.* 1995). In a glass aquariums study sulfosulfuron was applied at 25- 100 g/ha. Residues of sulfosulfuron in the fishes were found to be 1.09-3.52 µg/g after 10 and 90 days, residues in the fishes were reached to below the MRL (Sondhia 2008, 2012). In another study, fishes (*Channa punctata*) were exposed for 10 days to sub lethal concentration ($1/5^{th}$ of static LC_{50}) of butachlor. Residue of butachlor after 10 days were found 0.1255 mg/kg in gills, 0.3515 mg/kg (Bloch) liver in (Bloch) liver, 0.3145 mg/kg in kidney and 0.2350 mg/kg in brain traces muscle of *Channa punctata*. The results of this study and other revealed that prolonged exposure to sub lethal concentrations led to increase in the accumulation of residues in different tissues, causing toxicity to the fish which ultimately results in biomagnifications through the food chain (Tilak 2007, Sondhia 2012, 2013, **Figure 6**).

High doses or long exposure might lead to adverse effects on non-target organisms and limit their survival rate. In a study, fenoxaprop and metolachlor were found to be conjugated to earthworm (*Eisenia fetida*) at low rates. The metabolism of the Gram-negative bacteria *Stenotrophomonas maltophilia*, generally found in the rice field irrigation channels, could be negatively affected by 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 demonstrated the induced oxidative stress caused by the herbicides. Bensulfuron-methyl did not affect bacterial population significantly, either in the overlying water or in the surface paddy soil, but the nitrification potential was significantly suppressed. Butachlor application suppressed nitrogen-fixing ability few days after its application but was augmented after 37 days in the soil layers. N-fixing cyanobacteria were reported to be relatively tolerant to 2, 4-D under field conditions.

7. Non targeted effect of herbicides

Disappearances of some of the plants species including weed species is another result of the use of herbicides from the agricultural fields. 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. In addition, 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. This applies to *Anagallis arvensis, Arenaria serpyllifolia, Atriplex patula, Cerastium caespitosum, Galium aparine, Plantago major, Silene noctiflora* and several species belonging to the genus Veronica. However, studies of sensitivity indicated that for some species, like *Anagallis arvensis*, herbicides caused a major impact (Boutin *et al*. 2004).

It has been found that some crop plants are very sensitive to presence of herbicide residues in the soil, for example, sorghum and cucumber plants are found to be very sensitive plants to detect metribuzin residues in the soil. In general, residue problems can be linked with the use of long persisting soil-residual herbicides. High level of chemicals remaining at the site into the following growing season is referred to as carryover which results in stunted or malformed plants or lack of seedling emergence (**Figure 7**). Factors contributing to persistence involve misapplication, environmental condition, soil texture, organic matter content, temperature, rainfall, moisture, water holding capacity and percolation rate. Dry weather for first month after application increase chances of carryover. For example, high pH (>7) may increase carryover of sulfonylureas and triazine herbicides in the soil. Whereas low pH (<6) reduce microbial degradation of sulfonylureas and imidazolines herbicides in the soil. The polar molecules, such as glyphosate, permeate membranes slowly and can enter phloem sieve tubes and retained to allow for long-distance transport. Glyphosate often runs off to fields where it is applied and can be translocated by plant roots. Glyphosate can affect plant functioning in non-target plants found in agricultural ditches (Saunders and Pezeshki 2015). Glyphosate may also be transported within the plant xylem in the apoplastic pathway when taken up by roots. For both foliar and root uptake, glyphosate translocation may be basipetal or acropetal, moving toward sink tissues, such as meristems, flowers and fruits. Absorption of glyphosate through roots has been shown in several crop species, such as beets, barley, cotton, maize and rapeseed. This exposure pathway is significant, because roots are the main intercept of glyphosate in field runoff. In Table 6, examples of some re-cropping restriction after herbicide application are given.



Bleaching by acifluorfen **Stundted growth**

Figure 7: Crop injury due to herbicides (Adopted from Romeethredge 2013)

Table 6: Some re-cropping restriction after herbicide application

Herbicides	Re-cropping restriction
Sulfonylureas	Pea, lentil
Imidazoline	Soybean, sunflower
2,4-D	Tomato
Fluroxypyr,	Wheat, barley, oats, rye, corn, flax, canola, mustard, lentils, peas
Clopyralid	Wheat, barley, oats, rye, corn, flax, canola, mustard, lentils, sugar beets
Metosulam	Wheat, lupins
Pendimethalin	Mungbean

7.1 Herbicide and human heath

Though herbicide are designed to applied to control weeds in cropped and non-cropped condition, still misuse of herbicides is found in many cases and even many person find their way to use these chemicals as direct ingestion to kill their lives which is not at all recommended by these chemicals. The purpose of this information here is to aware and warn the readers on the severe toxicity of herbicide on the human if ingested intentionally or unintentionally. Through, indirect effects of herbicides on human are not common in India. However increasing incidences of acute herbicide self-poisoning by butachlor, fluchloralin, paraquat, 2, 4-D, pendimethalin, glyphosate *etc*. are imposing a warning situation in parts of Asia (Senarathna *et al.* 2009). In a study, low vapour pressure caused the formation of large droplets, thus inhalation of paraquat spray used in the open environment has not been shown to cause any significant systemic toxicity; however, inhalational exposure to paraquat in confined spaces, such as a greenhouse, is known to be associated with fatal pulmonary disease. The oxidative role of butachlor in intracellular ROS production, and consequent mitochondrial dysfunction, oxidative DNA damage, and chromosomal breakage, which eventually triggers necrosis in human PBMN cells, is also reported (Suntres 2002; Dwivedi *et al*. 2012). Hemoperfusion using activated charcoal has been shown to decrease paraquat level, but data to support survival benefit in humans is insufficient. It is only effective if initiated within 4 h of ingestion; as peak paraquat concentration in the lung is achieved in 5–7 hours. Atrazine have an adverse effect on endocrine, immune and nervous system function. Glyphosate damages and kills human cells at levels below those used in agriculture and at residual levels to be expected in food and feed derived from roundup-treated crops.

Intentional paraquat poisoning is an uncommon entity in India, and is associated with a high mortality rate (Agarwal *et al*. 2005; Kondle *et al*. 2013). These cases are reported in India to highlight the high mortality rate associated with paraquat poisoning in spite of advances in treatment and supportive care (Khosya and Gothwal, 2012).

Nair *et al.* (2000-5) demonstrated that 2, 4-D is capable of inducing higher DNA damage as well as chromosomal aberrations in human lymphocytes. In an Indian series of 17 patients of herbicide poisoning, the most common symptoms were vomiting (100%), followed by altered sensorium (59%), oral ulceration or dysphagia (53%), dyspnea (41%), or loose stools (24%) (Sandhu *et al*. 2003). Acute respiratory distress syndrome because of paraquat usually appears 24–48 h after ingestion (Singh *et al.* 1999, 2003).

8. Mitigation methods to minimize herbicide residue risk

When applied at recommended rates most herbicides breakdown within a few days or weeks after application and did not impose harmful effects to the next crop or cropping options to the 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 for long duration crops as the residues prevent growth of sensitive weed species throughout the season. However, these residues can restrict the crop that can be grown in rotation. Various management techniques including early detection by bioassay method have been developed which can be adopted to minimize the herbicide residue hazards in the soil as described below:

8.1 Use of optimum dose of herbicide, selection and time of application of herbicides

Theoretically, the rate of herbicide applied should never be more than the amount required to achieve an acceptable level of weed control. This practice will reduce the potential for carry-over. Hazards from residues of herbicides can be minimized by the application of chemicals at the lowest dosage by which the desired weed control is achieved. Several workers have reported no adverse residual effect of herbicides applied at optimum dose for rice on succeeding crops.

Choosing a herbicide with little or no carry-over given in soil and crop weather conditions will eliminate future crop injury problems. Research has shown that early removal when the weeds are 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.

8.2 Ploughing/cultivating the land and irrigation

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 case of deep

ploughing the herbicide layer is inverted and buried in deeper layers and thereby the residual toxicity reduced (**Figure 10**).

Village operation help in distributing herbicide evenly and therefore dilute residue concentration in the soil, allowing maximum exposure to the microorganism, clay and organic matter that adsorb herbicides. Tillage also enhanced aerobic microbial activity. Sometimes tillage invert residual herbicides and concentrating residue on upper soil depths that usually remained in the lower depth for longer period. The herbicide residue than can be brought back to the plant root zone with subsequently deep plough operation exposing future crop to carryover. Therefore it is necessary to thoroughly distribute herbicide residue in the soil.

Decontamination of herbicide residues by means of controlled irrigation practices alone or in combination with tillage, cropping and use of soil amendments has been achieved with success. While controlled irrigation enhances all modes of deactivation, heavy irrigations leach herbicides out of the root zone of the crop. Continuous moist soils often result in more rapid breakdown of herbicides due to creation of favourable conditions for microbial activity.

8.3 Addition of organic matter

Herbicides are also inactivated by plant residues or organic matter incorporated into soil. Farm yard manure application is an effective method to mitigate the residual toxicity of herbicides. Application of FYM 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 FYM 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) in sandy loam soil. A 50 t/ha of muck+peat and FYM application at 10 t/ha added to soil can also eliminate triazines and sulfonylurea herbicide residues from soil.

8.4 Crop rotation/growing of tolerant crops

When planning crop rotations, farmers must consider the injury potential to subsequent crops from herbicide residues. Visual injury and reduced yield of spinach planted 3-4 months after treatment with imazaquin and imazethapyr in southern pea (*Vigna unguiculata* L.) is reported. Herbicide residues in the soil can be decontaminated by crop rotation, i.e., sowing of crop plants that are resistant to the particular herbicide. Herbicides may be lost from the soils by absorption into crop plants (and detoxified there), which may theoretically be used as a trap crop. Application of atrazine to maize, diuron to cotton and chloramben to soybean produced no direct or residual effect on succeeding

crop in cotton-maize-soybean rotation. When herbicide residue is detected or suspected, a tolerant crop should be grown. A tolerant crop has the ability to either store or degrade the residue to non-toxic compounds. For example, when carry-over due to imazethapyr is suspected, crops such as canola and flax should be avoided. There can be differences in tolerance levels between varieties within a crop. The addition of fertilizer enhances the growth of tolerant plants, which increases the uptake of herbicide from the soil. It also promotes the growth of microflora, increasing biological breakdown of herbicide in the soil. For example, addition of phosphate fertilizer enhances the microbial breakdown of the phenoxy herbicides and 2, 4-D.

8.5 Addition of absorbents, antidotes, non phytotoxic oil and safeners

Activated charcoal (or carbon) effectively reduce herbicide contamination in specific areas and can also be used as a root dip to protect transplants (Tomatoes, peppers, strawberries, ornamentals, etc.). It is very effective to mitigate high level of residues of trifluralin, 2, 4-D, and other class viz. chloroacetamide triazine, substituted urea and sulfonylureas herbicides in the soil. Activated charcoal has a high adsorptive capacity because of its extremely large surface area which vary from 600-1200m^2/g. Activated charcoal can either be broadcasted or applied as narrow band over the seed at the time of planting. In a study incorporation of 50 kg/ha of activated charcoal completely inactivated chlorsulfuron residues applied at 1.25 and 2.50 kg/ha and did not affect the yield of maize compared to 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.

Qiu *et al.* (2009a) observed enhanced degradation of atrazine with increasing amount of wheat char added to the sandy loam soil from 0.1 to 1%. These increases were hypothesized to result from the nutrients present in char, and especially P, which could stimulate the microorganisms activity thereby enhancing the biodegradation. Atrazine residual hazard can be reduced by mixing in non phytotoxic oil. 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.

Biomass is recognized as a potential renewable energy source, and pyrolysis is considered the most promising thermo-chemical conversion of biomass into bioenergy products (Özçimen and Karaosmanoğlu 2004). Biochar be defined as the solid residual remaining after the thermo-chemical transformation of biomass whose main intended purpose is as a means of C sequestration. The use of biochar increase herbicide sorption on soil, decrease its mobility and reduce the contamination risks of surface and ground waters. The effect of biochar on the dissipation and degradation of pesticides in amended

soils has been reported for atrazine (Spokas *et al.* 2009; Jablonowski *et al.* 2010), acetochlor (Spokas *et al.* 2009), isoproturon (Sopeña *et al.* 2010). An increase in the degradation of atrazine was found by Jablonowski *et al.* (2010) in a clay soil adapted to atrazine and amended with biochar from hardwood at 450-500 °C. The increase in mineralization and degradation of the herbicide is attributed to the stimulation of the soil microflora by the nutrients provided by biochar. In **Figure 9** variability in the stability of biochars was placed in context of the spectrum of potential black C products with the molar ratio of oxygen: carbon (O: C) (Spokas 2009 b). However, bioavailability of diuron to soil microorganisms was decreased by the presence of wheat char in the soil, due to the increase in herbicide sorption. For weak acidic herbicide MCPA, a decrease in biodegradation because of wheat ash amendment was also reported by Hiller *et al.* (2009).

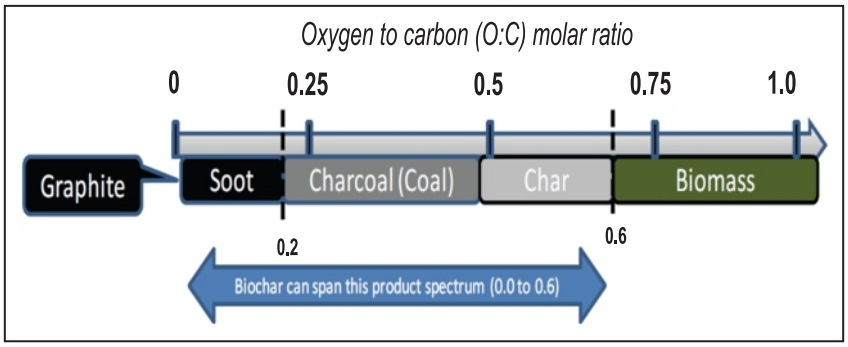


Figure 9: Spectrum of black C products based on the oxygen to carbon ratio in the residual solid product. [Adapted from Hedges et al. (2000), Bansal & Goyal (2005) and Spokas (2009)]

8.6 Tank-mixture opportunities

Combining a non-residual herbicide with the lowest recommended rate of a residual herbicide in a tank-mixture can reduce carry-over potential. It is important to use only registered tank-mixes and to apply according to the application instructions on the product labels.

8.7 Microbial mitigation

Some soil microbes such as bacteria and fungi play an important role in deactivating residues. *Aspergillus flavus* and *Aspergillus terricola* rapidly degraded metolachlor applied at 10 kg/ha up to 92 and 87 % after 20 days in sterile and non-sterile soils, respectively. *Penicillium chrysogenum* and *Aspergillus sps.* were found as potent pyrazosulfuron-ethyl and penoxsulam degrading fungi (Sondhia *et al.* 2013, 2016). It has been found that bacteria *Pseudomonas* sp. found to enhance the rate of degradation of atrazine into soil that had been maintained with and without switchgrass (*Panicum virgatum*). More than 99% of applied ^{14}C-atrazine was degraded within the first 72 hours

post-inoculation with 54.5% of applied ^{14}C-atrazine mineralized to CO_2. *Aspergillus niger* was found to degrade higher concentration of iodosulfuron in the soil.

8.8 Use of adsorptive materials

Polyacrylamides (PAMs) are polymer-based materials generally used to facilitate erosion control and decrease soil sealing by binding soil particles, especially clays, to hold them on site. In addition, these types of materials may also be used as a water treatment additive to remove suspended particles from runoff. PAM increases the soil available pore volume, thus increasing infiltration and reducing the quantity of runoff water that can cause erosion. Suspended sediments from PAM treated soils exhibit increased flocculation over untreated soils. The increased flocculation aids in their deposition, thus reducing storm water runoff turbidity and improving water quality. PAMs may be used as a water treatment additive to remove suspended particles from runoff. PAMs may also be used to provide an appropriate medium for the growth of vegetation for further stabilization.

Disadvantage of PAM is that the specific PAM copolymer formulation must be anionic. Cationic PAM shall not be used in any application because of known aquatic toxicity problems. It is not effective when applied to pure sand or gravel with no fine silts or clays, nor when applied over snow cover. Some PAMs are more toxic and carcinogenic than others. Only the most environmentally safe PAM products should be used. Materials are soil type-specific so a contractor cannot use leftover material at another site or bulk order for multiple sites.

8.9 Electrochemical deactivation and ozonation

Remediation of the *s*-triazine herbicides such as prometryne, desmetryne and terbutryne through electrochemical behaviour (DC and DPpolarography) on mercury electrodes was also demonstrated in the acidity range 2.25 MH_2SO_4 to pH 6.5. Electron irreversible reduction processes were found suitable with adsorption. Electrochemical deactivation at pH 3.5 and at potentials around –1.10 V (*vs* the Ag/AgCl/KCls at electrode) can be a valid method to deactivate these molecules in the contaminated water. Finally, the reductive route can be an alternative environmental degradative process in waters under strong reductive conditions, with pH values equal or lower than 3.5 pH-units, and rich in carbonaceous materials on clays. In these ambient oxidative photolytic detoxification of herbicides cannot occur.

Ozonation process at the output of 200 mg/hour at 0.15 kg/cm^2 for 15-30 minutes removed some pesticides from tomato up to 20.2 to 90.8% and can be utilized as post harvest technique for reduction of pesticides load from the mature vegetables/fruits.

8.10 Use of tolerant plant

Sometimes use of tolerant crop plants serve as an effective way to minimize herbicide residues from the soil. Maize, and sorghum for instances is a good candidate for decontaminating a field containing triazine and sulfonylurea herbicides. Pea and lentil can be used to detect sulfosulfuron residues in the contaminated soil.



Figure 10: Decontamination of herbicides, a) Deep ploughing; b) growing of Sesbania in affected soil; c and d) mixing of Sesbania in the affected soil; e) crop without phytoremediation; f) crop after phytoremediation technique

8.11 Use of weeds for retaining herbicides from agricultural runoff mitigation

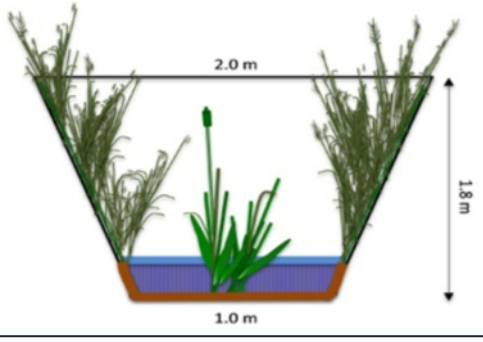
The use of a hydroponic system is a first step toward comprehensive fate of herbicide in plants, but is also a useful tool for assessment of phyto-treatment of industrial wastewater, agricultural runoff, surface and groundwater contaminated with pesticides.

Experiments showed tolerant of vetiver sps. to 20 ppm atrazine for 6 weeks, even with a maximum bioavailability created by the use of a hydroponic system. Atrazine resistance could be explained by plant metabolism, dilution of active ingredient into plant biomass, chloroplastic resistance, and sequestration of atrazine before it reaches its target site in leaves. *Vetiver thylacoids* was found to sensitive to atrazine, excluding therefore chloroplastic resistance. Plants known metabolism of atrazine relies on hydroxylation mediated by benzoxazinones, conjugation catalyzed by glutathione-*S*-transferases and dealkylation probably mediated by cytochromes P 450.

Plant metabolism took place in vetiver and small amounts of dealkylated products were found in roots and leaves, and conjugated atrazine was detected mainly in leaves, confirming *in vitro* tests. Atrazine metabolism study was successfully conducted in entire *Vetiver* plants in hydroponic system. However, such a system had limitations for understanding plant effect on atrazine removal from a soil environment.

8.12 Vegetated ditch for herbicide mitigation from water

Use of vegetated ditch for mitigation and control of mobile herbicides is also increasing. Vegetated ditch for mitigation of mesotrione, S-metolachlor and terbuthylazine after an extreme runoff was determined, the ditch was flooded with water containing herbicides release. Ditch can immediately reduce runoff concentration of herbicides by at least 50% even in extreme flooding conditions. The half-distances were about 250 m. As a general rule, a runoff of 1 mm from 5 ha is mitigated by 99% in 100 m of vegetated ditch. It was suggested that shallow vegetated ditches can be included in a general agri-environment scheme for the mitigation of herbicide runoff together with wetlands and linear buffer strips as given in **Figure 11 and 12** (Otto *et al.* 2015).



Compartment	Volume (m^3)	%
Soil	0.025	0.94
Sediment	0.006	0.21
Susp. Solid	0.000	0.00
Air	2.514	93.10
Water	0.154	5.69
Biota	0.000	0.00
Root	0.001	0.02
Stem	0.0005	0.02
Leaves	0.000	0.01
Sum	**2.700**	**100.00**
Liquid/Solid	4.9	4.9



Figure 11: Vegetated ditches for the mitigation of pesticides runoff (Adopted from; Otto *et al.* 2015)

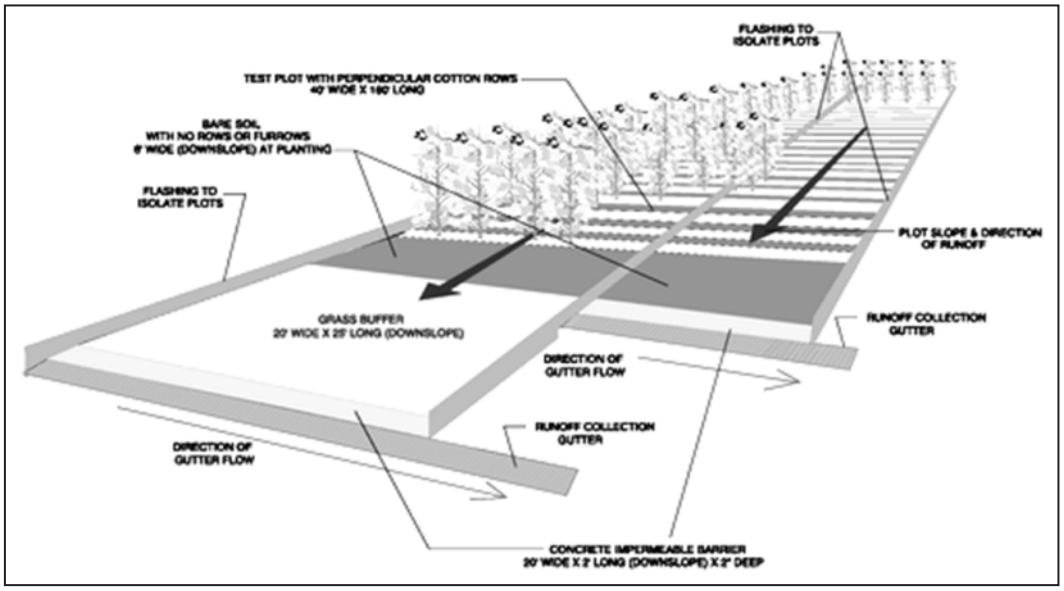


Figure 12: Removal of herbicides by vegetated filter strips

8.13 Removal of herbicides from air

Versi-Dry Lab Soakers (Kimbies) were also used to collect the diazinon spray particles within the orchard and outside the orchard. Kimbies were hung vertically in trees as well as placed horizontally under trees of the first tree row adjacent to the open field sampling area **(Figure 13)**. This can absorb herbicides for surrounding air.

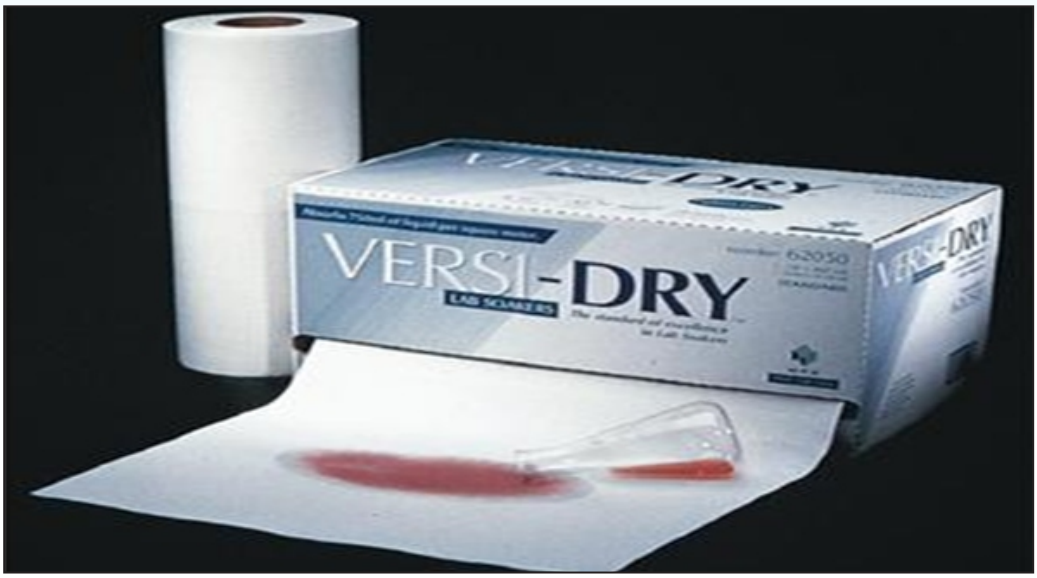


Figure 13: Versi-Dry Lab Soakers (Kimbies) to collect spray particles

8.14 Reducing herbicide poisoning in human

Hemoperfusion using activated charcoal has been shown to decrease paraquat level, but data to support survival benefit in humans is insufficient. It is only effective if initiated within 4 h of ingestion, as peak paraquat concentration in the lung is achieved in 5–7 h (Sandhu *et al.* 2003). Hemodialysis is used as a support of acute renal failure, but it does not increase clearance of the substance as it is rapidly distributed to the lungs and other organs (Sandhu *et al.* 2003). Immuno-suppression with combination of cyclophosphamide and methylprednisolone was shown to be beneficial in moderate-to-severe cases by prevention of ongoing inflammation (Agarwal *et al.* 2005). Unfortunately, none of the studied treatments, including controlled hypoxia, superoxide dismutase, vitamins C and E, N-acetylcysteine, desferrioxamine, and nitrous oxide, has been proven to be effective (Suntres 2001; Eddleston *et al.* 2003).

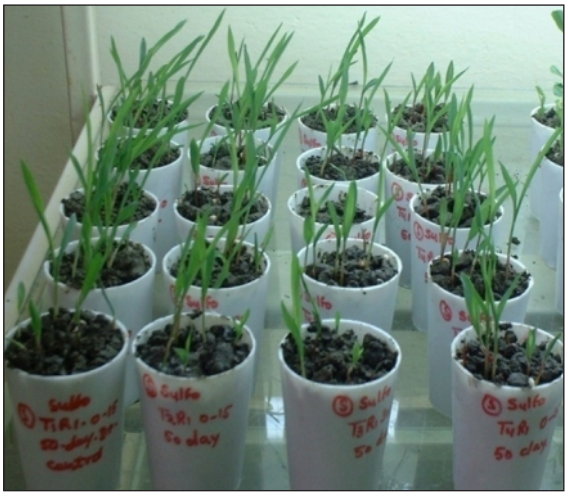
9. Use of bio-indicator plant for detection of residues

Determination of herbicide residues can be challenging due to the very low herbicide concentrations that can persist and remain bioactive in soil. These small amounts of residues may cause injury to sensitive rotational crops. Plant bioassays are a valuable alternative to instrumental procedures for determination of herbicides in the soil. Instrumental methods such as gas chromatography or high performance liquid chromatography require solvent or solid phase extractions before sample analysis, and

these highly efficient extractions enable the determination of total amount of herbicide in the soil. In contrast, bioavailable herbicide can be easily determined by bioassay procedures because plant response varies with soil types (Grey *et al.* 1997; Szmigielski *et al.* 2009).

Bioassays using sensitive plants species exposed to paraquat in solution have shown that it is highly active against plant roots, with wheat roots being particularly sensitive. The availability of paraquat to the plants present in soils appeared to depend on the nature of the soil, its adsorption capacity, and the concentration of paraquat in soil solution, the latter being available for uptake by roots. An acute 12-well plate phytotoxicity assay for the PSII herbicide diuron using isolated *Halophila ovalis* leaves by fluorescence images also can be used to test higher concentration of diuron in water (Wilkinson *et al.* 2015).

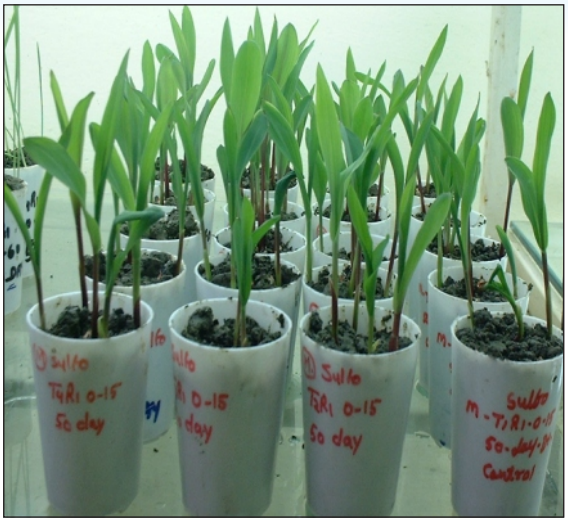
Typically, ALS-herbicides are detected using root inhibition bioassays, and various susceptible plant species including oriental mustard (Eliason *et al.* 2004; Szmigielski *et al.* 2009, 2011), corn, red beet (Jourdan *et al.* 1998), sunflower (*Helianthus annuus* L.) (Hernández-Sevillano *et al.* 2001); and pea, sorghum (Sondhia 2008). **Figure 8** shows the phytotxic effect of syulfosulfuron residues as a result of higher application rate (50 and 100 g/ha doses) on pea and lentil. Protox inhibiting herbicides influence mainly shoot development of sensitive plants. Cotton (Main *et al.* 2004; Grey et al. 2007) and sugar beet (Blanco and Velini 2005; Szmigielski *et al.* 2009, 2011) have been reported as a suitable species for sulfentrazone detection in the soil.



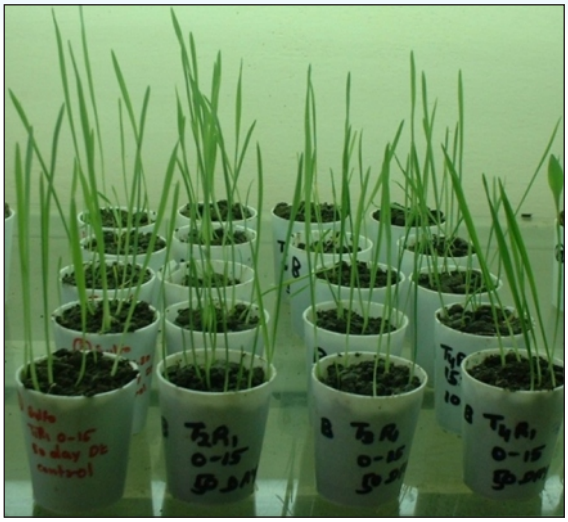
Effect of sulfosulfuron on maize after 50 days



Effect of sulfosulfuron on peas after 50 days



Effect of sulfosulfuron on sorghum after 50 days



Effect of sulfosulfuron on barley after 50 days

Figure 8: Use and effect of sulfosulfuron on pea and sorghum

Szmigielski *et al.* (2012) used sugar beet as a bio-indicator plant for detection of both flucarbazone and sulfentrazone by measuring both root and shoot length reduction of sugar beet. By sugar beet bioassay, concentration of approximately 2 ppb of flucarbazone based on root length measurements and of approximately 20 ppb of sulfentrazone using shoot length measurements may be detected. However, bioassay detection limits vary with soil type and are generally lower in sandy soils of low organic matter content and high pH (Eliason *et al.* 2004; Szmigielski *et al.* 2009). Because sugar beet plants respond both to flucarbazone and sulfentrazone, a sugar beet bioassay allows for detection of these two herbicides in the soil by evaluating both root and shoot inhibition. Growing sugar beet plants in Whirl-PakTM bags is a simple technique and provides a convenient method for assessing shoot and root length. Shoots are measured above the soil level and do not need to be harvested, this helps particularly with measuring shoots that are short and brittle at phytotoxic concentrations of herbicide. Roots are recovered from soil with water and consequently roots do not get broken or damaged before being measured.

So these or other sensitive bioassay plants can be grown to detect presence of suspected persisting residues in the field and therefore a suitable cropping sequence can be followed in the same field. Sensitive crop should not be grown or planted in the same field.

10. Precautionary measure to minimize herbicide risk

As stated earlier, herbicides are also synthetic chemicals and designed to kill weed plants and may be considered as poison hence their improper and excessive sue may use result in severe damage to the standing or successive crops and resulting higher persistence and residues in the soil and crop plants. Apart from harmful effects to the crops, the avoidance of safety instructions and kit during preparation, spraying of herbicide and disposal may severely affect the physical health of person/farmers. It is always recommended to follow safety instruction and use of safety kit **(Figure 14)** not only for herbicides but other class of pesticides too.

- Use only registered and recommended formulations/brands in accordance with state laws and regulations.
- Ensure to read, understand and follow all of the label directions when mixing and applying herbicides. Take particular note of the toxicity of the herbicide and any adverse effects it will have on other crops, trees, wildlife or human health.
- Remember, more is not better. Use the application rate on the label.
- Some herbicides are selective, and only kill certain types of plants, while others are non-selective and kill almost any type of plant.
- Some herbicides kill weeds quickly, others can take up to a week or more, proper care and patience is required.
- Some herbicides persist in plants and soils for longer duration, while others only remain in plants or soil for a short time. Some herbicides have active ingredients that are more likely to move through soils towards groundwater. Others are much less likely to move through soils.
- Adopt methods to reduce drift. For example, using low pressure nozzles or low nozzle height. Remember that no current method eliminates drift.
- Assess the risks and decide if they are worth taking. For example, if you are spraying a selective herbicide in wheat and down wind there are other wheat crops, you are probably fairly safe to spray in a strong wind. On the other hand, if you are spraying knock-downs and down-wind there is a belt of new plants you have been trying to establish, wait for more favourable spraying conditions.
- Wind speed is the main factor to be considered at the time of spraying. Do not spray if

the maximum wind speed is greater than the speed at which you are spraying. If the wind speed is greater than your speed of travel, you risk to come into contact with the drift is high when spraying with the wind behind you.

- Individuals who are mixing, loading, transporting and applying herbicides can minimize their exposure by wearing the personal protective equipment (PPE) (**Figure 14**). Standard PPE used for most types of herbicide applications includes rubber boots, protective aprons or suits face mask, goggles and rubber gloves.
- Contaminated water as a result of the washing the spraying equipments must be disposed of by scattering over the barren land.
- Discontinue use of herbicides that are ineffective, or out dated.
- Do not blow, suck or apply your mouth to any sprinkler, nozzle or other spraying equipment. Spray should always be done in the direction of the blowing wind to avoid skin exposure and inhalation.
- Do not use the empty containers of herbicides for any other purpose. Destroy them by making holes and bury them afterwards in to the soil.



Figure 14: Herbicides protection kit

11. Do's and don'ts of herbicides

- Always read the label carefully before you buy a product and make sure the product is intended for your specific use. Store all herbicide safely out of reach of children and pets.
- Make sure kids, pets, and anyone non-essential to the application is out of the area before mixing and applying pesticides.
- Be sure to wear clothing that will protect you when using herbicides. Consider wearing a long sleeve shirt, long pants, and closed-toe shoes in addition to any other protective clothing or equipment mentioned in the label.
- Mix herbicides outdoors or in well-ventilated areas.
- Mix only what you need to use in the short term to avoid storing or disposing of excess pesticide.
- Be prepared for any possible herbicide spill. Have paper towels, sawdust or kitty litter, garbage bags, and non-absorbent gloves on hand to contain the spill. Avoid using excessive amounts of water, as this may only spread the herbicide and could be harmful to the environment.
- Read the first aid instructions on the label before using the product. Contact the emergency services in case of medical emergency.
- Remove personal items, such as toys, clothing, or tools from the spray area to avoid contamination.
- When spraying herbicide indoors, make sure the area is well ventilated.
- When applying herbicide as a spray or dust outside, avoid windy conditions and close the doors and windows of your home.
- After using herbicides, wash your hands with soap and water properly before smoking or eating.
- Use the appropriate amount of herbicide according to area to be sprayed. Applying more herbicide than the recommended dose may waste money and may harm people, pets or the environment.
- Do not assume a herbicide purchased for one type of weed control in a particular crop can be used in other crop for control of same or other weeds, always remember herbicide are crop and weed specific.
- Buy only what you need. Storing and disposing of leftover herbicide can lead to unnecessary risks.
- Review the storage and disposal section of the label for information on how the product should be stored and disposed of, including the empty container.

- Always read the label before using or re-using a herbicide.
- Do not use herbicide in any manner other than those specifically listed on the label.
- Never remove a herbicide label from the container, or use unlabeled herbicides.
- Always keep required personal protective equipment , first aid, emergency telephone numbers and instructions regarding mixing, application, use rates and labeled sites near the spraying field.

12. Guidelines for safely mixing and loading of herbicides

- Only authorized herbicide handlers or supervisors should be in the mixing and loading area. All handlers should be wearing proper personal protective equipment (PPE). No other persons, and no animals, should be present.
- To prevent spills, place herbicide containers in a secure place.
- Take proper position when you are opening and handling them.
- Read and follow label directions. Pay special attention to warnings and precautions.
- Work only in a well-ventilated and well-lighted area.
- Never stir herbicide with your hands. Always use a stir-stick.
- Use a collecting basin, a container within a container-to further prevent inadvertent spills.
- Never pour herbicide at eye level. Never lift any open herbicide container higher than your chest. Mix and pour concentrated herbicide no higher than waist level. A spill or splash could be disastrous.
- If herbicide are spilled or splashed on you, remove your clothing immediately and wash yourself thoroughly within two minutes. Then wash your clothing.
- Protect your eyes with splash-proof goggles.
- Stand with your back to the wind so any fumes or dusts are blown away from you.
- Be precautious and never pour herbicide directly into a spray tank. Always mix and dilute the herbicide in a small container.
- Always pour the herbicide into water. Never pour water into the herbicide. When pouring, keep your head well above and to one side of the spray tank opening. This will reduce the chance of your being splashed in the face.
- Avoid mixing or loading near surface water or a well head.
- Do not leave a herbicide tank unattended while you are filling.
- Never allow a spray tank to overflow. The cleanup could be a costly and dangerous and may be of all-day, all-night task.

13. Cleaning equipment and containers

Rinse equipment at seperate sites in the field. Triple-rinse or pressure-rinse empty herbicide containers at the mixing site before you recycle them or dispose of them. Do this after emptying the containers. Add the rinse water to the sprayer tank and spray it out over an approved site, or use it to mix the next batch.

Conclusion

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. For this, herbicide use should be always carry out following the given guidelines and instruction given in the commercial products. Over and repeated use of herbicide should always be avoided to reduce phytotoxic effects on succeeding crops plants. Herbicide must be applied in proper dose and time, based on the physico-chemical properties of herbicides, soil, water, and weather parameters to avoid residue problem. The improper use of herbicides even may lead to higher residues level in the soil and crop produce and can contaminate ground water besides adverse effects on human and animal. It has to be noted that as a result of a heavy dependence on selective herbicides for weed control worldwide, several weed species have developed resistance against herbicides. Therefore, mitigation strategies of herbicide residue hazard need to be followed to lessen their effect on environment by reducing adverse impacts to less than significant levels. Sensitive crops should be avoided after using a soil residual herbicide. A remedial measure should be advocated to the growers/farmers along with chemical weed control methods to deal with high residues and to avoid any carryover effect. A field bioassay can be performed if suspecting a carryover effect. Herbicides in most instances when applied at recommended doses did not result in residues in food chain or in the soil at level that should cause concern. Even though the switch to low-dose herbicides has significantly reduced herbicide consumption, still most surface water and groundwater samples still contain some quantity of herbicides, sometimes at levels harmful for human health and for environment.

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. Central laws and policies regulate many aspects of herbicides including labeling, registration, and application. However, risks are always present with any herbicide use, but improper use or misapplication can further increase these risks and necessitate use of a remediation measures.

References

Agarwal R, Srinivas R, Aggarwal AN and Gupta D. 2006. Experience with parquet poisoning in a respiratory intensive care unit in North India. *Singapore Medical Journal* 47(12): 1033–1037.

Aktar MW, Gupta D, Alam S and Chowdhury A. 2009. Degradation dynamics of a di-nitro aniline herbicide (trifluralin) in/on black gram (*Vigna mungo*) under East-Indian climatic condition. *Electronic Journal of Environmental, Agricultural and Food Chemistry* 8 (11): 1172-1177.

Aktar MW, Gupta A and Gade V. 2007. Bhattacharyya fate and behavior of benthiocarb a herbicide in transplanted paddy under east-Indian climatic condition. *Bulletin of Environmental Contamination and Toxicology* 79: 646–649.

Arora A, Tomar SS and Sondhia S. 2013. Efficacy of herbicides on wheat and their terminal residues in soil, grain and straw. *Indian Journal of Weed Science* 45(2): 109–112.

Aslam M, Alam M and Rais S. 2013. Detection of atrazine and simazine in ground water of Delhi using high performance liquid chromatography with ultraviolet detector current. *World Environment* **8**(2): 323-329.

Bansal R C and Goyal M. 2005. Activated carbon adsorption, CRC Press Taylor and Francis Group LCC, ISBN 0-8247-5344-5, Boca Raton, Florida, USA.

Blanco FMG and Velini ED. 2005. Sulfentrazone persistence in soybean-cultivated soil and effect on succession cultures. *Planta Daninha* 23(4): 693-700.

Biswas PK, Kumar S, Mitra SR and Bhattacharyya A. 2007. Persistence of napropamide in/on tea under north-east Indian climatic condition. *Bulletin of Environmental Contamination and Toxicology* 79: 566–569.

Boutin C, Elmegaard N and Kjær C. 2004. Toxicity testing of fifteen noncrop plant species with six herbicides in a green house experiment: implications for risk assessment. *Ecotoxicology* 23: 349-369.

Deepa and Jayakumar 2006. Persistence of pretilachlor in water at different pH level. *Pesticide Research Journal* 18(2):199-200.

Devi MP, Reddy CN and Reddy NV. 1998. Crop tolerance studies to oxyfluorfen and its persistence in soil. *Indian Journal of Weed Science* 30(3-4): 214-215.

Devi MP, Reddy CN, Reddy NV, Reddy DJ and Babu TR. 2000. Metolachlor and pendimethalin dissipation in red sandy loam soil and their movement in Alfisols and Vertisols. *Journal of Research ANGRAU* 29: 4, 95-99.

Dwivedi S, Saquib Q, Abdulaziz A, Al-Khedhairy, Musarrat J. 2012. Butachlor induced dissipation of mitochondrial membrane potential oxidative DNA damage and necrosis in human peripheral blood mononuclear cells. *Toxicology* 302(1): 77–87.

Eddleston M, Wilks MF and Buckley NA. 2003. Prospects for treatment of paraquat induced lung fibrosis with immunosuppressive drugs and the need for better prediction of outcome a systematic review *QJM* 96(11): 809–824.

Eliason R. Schoenau JJ, Szmigielski AM and Laverty WM. 2004. Phytotoxicity and persistence of flucarbazone-sodium in soil. *Weed Science* 52 : 857-862.

Grey TL, Walker RH, Wehtje GR and Hancock, HG. 1997. Sulfentrazone adsorption and mobility as affected by soil and pH. *Weed Science* 45: 51-56.

Grey TL, Vencill WK, Mantrepagada N and Culpepper AS. 2007. Residual herbicide dissipation from soil covered with low-density polyethylene mulch or left bare. *Weed Science* 55: 638-643.

Gupta S and Gajbhiye VT. 2002. Adsorption-desorption, persistence and leaching behavior of dithiopyr in an alluvial soil of India. *Journal of Environmental Science and Health, Part B: Pesticides, Food Contaminants, and Agricultural Wastes* 37(6): 573-586.

Hedges JI, Eglinton G, Hatcher PG, Kirchman DL, Arnosti C, Derenne S, Evershed RP, Kogel-Knabner I, de Leeuw JW, Littke R, Michaelis W and Rullkotter J. 2000. The molecularly-uncharacterized component of nonliving organic matter in natural environments. *Organic Geochemistry* 31 (10): 945-958.

Hernández-Sevillano E, Villarroya M, Alonso-Prados JL and García-Baudín JM. 2001. Bioassay to detect MON-37500 and triasulfuron residues in soil. *Weed Technology* 15: 447–452.

Hiller E, Bartal M, Milicka J and Cernansky S. 2009. Environmental fate of the herbicide MCPA in two soils as affected by the presence of wheat ash. *Water Air and Soil Pollution* 197 (1-4): 395-402.

Janaki P, Rathika S, Chinnusamy C and Prabhakaran NK. 2013. Field dissipation of metamitron in soil and sugar beet crop. *Bulletin of Environmental Contamination and Toxicology* 90:116–119.

Jablonowski ND, Hamacher G, Accinelli C, Berns AE, Meng F, Martinazzo R, Langen U, Walraf C, Linden A and Burauel P. 2010. Influence of biochar and activated char amendment on the biodegradation of 14C-atrazine in atrazinem adapted soils from Belgium and Brazil. In Setac Europe 20th Annual Meeting, Seville, May 2010.

Jayakumar R and Sankaran S 1995. Evaluation of anilofos 50 EC residues in transplanted rice. *Madras Agricultural Journal* 82 (4): 296-298.

Johnson EN, Moyer JR, Thomas AG, Leeson JY, Holm FA, Sapsford KL, Schoenau JJ, Szmigielski AM, Hall LM, Kuchuran ME and Hornford RG. 2005. Do repeated

applications of residual herbicides result in herbicide stacking? In Soil Residual Herbicides: Science and Management. Topics in Canadian Weed Science, Ed. R.C. Van Acker. Sainte-Anne-de Bellevue, Québec: Canadian Weed Science Society – Société canadienne de malherbologie, P 53-70, Volume 3 ISBN: 0-9688970-3-7.

Jourdan SW, Majek BA and Ayeni AO. 1998. Imazethapyr bioactivity and movement in soil. *Weed* Science 46: 608-613.

Kathpal TS, Gupta K, Kamboj RK and Kairon MS. 1980. Contamination of cotton leaves with 2,4-D herbicide residues. *Haryana Agricultural University Journal of Research* 10(2): 258-260.

Kaur R and Gill BS. 2012. Analysis of herbicide residues in celery seeds. *Indian Journal of Ecology* 39(2): 258-260.

Khosya S and Gothwal S. 2012. Two cases of paraquat poisoning from Kota, Rajasthan, India case reports in critical care. https://doi.org/10.1155/2012/652146

Kondle Raghu, Vidavalur Mahesh, Parri Sasidhar, Polam R Reddy, Vajja Venkataramaniah, and Agrawal A. 2013. Paraquat poisoning: A case report and review of literature. *Case Report* 20(3): 198-200.

Kulshrestha G, Singh SB and Gautam KC. 1995. Residues of fluazifop-p-butyl following application to soybean. *Bulletin of Environmental Contamination and Toxicology* 55 (2): 276-282.

Kumar B. 2011. Residues of pesticides and herbicides in soils from agriculture areas of Delhi region, India. *Journal of Environment and Earth Science* 12(1): 8.

Kumari D, Kumari B, Kathpal TS, Yadav A and Malik RK. 2004. Determination of 2 4 D sodium salt residues in soil and wheat using HPLC. *Annals of Agri-Bio Research* 9 (1): 59-61.

Leela D. 1993. Weedicides for vegetables Indian-Horticulture. 38(2) : 13-15.

Lewis SE, Smith R, Brodie JE, Bainbridge ZT, Davis AM and Turner R. 2011. Using monitoring data to model herbicides exported to the Great Barrier Reef, Australia. 19th International Congress on Modelling and Simulation, Perth, Australia, 12–16 December 2011, p-2051-2056. http://mssanz.org.au/modsim2011.

Main CL, Mueller TC, Hayes RM, Wilcut JW, Peeper TF, Talbert RE and Witt WW. 2004. Sulfentrazone persistence in southern soils: bioavailable concentration and effect on a rotational cotton crop. *Weed Technol*ogy 18: 346-352.

Mandal K, Sahoo SK, Battu RS and Singh B. 2014. Estimation of quizalofop ethyl residues in black gram (*Vigna mungo* L.) by gas liquid chromatography. *Bulletin of Environmental Contamination and Toxicology* 92(1):115-118.

Mukherjee I and Gopal M. 2005. Evaluation of fentrazamide for weed control and estimation of its residues in rice. *Bulletin of Environmental Contamination and Toxicology* 74: 667–672.

Mukherjee A, Dutta S, Karmakar PR, Kole RK and Bhattacharyya A. 2010. Dissipation pattern of the herbicide pyrazosulfuron-ethyl in alluvial and red lateritic soils of West Bengal. *Journal of Crop and Weed* 2(2): 65-69.

Mukhopadhyay S, Bhattacharyya A and Das S. 2012. Fate and persistence of herbicide quizalofop-p-tefuryl on black gram. *Journal of Crop and Weed* 8(1): 190-192.

Muniappa VT, Manjunatha V, Babu VS and Shivkumar HR. 1995. Efficacy of post emergent herbicides on control of water hyacinth (*Eichhornia crassipes* Mart.) and their effect on fishes. *World Weeds* 2:117-121.

Nag SK and Das SK. 2009. Persistence of atrazine in soil under fodder sorghum. *Journal of Crop and Weed* 5(2): 131-135.

Nair RS, Paulmurugan R and Wilsanand V. 2005. Genotoxix effects of coomonly used pesticides of south india in human lymphocytes. *Pollution Resarch* 24 (1): 7-12.

Naveen DV, Gowda RC and Mamatha B. 2012. Field studies on persistence of pyrazosulfuron-ethyl in soil, ground water and residues in transplanted rice. *Asian Journal of Soil Science* 89(5): 1032-1036.

Otto S, Pappalardo SE, Cardinali A, Masin R , Zanin G and Borin M. 2016. Vegetated ditches for the mitigation of pesticides runoff in the Po Valley. PLoS One. .doi.org/10.1371/journal.pone.0153287.

Özçimen D and Karaosmanoğlu F. 2004. Production and characterization of bio-oil and biochar from rapeseed cake. *Renewable Energy* 29 (5): 779-787.

Pekarek RA, Garvey PV, Monks DW, Jennings KM and MacRae AW. 2010. Sulfentrazone carryover to vegetables and cotton. *Weed Technology* 24: 20–24.

Qiu Y, Xiao X, Cheng H, Zhou Z and Sheng GD. 2009. Influence of environmental factors on pesticide adsorption by black carbon: pH and model dissolved organic matter. *Environmental Science and Technology* 43(13): 4973-4978.

Parmar NB, Maraviya GV, Shah PG, Patel BK, Ghelani LM and Patel AM. 1998. Pendimethalin residues in tobacco plant. *Tobacco Research* 24(1): 57-59.

Radhamani S, Sankaran S and Jayakumar R. 1997. Degradation and persistence of herbicides in direct seeded puddled rice. *Madras Agricultural Journal* 84 (4): 194-196.

Rai AK, Chhonkar PK and Agnihotri NP 2000. Persistence and degradation of pendimethalin and anilofos in flooded versus non-flooded soils. *Journal of the Indian Society of Soil Science* 48 (1): 57-62.

Raj MF, Patel BK, Shah PG and Barevadia TN. 1999. Pendimethalin, fluchloralin and oxadiazon residue in onion. *Pesticide Research Journal* 11(1**):** 68-70.

Ramesh A and Maheswari S T.2004. Dissipation of alachlor in cotton plant soil and water and its bioaccumulation in fish. *Chemosphere* 54: 547-652.

Ramesh A and Maheswari ST. 2003. Dissipation of sulfosulfuron in soil and wheat plant under predominant cropping conditions and in a simulated model ecosystem. *Journal of Agricultural and Food Chemistry* 51: 3396–3400.

Randhawa SK and Sandhu KS. 1997. Persistence of metoxuron in soil. *Journal of Research Punjab Agricultural University* 34 (2): 136-137.

Reddy KN and Reddy H. 2010. Pesticide residues in surface water of lakes around Hyderabad, India. *Pesticide Research Journal* 22(2):111-115.

Reddy KN, Rao B N, Sultan MA, Reddy D J and Babu TR. 1998. Residues of butachlor in paddy. *Journal of Research ANGRAU* 26(3-4) : 48-49.

Romeethredge. 2013. Reflex Herbicide Injury on Soybean. Seminole Crop E News. Agricultural news for farmers and agribusiness in SW Georgia. https://seminolecropnews.wordpress.com/2013/06/12/reflex-herbicide-injury-on-soybean/

Saikia TP and Pandey J. 1999. Dissipation of fluchloralin in chickpea (*Cicer arietinum* L.). *Journal of the Agricultural Science Society of North East India* 12(2): 236-238.

Sandhu JS, Dhiman A, Mahajan R and Sandhu P. 2003. Outcome of paraquat poisoning a five year study. *Indian Journal of Nephrology* 13: 64–68.

Saunders LE and Pezeshk Ri 2015. Glyphosate in runoff waters and in the root-zone: A Review. *Toxics* 3(4): 462-480.

Senarathna L and Eddleston MF. 2009. Prediction of outcome after paraquat poisoning by measurement of the plasma paraquat concentration *QJM* 102 (4): 251–259.

Sharma KK. 2002. Degradation of alachlor in water and tropical soil of India. *Bulletin of Environment Contamination and Toxicology* 68: 394-399.

Singh S, Bambery P, Chaudhry D, Makharia G, Kakkar N and Singh D. 1999. Fatal paraquat poisoning: report of two cases. *Journal of Association of Physicians of India* 47(8): 831–832.

Singh S, Yadav S, Sharma N and Malhotra P. Bambe. 2003. Fatal 2, 4-D (ethyl ester) ingestion. *Journal of Association of Physicians of India* 51: 609-610.

Sondhia S and Saraswat VN 2000. Spectrophotometeric determination of atrazine residues in maize grains and soil. In: Proceedings of the international conference on natural resource management, New Delhi, India, 14–18 February, 2000, pp. 226–227.

Sondhia S. 2001.Determination and assessment of atrazine residues in potato (*Solanum tuberosum L.*) soil. *Geobios- Jodhpur* 28(2/3): 140-142.

Sondhia S. 2005. Phytotoxicity and persistence of metribuzin residues in black soil. *Toxicological and Environmental Chemistry* 87: 387-389.

Sondhia S. 2005. Phytotoxicity and persistence of metribuzin residues in black soil. *Toxicological and Environmental Chemistry* 87(3): 389-397.

Sondhia S. and Yaduraju NT. 2005. Evaluation of leaching of atrazine and metribuzin in sandy clay loam soil. *Indian Journal of Weed Science* 37(3&4) : 298-300.

Sondhia S. and Dubey RP. 2006. Terminal residues of butachlor and pendimethalin in onion. *Pesticide Research Journal* 18: 185-186.

Sondhia Shobha, Singh VP and Yaduraju NT. 2006. Persistence of butachlor in sandy clay loam soil and its residues in rice grains and straw. *Annals of Plant Protection Sciences* 14(1): 206-209.

Sondhia S. 2007a. Fluazifop-butyl residues in soybean crop and soil. *Pesticide Research Journal* 19: 248–250.

Sondhia S. 2007b. Evaluation of leaching potential of pendimethalin in clay loam soil pesticide. *Research Journal* 19(1): 119-121.

Sondhia S. 2007. Determination of imazosulfuron persistence in rice crop and soil. *Environmental Monitoring and Assessment* 137(1-3): 205-211.

Sondhia S. and Dixit A. 2007. Determination of terminal residues of oxyfluorfen in onion. *Annals of Plant Protection Sciences* 15(1): 232-234.

Sondhia S. 2008. Evaluation of leaching potential of butachlor in clay soil. *Geobios* 36(4):249.

Sondhia S. 2008. Terminal residues of imazethapyr in soybean grains, straw and soil. *Pesticide Research Journal* 20(1): 128-129.

Sondhia S. and Singhai B. 2008. Persistence of sulfosulfuron under wheat cropping system. *Bulletin of Environmental Contamination and Toxicology* 80 (5): 423-427.

Sondhia S. 2008. Persistence of metsulfuron-methyl in wheat crop and soil. *Environmental Monitoring and Assessment* 147(1-3): 463-469.

Sondhia S. and Singhai B. 2008. Persistence of sulfosulfuron under wheat cropping system. *Bulletin of Environ. Contamination and toxicology* 80(5): 423-427.

Sondhia S. 2009. Persistence of metsulfuron-methyl in paddy field and detection of its residues in crop produce. *Bulletin of Environment Contamination and Toxicology* 83: 799–802.

Sondhia S. and Singhai B. 2009. Persistence and leaching of sulfosulfuron under wheat cropping system. *Indian Journal of Agricultural Sciences* 79 (6): 484-487.

Sondhia S. 2009. Persistence of oxyfluorfen in soil and detection of its residues in rice crop. *Toxicological and Environmental Chemistry* 91(3): 425-433.

Sondhia S. and Varshney JG. 2010. Herbicides. *Satish Serial Publication House, New Delhi*.

Sondhia S. 2010. Persistence and bioaccumulation of oxyfluorfen residues in onion. *Environmental Monitoring and Assessment* 162(1&4): 163-168.

Sondhia S and Dixit A. 2012. Bioefficacy and persistence of ethoxysulfuron in rice. *ORYZA-An International Journal on Rice* 49(3): 178-182.

Sondhia S 2013. Evaluation of imazethapyr leaching in soil under natural rainfall conditions. *Indian Journal of Weed Science* 45(1): 58–61.

Sondhia S, Waseem U and Varma RK. 2013. Fungal degradation of an acetolactate synthase (ALS) inhibitor pyrazosulfuron-ethyl in soil. *Chemosphere* 93(9): 2140–2147.

Sondhia S 2013. Harvest time residues of pendimethalin in tomato, cauliflower and radish under field conditions. *Toxicological and Environmental Chemistry* 95(2): 254-259.

Sondhia S and Mishra JS. 2006. Determination of terminal residue of clodinafop propargyl in soil, wheat grains and straw. *Indian Journal of Weed Science* 37(3&4): 296-297.

Sondhia S and Dixit A. 2005 Persistence of oxyfluorfen residues in the soil of paddy field and detection of its residues in crop produce *Indian Journal of Agricultural Science* 80(10): 926-929.

Sondhia S and Singh VP. 2006. Persistence of isoproturon in soil and detection of its residues in wheat grains and straw. *Geobios-Jodhpur* 33(2/3): 209.

Sondhia S. 2014. Herbicides residues in soil, water, plants and non-targeted organisms and human health implications: an Indian perspective. *Indian Journal of Weed Science* 46(1): 66–85.

Sondhia S. 2012a. Dissipation of pendimethalin in soil and its residues in chickpea (*Cicer arietinum* L.) under field conditions. *Bulletin of Environmental Contamination and Toxicology* 89(5): 1032–1036.

Sondhia S, Singh S and Varma RK. 2016. Biodegradation of the herbicide penoxsulam (triazolopyrimidine sulphonamide) by fungal strains of Aspergillus in soil. *Applied Soil Ecology* 105: 196-205.

Sondhia S. 2018-19. Environmental risk assessment of herbicides under wheat based cropping system and their mitigation measures**.** In Annual report ICAR-Directorate of Weed Research, Jabalpur 2018-19, p 56-59.

Sopeña F, Semple K, Sohi S and Bending GD. 2010. Isoproturon bioavailability in soil amended with biocharcoal. In Setac Europe 20th Annual Meeting, Seville, May 2010.

Srivastava A, Pandey S and Tandon S. 2006. Fate of pendimethalin herbicide in soil and pea plant (*Pisum sativum* L.). *Environmental Science: An Indian Journal* 1: 29–33.

Srivastava AK, Trivedi P, Srivastava MK, Lohani M, Srivastava LP . 2011. Monitoring of pesticide residues in market basket samples of vegetable from Lucknow City India: QuEChERS method. *Environmental Monitoring and Assessment* 176(1-4): 465–72.

Spokas KA and Reicosky DC. 2009. Impacts of sixteen different biochars on soil greenhouse gas production. *Annals of Environmental Science* 3: 179-193.

Spokas K, Koskinen WC, Baker JM and Reicosky DC. 2009b. Impacts of woodchip biochar additions on greenhouse gas production and sorption/degradation of two herbicides in a Minnesota soil. *Chemosphere* 277(4): 574-81.

Suntres ZE. 2002. Role of antioxidants in paraquat toxicity. *Toxicology* 180(1): 65–77.

Sushilkumar, Sondhia S and Vishwakarma K. 2003. Final report ICAR, ADHOC Project on role of insects in suppression of problematic alligator weed (*Alternanthera philoxeroides*) and testing of herbicides for its integrated management. pp 48.

Szmigielski AM Schoenau JJ, Johnson EN, Holm FA, Sapsford KL and Liu J. 2009. Development of a laboratory bioassay and effect of soil properties on sulfentrazone phytotoxicity in soil. *Weed Technol*ogy 23: 486-491.

Szmigielski AM, Schoenau JJ, Johnson EN, Holm FA and Sapsford KL. 2011. Determination of thiencarbazone in soil by the mustard root length bioassay. (Unpublished data).

Szmigielski AM, Schoenau JJ, Johnson EN and Fedrick AH. 2012. Determination of thiencarbazone in soil by oriental mustard root length bioassay. *Weed Science* 60(3): 468-473.

Tilak KS, Veeraiah P, Thathaji and Butchiram MS. 2007. Toxicity studies of butachlor to the freshwater fish *Channa punctata* (Bloch). *Journal of Environmental Biology* 28(2): 485-487.

Yadav A, Bhatnagar A and Kaur M. 2013. Aberrations in the chromosomes of *Cirrhinus mrigala* (Hamilton) upon exposure to butachlor. *Iranian Journal of Toxicology* **7** (21): 858-865.

Ying GG and Williams B. 2000. Dissipation of herbicides in soil and grapes in a south Australian vineyard. *Agriculture Ecosystem and Environment* 78: 283–289.

Wilkinson A, Collier FF Mercurio P, Brien JO, Ralph P and Negri AP. 2015. A miniature bioassay for testing the acute phytotoxicity of photosystem II Herbicides on Seagrass 2015. PLoS ONE 10(2). DOI: 10.1371/journal.pone.0117541.

Annexure I

Herbicide registered in India under section 9(3) of the Insecticides Act, 1968 for use in the Country: (As on 31/1/2020)

Name of the Pesticide	
1.	2,4-D Amine salt
2.	2,4-Dichlorophenoxy Acetic Acid
3.	Alachlor
4.	Ametryn
5.	Anilophos
6.	Atrazine
7.	Azimsulfuron
8.	Bensulfuron-methyl
9.	Bentazone
10.	Bispyribac Sodium
11.	Butachlor
12.	Carfentrazone- ethyl
13.	Chlorimuron-ethyl
14.	Chlorpropham
15.	Cinmethylene
16.	Clodinafop-propargyl
17.	Clodinafop-propargyl + Sodiumacifluorfen
18.	Clomazone
19.	Copper Sulphate
20.	Cyhalofop-butyl
21.	Diclofop-methyl
22.	Diclosulam
23.	Diuron
24.	Ethoxysulfuron
25.	Fenoxaprop-p-ethyl
26.	Fluazifop-p-butyl
27.	Flucetosulfuron
28.	Fluchloralin
29.	Flufenacet
30.	Flumioxazin
31.	Glufosinate Ammonium
32.	Glyphosate
33.	Haloxyfop-R-methyl
34.	Halosulfuron methyl
35.	Hexazinone
36.	Imazamox
37.	Imazethapyr
38.	Imidacloprid
39.	Indaziflam+ glyphosate ammonium (FI)
40.	Isoproturon
41.	Mepiquate Chloride
42.	Mesosulfuron-methyl + iodosulfuron-methyl Sodium
43.	Methabenzthiazuron
44.	Methyl Chlorophenoxy Acetic Acid (MCPA)
45.	Metolachlor
46.	Metribuzin
47.	Metsulfuron-methyl
48.	Orthosulfamuron
49.	Oxadiargyl
50.	Oxadiazon
51.	Oxyfluorfen
52.	Paraquat dichloride
53.	Penoxasulam
54.	Pendimethalin
55.	Penoxsulam
56.	Pinoxaden
57.	Pretilachlor
58.	Propanil
59.	Propaquizafop
60.	Pyrazosulfuron-ethyl
61.	Pyrithiobac sodium
62.	Quizalofop ethyl
63.	Quizalofop-P-tefuryl
64.	Sulfentrazone
65.	Sulfosulfuron
66.	Tembotrione
67.	Topramezone
68.	Triafamone (Triafamone 20% w/w + ethoxysulfuron 10% WG % w/w SC FI)
69.	Triallate
70.	Triasulfuron
71.	Trifluralin

Annexure II

Toxicological data of important herbicides (acceptable daily intakes (ADI) are extracted from agricultural and Veterinary Chemicals, Australian government, Department of health, office of chemical safety current as of 30 June 2014 and Acute reference dose (Rfd)** doses extracted from www.epa.gov, Instead of ARfd (Acute reference dose), AOEL*** (Acceptable Operator Exposure Level)

Herbicide	Rat Oral LD50 (mg/kg)	Toxicity Rating	ADI* mg/kg bw/day
Alachlor	930	III	0.0025
Acifluorfen	4790	III	0.0125
Ametryn	1950	III	0.02
Anilofos	472	II	0.001
Atrazine	1886	III	0.005
Butachlor	3300	III	0.005
Bensulfuron-methyl	> 5000	IV	0.20
Carfentrazone	5143	IV	0.03
Chlorimuron-methyl	>5000	IV	0.02
Clodinafop-propargyl	>2276	III	0.004
Clomazone	2343	III	0.1
Clopyralid	4300	III	0.5
Cyhalofop-butyl	>5000	IV	0.003
Dalapon	9330	IV	0.03
Dicamba	2629	III	0.03
Dithiopyr	>5000	IV	0.005
2, -4-D	>1000	III	0.01
2,4 -DB	877	III	0.02
Diclofop-methyl	428 -636	II-III	0.002
Diquat	230	II	0.002
Diuron	3400	III	0.007
Ethoxysulfuron	3270	III	0.06
Fenoxaprop	3310	III	0.004
Fluazifop-p-butyl	>5000	IV	0.003
Fluchloralin	1550	III	0.003
Flumetsulam	371 -1365	III	1
Flumioxazin	>5000	IV	0.003
Fluroxypyr	>2000	III	0.2
Flufenacet	371 -1365	II< III	-
Glufosinate ammonium	2170	III	0.02
Glyphosate	>5000	IV	0.3
Haloxyfop-methyl	2870	III	0.0007

Haloxyfop	337	II	0.0003
Imazethapyr	>5000	IV	2.8
Imazamox	5000	IV	2.8
Imazapyr	>5000	IV	2.5
Iodosulfuron -methyl sodium	>5000	IV	0.03
Isoproturon	1826	III	0.0062
Imazosulfuron	>5000	IV	0.75
Linuron	1200 -1500	III	0.01
Mefenacet	>5000	IV	0.0036
Methabenzthiazuron	>5000	IV	0.004
Metamifop	>2000	III	0.017
Metolachlor	2877	III	0.08
Metoxuron	>3200	III	0.02
Metribuzin	1090	III	0.02
Metsulfuron - methyl	>5000	IV	0.01
Mesosulfuron - methyl	> 5000	IV	1.0
Oxadiazon	>5000	IV	0.05
Oryzalin	>500	III	0.1
Oxadiargyl	>802	III	0.008
Oxyfluorfen	>2000	IV	0.025
Paraquat dichloride	40 -150	I-II	0.004
Pendimethalin	4075	III	0.1
Pinoxaden	5000	IV	0.1
Penoxsulam	>5000	IV	0.05
Pretilachlor	6099	IV	0.018
Propanil	3269	III	0.2
Pyrazosulfuron -ethyl	>5000	IV	0.043
Prometryn	4550	III	0.03
Propaquizafop	5000	IV	0.015
Quizalofop -p-butyl	6600	IV	0.01
Quizalofop -p-tefuryl	1012	III	0.013
Simazine	>5000	IV	0.005
Sulfentrazone	2855	III	0.05
Sulfosulfuron	> 5000	IV	0.2
Tribenuron -methyl	>5000	IV	0.01
Thiobencarb	1033	III	0.007
Triasulfuron	>5000	IV	0.005
Tri -allate	1100	III	0.025
Triclopyr	1581	III	0.005
Trifluralin	>5000	IV	0.02

भा.कृ.अनु.प. – खरपतवार अनुसंधान निदेशालय
ICAR - Directorate of Weed Research
जबलपुर, मध्य प्रदेश
आई.एस.ओ. 9001 : 2015 प्रमाणित
ISO 9001 : 2015 Certified

Amrit # 8349634350