Herbicides residues in soil, water, plants and non-targeted organisms and human health implications: an Indian perspective

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ABSTRACT

Herbicides use is increasing throughout the globe due to increasing labour cost, choice of application of herbicides, quick weed control in crop and non-crop areas. In India, herbicide use has increased up to 30% during the last 10 years in the country. Herbicides are chemical in nature, therefore, excessive and repeated use may pose residue problems, phytotoxicity to crop plants, residual effects on susceptible intercrops or succeeding crops, adverse effects on non-target organisms and ultimately health hazards to human and animals. Many herbicides are found as bound residues which make them not only unavailable to the targets but also polluting the soil ecosystem in a number of ways. Thus monitoring of these residues in soil, water, plants, fishes and other matrices is very much important. The fate of herbicide in soil depends on adsorption, absorption, volatilization, leaching, runoff, photodecomposition, degradation by microbial and chemical processes etc. In Indian tropical conditions, the half-life of imidazoline, phynylureas, sulfonylureas, triazines, chloroacetanilides, dinitroanilines, diethyl ethers, thiocarbamates, and fop group of herbicides in soil are found to varied 57-71, 13-60, 13-147, 12-58, 12-77, 19-29, 19-24, and 8-24 days. At harvest, herbicides in various commodities were found either below the maximum residue limit or below detectable limits. Indirect effects of herbicides are not common in India. However increasing incidences of intentionally acute poisoning by some of the herbicide such as butachlor, fluchloralin, paraquat, 2,4-D, pendimethalin, glyphosate etc. are emerging problem in India. Paraquat poisoning is an uncommon entity in India, and is associated with a high mortality rate. It can be concluded that in India herbicide contamination of soil, plants and natural waters occurs infrequently and at low levels.

Key words: Health hazard, Herbicides residues, Implication, Monitoring of residue, Non-targeted organisms

Over the years herbicides have emerged as an important tool in management of weeds. Herbicides use is increasing throughout the globe due to increasing labour cost, choice of application of herbicides, quick weed control in crop and non-crop areas etc. After the discovery and use of 2,4-D as a herbicide following 2nd World War, there has been a phenomenal growth in development of new molecules as herbicides. Due to intensive research in herbicide discovery and mode of action of herbicides, many new molecules are available to cater the farmers need. Globally consumption of herbicides is 44% followed by the insecticides (22%), fungicides (27%) and others (7%). In India, herbicide use has increased to 30% during the last 10 years in managing weeds in the country. As herbicides are chemical in nature and thus excessive and repeated use may pose residue problems, phytotoxicity to crop plants, residual effect on susceptible intercrops or succeeding crops or non-targets organisms and ultimately health hazards due to accumulation of herbicide residues in the soil, crop produce and ground water. Many herbicides are found as bound residues which make them not only unavailable to the targets but also polluting the soil ecosystem in a number of ways. There is a need to monitor herbicide residues in various commodities to assess buildup, bioma gnifications and bioaccumulation of residues and adverse effects if any. Thus an exhaustive study on fate, degradation and monitoring of herbicide residues in soil, water, crop plants, fishes etc. have been conducted by Sondhia between 1999-2014 at Directorate of Weed Science Research, Jabalpur. Residue data was further strengthen by incorporating data from other studies conducted across the country.

Herbicide use pattern

In India, currently 51 herbicides are registered for use in various crops. Out of these, one belongs to category I of pesticide class (extremely hazardous), four belongs to highly hazardous, 26 belongs to moderately hazardous and 24 belongs to fourth category that is unlikely to cause any harmful effects with LD50 value > 5000 mg/kg (Table 1)
Out of the total consumption of pesticides, 80% are in the form of insecticides, 15% are herbicides, 1.46% is fungicide and less than 3% are others. In comparison, the worldwide consumption of herbicides is 47.5%, insecticides are 29.5%, and fungicides 17.5% and others account for 5.5% only. Herbicide application is more common in wheat crop (44%), followed by rice (31%), plantation crop (10%), soybean (4%), and other crops (11%) (Fig. 1).

Herbicide residues

According to World healthorganization (WHO) “any substance or mixture of substances in food for man or animals resulting from the use of a pesticide and includes any specified derivatives, such as degradation and conversionproducts, metabolites, reaction products, and impurities that are considered to be of toxicological significance” are defined as herbicide/pesticide residues.

Table 1. Herbicides registered in India under/section 9 (3) of the insecticide Act 1968 as on January 2014

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Oral LD₅₀ (mg/kg)</th>
<th>Toxicity rating</th>
<th>Herbicide</th>
<th>Oral LD₅₀ (mg/kg)</th>
<th>Toxicity rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,4-Dichlorophenoxy acetic acid</td>
<td>375-1200</td>
<td>II-III</td>
<td>Linuron</td>
<td>1254</td>
<td>III</td>
</tr>
<tr>
<td>Alachlor</td>
<td>930-1350</td>
<td>III</td>
<td>Mepiquate chloride</td>
<td>500-2000</td>
<td>II-III</td>
</tr>
<tr>
<td>Anilophos</td>
<td>&gt;2000</td>
<td>III</td>
<td>Mesosulfuron-methyl</td>
<td>5000</td>
<td>IV</td>
</tr>
<tr>
<td>Atrazine</td>
<td>3090</td>
<td>III</td>
<td>Iodosulfuron-methyl sodium</td>
<td>5000</td>
<td>IV</td>
</tr>
<tr>
<td>Azimsulfuron</td>
<td>5000</td>
<td>IV</td>
<td>Methabenzthiazuron</td>
<td>1000</td>
<td>III</td>
</tr>
<tr>
<td>Bensulfuron -methyl</td>
<td>&gt;5000</td>
<td>IV</td>
<td>Metolachlor</td>
<td>2877</td>
<td>III</td>
</tr>
<tr>
<td>Bispyribac Sodium</td>
<td>4111</td>
<td>III</td>
<td>Metribuzin</td>
<td>1090</td>
<td>III</td>
</tr>
<tr>
<td>Butachlor</td>
<td>3300</td>
<td>III</td>
<td>Metsulfuron- methyl</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Carfentazone ethyl</td>
<td>5143</td>
<td>IV</td>
<td>MCPA</td>
<td>700</td>
<td>III</td>
</tr>
<tr>
<td>Chlorimuron- ethyl</td>
<td>&gt;5000</td>
<td>IV</td>
<td>Orthosulfuron</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Clodinafop-propargyl</td>
<td>2276</td>
<td>III</td>
<td>Oxadiargyl</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Croma zone</td>
<td>1326</td>
<td>III</td>
<td>Oxadiazon</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Copper sulphate</td>
<td>30</td>
<td>I</td>
<td>Oxyfluorfen</td>
<td>&gt;2000</td>
<td>III</td>
</tr>
<tr>
<td>Cyhalofop-butyl</td>
<td>&gt;5000</td>
<td>IV</td>
<td>Paraquat dichloride</td>
<td>40-150</td>
<td>I-II</td>
</tr>
<tr>
<td>Dazomet</td>
<td>&gt;2000</td>
<td>III</td>
<td>Pendimethalin</td>
<td>4050</td>
<td>IV</td>
</tr>
<tr>
<td>Diuron</td>
<td>3400</td>
<td>III</td>
<td>Penoxsulam</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Diclofop-methyl</td>
<td>563-693</td>
<td>III</td>
<td>Pinoxaden</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Ethoxy sulfuron</td>
<td>3270</td>
<td>IV</td>
<td>Pretilachlor</td>
<td>6099</td>
<td>III</td>
</tr>
<tr>
<td>Fenoxaprop-p-ethyl</td>
<td>3110</td>
<td>III</td>
<td>Propanil</td>
<td>3269</td>
<td>III</td>
</tr>
<tr>
<td>Fluazifop-p-butyl</td>
<td>&gt;5000</td>
<td>IV</td>
<td>Propaquizafop</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Fluchloralin</td>
<td>5580</td>
<td>IV</td>
<td>Pyrazosulfuron-ethyl</td>
<td>5000</td>
<td>III</td>
</tr>
<tr>
<td>Flufenacet</td>
<td>371-1365</td>
<td>II-III</td>
<td>Quizalofop ethyl</td>
<td>1210-1670</td>
<td>III</td>
</tr>
<tr>
<td>Glufosinate ammonium</td>
<td>2170</td>
<td>III</td>
<td>Quizalofop-p-tefuryl</td>
<td>1012</td>
<td>III</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>&gt;2000</td>
<td>III</td>
<td>sulfosulfuron</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Hexazinone</td>
<td>1690</td>
<td>III</td>
<td>Thiobencar (bentiocarb)</td>
<td>1033</td>
<td>III</td>
</tr>
<tr>
<td>Imazamox</td>
<td>&gt;5000</td>
<td>IV</td>
<td>Triallate</td>
<td>1200</td>
<td>III</td>
</tr>
<tr>
<td>Imazethapyr</td>
<td>&gt;5000</td>
<td>IV</td>
<td>Triasulfuron</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>&gt;2000</td>
<td>III</td>
<td>Trifluralin</td>
<td>&gt;5000</td>
<td>IV</td>
</tr>
</tbody>
</table>

Source: Central Insecticidal Board and Registration Committee

*I= Extremely hazardous, II= Highly hazardous, III= Moderately hazardous, IV= Unlikely to pose any hazards

Fig. 1. Herbicide consumption in different crops

Source: Shobha Sondhia

Fate and persistence of herbicide

As soon as a herbicide is applied, a number of processes immediately begin to remove the compound from the original site of application. For the herbicide which is intercepted by plants, the chemicals may
be taken up by the plant itself, may be washed off by precipitation onto the soil, may undergo chemical/microbial and/or photodegradation on plant surface or may volatile back into the air. Herbicides persistence in the soil is expressed as half-life or time required to degrade fifty percent of the original molecule (Table 2). However the half-life is not absolute because it depends on the soil type, temperature, and concentration of the herbicide applied. The persistence varies with the nature of a chemical, soil properties and climatic conditions. The herbicide should persist long enough to check weeds until the end of critical period of weed competition but not persist beyond the crop harvest, as it would be injurious to the sensitive crops grown in rotation (Buchholtz 1965, Cornish 1992, Brandenboger 2007, Sondhia 2009, 2013). Beside herbicides structure, soil conditions prevailing during and after the application of a herbicide as well as herbicide application methods influence the fate of the herbicides in the soil (Eleftherohorinies 1987, Webster and Show 1996, Latchana 1987, Sondhia 2005, Sondhia and Singh 2009). Heavy rainfall will cause greater leaching and runoff. Sandy soil would have a higher leaching potential than a clay soil due to larger pore spaces and lower CEC (Sondhia and Yaduraju 2005, Sondhia 2007, Sondhia 2008, 2009).

Higher humidity enhances the soil microflora proliferation. Similarly the persistence of herbicides in dry soil is greater as compared in wet soil. There are many chemical reactions which govern chemical degradation of herbicide in soil. Chemical degradation by redox reactions is common with anilines, phenols and dinitroanilines. Hydrolysis, ester formation, oligomerization/polymerization reactions catalyzed by clay surfaces and photolysis are common with fluchloralin, bentazon, and olefins. Some common pathways of biotic transformations such as oxidative process is common with phenoxy alkanoic acids, aromatic compounds, anilines phenylurea etc. However alkenes, alkines and nitro compounds undergo reductive transformation. Carboxylic esters, sulfates, 2, 6-dchloroben-zonitriles etc undergo hydrolytic process of transformation are common by biotic reactions (Table 2).

Degradation of herbicides by biotic reactions is generally followed by oxidative processes such as beta-oxidation, C-cleavage, C-hydroxylation, N-oxidation, N-demethylation, either cleavage, C-reduction, N-reduction, hydrolysis and mineralization. Whereas oxidation, reduction, mineralization, hydrolysis, ester formation, photolysis, polymerization etc. reactions are common by abiotic degradation.

### Table 2. Half-lives of some herbicides in soil

<table>
<thead>
<tr>
<th>Herbicide</th>
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<td>13-58</td>
<td>Metribuzin</td>
<td>23-49</td>
</tr>
<tr>
<td>Butachlor</td>
<td>5-24</td>
<td>Metolachlor</td>
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<tr>
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<td>12-29</td>
</tr>
<tr>
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<td>12-46</td>
<td>Pendimethalin</td>
<td>15-77</td>
</tr>
<tr>
<td>Dithiopyr</td>
<td>11-25</td>
<td>Pretiachlor</td>
<td>10-11</td>
</tr>
<tr>
<td>Imazethapyr</td>
<td>57-71</td>
<td>Sulfosulfuron</td>
<td>3-27</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>13-21</td>
<td>2,4-D</td>
<td>7-22</td>
</tr>
<tr>
<td>Chlorsulfuron</td>
<td>31-93</td>
<td>Methylsulfuron-methyl</td>
<td>70-147</td>
</tr>
<tr>
<td>Chlorimuron</td>
<td>60</td>
<td>Thiobencarb</td>
<td>19-24</td>
</tr>
<tr>
<td>Flufenacet</td>
<td>9-22</td>
<td>pyrazosulfuron</td>
<td>16-21</td>
</tr>
</tbody>
</table>

Source: Sondhia and Varsheny (2010)

### Herbicide degradation and residues in the soil

A herbicide is said to be persistent when it may be found to exist in soil in its original or a closely related but phytotoxic form longer than one crop season after its original application (Sondhia 2005, 2011). Herbicide residues in crop produce above the safe level can cause health hazards to men and animals. Ultimate fate of herbicide in soil depends on number of processes such as volatilization, leaching, runoff and degradation by microbes, chemical processes and photodecomposition. Persistence of pyrazosulfuron-ethyl was studied in three different soils (Shimoga, Mandya and Chamrajnanagar) of Karnataka under three moisture regimes (maximum water holding capacity, half maximum water holding capacity and submergence). The persistence of pyrazosulfuron-ethyl indicated a close correspondence to first order exponential degradation kinetics in soils and mainly influenced by soil organic matter and moisture. Faster disappearance was noticed under submergence followed by maximum water holding capacity and half maximum water holding capacity and submergence. The addition of organic manure affects the bio-

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Source: Sondhia and Varsheny (2010)
under Middle Western Indian agro-climatic conditions in Indian mustard (*Brassica juncea* L.). FYM incorporation at a rate of 10 t/ha decreased herbicide persistence and relatively lower half-lives of 44.93 to 39.09 days were recorded with FYM incorporation, each at the rate of 0.5 and 1.0 kg/ha for pendimethalin, trifluralin and fluchloralin. On the other hand, the half-life in absence of FYM was higher for all three dinitroaniline herbicides. Triasulfuron residues dissipated from field soil with half-life of 5.8-6 days at two rates of application following a first-order-rate kinetics through biphasic degradation with faster rate initially ($t_{1/2} = 3.7$ days), followed by a slower dissipation rate at the end ($t_{1/2} = 9.4$ days). Similar trend was observed with non-sterile soil in laboratory with a longer half-life. Acidic pH and microbial activity contributed toward the degradation of triasulfuron in soil (Singh and Kulsherestha 2006).

Metsulfuron-methyl dissipated more rapidly in acidic silty loam soil as compared to high pH soil and light did not play any role in altering the persistence (Yadav et al. 1997). A bioassay technique could detect the residue of metsulfuron-methyl up to 30 days in surface soil, while, with HPLC, residues detectable upto 15 day only. The half-lives of metsulfuron-methyl was found 6.3-17.5 days (Paul et al. 2009). However residues of metsulfuron-methyl rice soil at 30 days was found 0.008-0.016 µg/g at 2-8 g/ha application rates. Whereas residue in soil, rice grains and straw at harvest was found below 0.001 µg/g (Sondhia 2009b). Sushilkumar et al. (2008) reported that metsulfuron-methyl residues were not detected after 60 days at 16 g/ha application rate, but at higher application rates 20-24 g/ha, 0.002 and 0.011 mg/kg residues were found in back soils of Jabalpur. However Sondhia and Singhai (2006) and Sondhia (2008b, 2009b) found residues below the detection limit in 3-5 g/ha application rates and 0.002 µg/g residues were detected at 8 g/ha, in wheat plants at harvest. The oxyfluorfen residue dissipated faster in wheat plants than in soil respectively, with a mean half-life of 6.1 and 11.2 days. Dissipation followed first-order kinetics. A sorption study revealed that the adsorption of oxyfluorfen to the soil was highly influenced by the soil organic carbon with the $K_{oc}$ value of 5450 and dissipation of oxyfluorfen in soil and onion was dependent on the physico-chemical properties of the soil and environmental conditions (Janaki et al. 2013). Ethoxyxsulfuron residues were found below <0.001 µg/g in rice soil at harvest at 15 to 20 g/ha doses, respectively (Sondhia and Dixit 2012).

Atrazine in soil showed a gradual degradation with advancement in maize plants growth and residue were not found at harvest whereas 0.056 mg/kg of residue in the post-harvest soil were found at double the recommended dose (Janaki et al. 2012). Bromacil and diuron residues at 3 kg/ha persisted on top 2.5 cm of the soil profile even after eight months (Leela 1984). Kulsherestha et al. (1977), Sandhu et al. (1994), Sondhia (2001, 2002), and Nag and Das (2009) and Janaki et al. (2012) reported that more than 95 percent of atrazine dissipated from the field at the time of crop harvest. The half-life values were found to be 9.38-21.54 days in soil. Pre-emergence applications of atrazine and simazine at 1.5 kg/ha persisted up to 47 and 83 days, respectively (Sharma and Angiras 1997). Kausik and Moolani (1974) reported 97% atrazine dissipation from the soil within 4 months in which maize plants were growing whereas about 83% atrazine dissipated from un-cropped soil. The persistence of fluazifop-p-butyl at two rates of application and at three temperature level revealed fast degradation in soil to corresponding acid, fluazifop-p-butyl as only 2% fluazifop-p-butyl was recovered after 24 h. The acid form of the herbicide had a half life of 19.8-23.9 days. Persistence was inversely related to the soil temperature (Raut and Kulshrestha 1991). The residue level of fluazifop-p in soil was found 0.051 to 0.079 µg/g at 125-500 g/ha application rates in soybean field (Sondhia 2007).

Sondhia et al. (2006) reported rapid dissipation of butachlor in rice field as compared to laboratory conditions with half-life of 18.1-23.0 days at 1.0-2.0 kg/ha. The butachlor degradation in soils were mainly influenced by soil organic matter and moisture and rapid disappearance was noticed at field capacity followed by submergence and air dry conditions in all soils. 2, 4-D at 0.4 kg/ha alone and in combination with anilofos persisted up to harvest with half-life of 18-22 days (Jayakumar and Ramulu 1993). Clodinafop-propargyl ester generally convert to acid (a major metabolites) and which is also responsible for herbicidal action. It was found that dissipation of clodinafop was not affected by specific soil pH and soil type. Residues of clodinafop in soil was found 0.093 to 0.081 µg/g in alluvial, red and black soil (Roy and Singh 2006, Sondhia and Mishra 2005). Fentazonam residues at 240 g/ha application rate were found 0.03 to 0.04 mg/kg in soil of rice field in a three year study with a half life of 20 days, however residues were below the detection limit in rice husk and straw (Tandon et al. 2012). Chlorophenyltetrazoline and cyclohexyl ethylamine have been iden-
tified as major and minor metabolites of flentazamide in soil (Mukherjee and Gopal 2005). In a monitoring study of four herbicides, butachlor residues alone contributed 61% followed by pendimethalin (36%), and fluchloralin (3%). Alachlor was not detected in all the locations. The total range of herbicides was <0.01 to 1.46 ng/g with a mean of 0.21 ng/g. The individual concentration of herbicides ranged 0.03-1.28 ng/g (pendimethalin), 0.02-1.22 ng/g (butachlor), 0.01-0.25 ng/g (Kumar 2011). The residues of pretillachlor dissipated to below detection limit within 30 days after application when applied with green manure, while at 0.75 to 1.5 kg/ha rates, it persisted up to 45 days with a half-life of 3.9 to 10.0 days (Dharumarajan et al. 2008).

Sorghum and cucumber plants were found very sensitive bioassay plants for metribuzin and could detect residues even at 0.010 and 0.046 mg/kg in the post harvest soil of potato crop (Sondhia 2005). At harvest no detectable residues of fenoxaprop-ethyl or acid were detected in soil, wheat grain and straw samples at recommended doses (Sondhia 2007, Singh et al. 2013). In paddy field benthicarb residue dissipated to 90% within 30 days in soil and no residues were detected in soil as well as in straw, grain and husk samples at harvest when applied at 1500 to 3000 g/ha in transplanted paddy field (Aktar et al. 2007). However, Kumar (1993) reported lower temperature and higher concentration resulted in greater persistence (Jayakumar and Ramulu 1993). 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 (Sethi and Chopra 1975). Sondhia (2002) reported that alachlor and fluchloralin residues were not detected in the soil at harvest at 1.0 kg/ha rate in the soybean field but at 1.2 and 1.5 kg/ha rates, 0.01 and 0.02 µg/g residues were detected at harvest. Whereas in sandy loam soil of Karnataka, alachlor persisted up to 60 days at 1.5 kg/ha application rate applied as pre-emergence in vegetable crops (Leela 1993).

Fluchloralin degraded at faster rate in flooded anaerobic soil than in aerobic soil and amendment of fluchloralin with organic matter enhanced degradation of flooded anaerobic soil and dealkylated fluchloralin, partially reduced fluchloralin and its cyclic product were detected as major degradation products (Singh and Kulshrestha 1995). Patel et al. (1996) found that persistence of the pre-plant incorporated fluchloralin at 0.67–1.35 kg/ha application rates was longer in the loamy soil as compared to sandy loam soil with the half-life values in both the soils ranged between 42.4 to 45.6 days. Fluchloralin translocated to leaves and roots of chicory crop and was detected on the 60th day of application and did not found at harvest. Kalpana et al. (1999) found that fluchloralin applied at 1.00 kg/ha in a sandy loam soil in onion crop showed first-order rate kinetics in a biphasic mode and residues were not found at harvest.

Dissipation of pendimethalin in the field peas (Pisum sativum L.) and chickpea soil followed first-order kinetics showing a half-life of 11.23-19.83 days averaged over all doses (Sondhia 2012, 2013). Kulshrestha et al. (2000) reported that repeated application of pendimethalin on the same soil led to rapid degradation of pendimethalin in each successive year with each successive crop. Pahwa and Bajaj (1997) found that persistence of pendimethalin and trifluralin was directly correlated with temperature and application rate. Pendimethalin in a sandy loam soil applied at 1 to 4 kg/ha rates in wheat crop showed persistence up to 200 days and caused phytotoxicity to the succeeding sensitive sorghum crop at higher dose (Yadav et al. 1995). Pendimethalin was found to be persistent in the soil of cabbage field however residues did not translocated to plant parts (Arora and Gopal 2004). Persistence of some herbicides under Indian tropical conditions in soil is given in Table 3.

Goyal et al. (2003) reported that intermittent wetting and drying resulted in a very high persistence (90-99%) of trifluralin whereas with continuous ponding, the persistence of trifluralin decreased to 22-40% in alluvial soil. Sondhia (2006) reported 0.008 µg/g imazethapyr residues at harvest in the soil of soybean crop at 100 g/ha application rate. Sondhia (2006, 2008) reported 0.002, 0.006, 0.0075 and 0.010 µg/g residue of imazosulfuron in the soil of transplanted rice field after 60 days at 30-60 g/ha application rates, however no residues were found after 90 and 120 days. Sulfosulfuron followed first order dissipation kinetics in soil at 25-50 g/ha application rates and residues were not detected in the soil at harvest under wheat cropping system (Ramesh and Maheshwari 2003, Sondhia and Singh 2008). However after 150 days residues were found below 0.001 µg/g in soil samples collected from 25 to 50 g/ha treated plots (Sondhia and Singhai 2008).

The adsorption–desorption revealed strong adsorption of dithiopyr in alluvial soil with Kd values ranging from 3.97–5.78 and Freundlich capacity factor (Kd) of 2.41. The leaching studies carried out under saturated flow conditions revealed that dithiopyr was highly immobile in alluvial soil. Strong adsorption of dithiopyr may cause a greater persistence in the soil (Gupta and Gajbhiye 2002). Singh and Kulshrestha (2006) reported dissipation of triasulfuron at 15 and 20 g/ha in soil under wheat crop with half-
Table 3. Persistence of some herbicides under tropical conditions in soil

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Persistence in soil (days)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>45-90</td>
<td>Kulshreshtha et al. (1977), Sandhu et al. (1994), Sharma and Angiras (1997), Nag and Das (2009)</td>
</tr>
<tr>
<td>2,4-D</td>
<td>45-90</td>
<td>Kumari et al. (2004), Sushilkumar et al. (2008)</td>
</tr>
<tr>
<td>Butachlor</td>
<td>100</td>
<td>Sondhia et al. (2006)</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>90-120</td>
<td>Yaduraju et al. (1993), Sondhia and Singh (2006)</td>
</tr>
<tr>
<td>Imazosulfuron</td>
<td>60</td>
<td>Sondhia (2006, 2008)</td>
</tr>
<tr>
<td>Metoxuron</td>
<td>80</td>
<td>Randhawa and Sandhu (1997)</td>
</tr>
<tr>
<td>Metribuzin</td>
<td>20-100</td>
<td>Sondhia (2002)</td>
</tr>
<tr>
<td>Oxadiazon</td>
<td>56-125</td>
<td>Leela (1993), Raj et al. (1999)</td>
</tr>
<tr>
<td>Pyrazosulfuron-ethyl</td>
<td>35-60</td>
<td>Mukherjee et al. (2010), Naveen et al. (2012), Sondhia et al. (2013)</td>
</tr>
<tr>
<td>Pyretilachlor</td>
<td>30-60</td>
<td>Dharumarajan et al. (2008), Kumar (2011), Sondhia (2012)</td>
</tr>
<tr>
<td>Tralkoxydim</td>
<td>28-45</td>
<td>Srivastava et al. (1995)</td>
</tr>
<tr>
<td>Thiobencarb (bentiocarb)</td>
<td>28-60</td>
<td>Jayakumar and Ramulu (1993), Akter et al. (2007)</td>
</tr>
<tr>
<td>Oxyflourfen</td>
<td>60-80</td>
<td>Devi et al. (1998)</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>40-190</td>
<td>Devi et al. (2000), Sanyal and Yaduraju (2008)</td>
</tr>
</tbody>
</table>

Life of 5.8 and 5.9 days. Isoproturon degraded to non-detectable level within 60 days at 0.94 kg/ha rate in Ludhiana, it took 75 days in Badruka, Kum Kalan and Chakkar district for its complete degradation (Walia et al. 2000). Isoproturon applied at 1.0 kg/ha rate in wheat crop degraded completely at harvest in black soil of Jabalpur (Randhawa and Sandhu 1997, Sondhia 2002, Sondhia and Singh 2006). Isoproturon residues at 0.5 and 1.0 kg/ha application rates were found 0.0213 mg/kg after 70 days and 0.0201 mg/kg after 120 days in soil of potato crop (Yaduraju et al. 1993). Gupta et al. (2001) found that flufenacet dissipated to about 98% in soil after 60 days and no residues were detected after 90 days under submerged conditions than field capacity. Sondhia (2002) reported that metribuzin applied at 0.85 and 1.20 kg/ha persisted up to harvest in black soil in potato crop in Jabalpur. Rai et al. (1997) found rapid degradation (40-61%) of anilofos after 30 days of incubation under flooded than non-flooded conditions. Anilofos at 0.4 kg/ha application rate persisted up to 56 days in direct seeded rice field (Radhamani et al. 1997).

Sondhia and Khare (2014) demonstrated sorption of cyhalofop-butyl in sandy clay loam and clayey soils using a batch equilibrium method. Adsorption of cyhalofop-butyl was found positively related with clay and organic carbon content and cyhalofop-butyl was highly adsorbed in clayey than sandy clay loam. Adsorption isotherm suggested a relatively higher affinity of the cyhalofop-butyl for the adsorption sites at low equilibrium concentrations. Metolachlor applied as pre-emergence at 1-2 kg/ha application rates was dissipated almost 100% in the soil at harvest under field condition (Singh et al. 1997). Dissipation of metolachlor occurred in two distinct phases. The initial slow rate could be due to degradation and adsorption on soil. After one month herbicide dissipated rather rapidly (Singh et al. 1997). Sanyal et al. (2000) demonstrated moderate persistence of metolachlor with a half-life of 27 days in the field conditions and leached to a depth of 15-30 cm in soil. It was found that fungi 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 (Sanyal and Kulshreshtha 2003). Following the first order kinetics, the diclosulam dissipates in soybean crop soil with half-life values ranging between 5.28-8.36 days in three consecutive seasons, irrespective of the doses (Bhattacharyya et al. 2012).
Herbicide residues in cereals

The analytical results of herbicide residues in various crops indicated global presence of residues but below the alarming level. Using the latest hi-tech analytical devices, the presence of herbicide residues can be easily detected at ppb level. Based on extensive herbicide residue work conducted at Directorate of Weed Science Research, Jabalpur, All India Coordinated project on Weed Control (AICRP-WC) and various sources in India, in about 80 percent samples, residues were found below detection limit (BDL), 13.4 percent below maximum residue limit (MRL) and 6.6 percent residues were found above MRL values.

Rice: Sondhia and Dixit (2012) demonstrated that ethoxysulfuron dissipated at faster rate in soil and plants and residues were found below 0.001 µg/g in grains and straw at harvest at 15-20 g/ha application rates. Imazosulfuron residues were found to be 0.009 and 0.039 µg/g at 50 and 60 g/ha rates, respectively, in rice and residues were not detected at 30-40 g/ha in rice grains and straw (Sondhia 2007, 2008). The residue level of butachlor in rice grain and straw samples were found 0.029 and 0.042 µg/g, respectively (Sondhia et al. 2006). Harvest time samples of paddy grains, rice bran and straw, treated with butachlor showed residues below the detectable levels in rice, 0.002 mg/kg in bran, 0.009 mg/kg in straw and 0.006 mg/kg in rice grains at 1.0 kg/ha and at 2 kg/ha, the residues were 0.001, 0.005, 0.010 and 0.025 mg/kg in rice, bran, straw and paddy grains, respectively (Reddy et al. 1998). Deka and Gogoi (1993) found 0.012 and 0.007 mg/kg residues in rice grains and straw after treatment with butachlor at 2.0 kg/ha rate.

In paddy straw 0.01-0.03 µg/g oxyfluorfen residues were detected at 240-500 g/ha rates. Residues were 0.028-0.03 µg/g in soil when oxyfluoruron was applied at 240-500 g/ha rates. However, in rice grains, 0.018-0.106 µg/g of oxyfluoruron residues were detected in 240-500 g/ha treated plots (Sondhia 2009). Residues of metsulfuron-methyl and pretilachlor in rice grains and straw at harvest were found below 0.001 µg/g (Dharumarajan et al. 2008, Sondhia 2009). In plant foliage collected at harvest traces of atrazine residues were detected in few samples in first year but in the second year’s residues were not detected (Nag and Das 2009). Fentazamide residues were below the detection limit in rice husk and straw at 240-420 application rates. Chlorophenyltetrazoline and cyclohexyl ethylamine have been identified as major and minor metabolites of fentazamide in soil (Mukherjee and Gopal 2005). Butachlor dissipated with half life varied from 12.5 to 21.5 days at 1.0 and 2.0 kg/ha application rates under with and without organic manures conditions. Low levels of residues were detected in rice grain (Rao et al. 2012). Devi et al. (1997) and Jayakumar and Sankaran (1995) reported that butachlor and anilofos residues in rice crop were found below the maximum permissible residue limit (0.25 mg/kg) in soil. Sondhia et al. (2004) reported that butachlor residues were not detected after 120 days in clay loam soil applied at 1.0 kg/ha in transplanted rice crop. The pre-emergence application of anilofos and thiobencarb applied at recommended doses continuously for four seasons in rice crop showed residues in soil, rice grains and plant parts below the maximum allowable level (Balasubramanian et al. 1999).

Wheat: In a field experiment, residues of isoproturon were found to be 0.006, 0.041 and 0.022 µg/g in post-harvest soil, wheat grain and straw, respectively, while 0.021 and 0.096 µg/g residues of clodinafop was present in soil and grain at higher level of application (Arora et al. 2013). At harvest, no residues of metsulfuron-methyl were detected in wheat grains at 3-4 g/ha rates. However 0.002 µg/g residues were detected in wheat straw at 5-8 g/ha application rates (Sondhia 2008). In wheat field soil, residues persisted beyond 30 days with a first order rate kinetics biphasic dissipation with initial faster dissipation followed by a slower dissipation during later period. Wheat grains, straw and soil collected at harvest (112 days) contained residues below detectable limits (Singh and Kulshrestha 2006). In a three year field trials revealed no detectable amount of tralkoxydim in treated samples of soil, wheat grain and straw at harvest of wheat (Srivastava et al. 1994, Srivastava et al. 1995).

Clodinafop residues were not detected in the wheat grain and straw at doses 60-120 g/ha however 0.0089 mg/kg residues were detected in wheat grains at 240 g/ha treatment (Sondhia and Mishra 2005). Sulfosulfuron residues were not found in wheat grains, straw and subsequent vegetables in natural ecosystem as well as in model ecosystem at recommended rates in wheat crop (Ramesh and Maheshwari 2003, Sondhia et al. 2007, Sondhia and Singh 2009). Isoproturon dissipated by 120 days in the soil of wheat crop applied at 1.0 kg/ha and residues were not detected in wheat grains and straw at harvest (Sondhia and Singh 2006). Persistence of clodinafop-propargyl evaluated at Ludhiana showed that it degraded to safe level by 60 days at 0.03 to 0.04 g/ha application rates and at higher doses, viz. 11 and 22 g/ha, residues persisted for more than 80 days. Whereas Singh et al. (2004) reported that clodinafop at 60 and 120 g/ha rates in wheat crop degraded completely by harvest and hence residues of clodinafop were not detected in wheat grains and soil at harvest. Metribuzin residues were
not found in the soil, grains and straw following an application at 210–420 g/ha in wheat crop at Pantnagar (Dubey et al. 1998). Fenoxaprop-p-ethyl residue in the soil of wheat field was found 0.0004–0.0011 µg/g at 70–400 g/ha application rates (Sondhia 2006). In an experiment initially 0.0434, 0.0888 and 0.1661 µg/g residues of fenoxaprop-p-ethyl, carfentrazone and pinoxaden were detected in the wheat soil which dissipated to 0.0026 µg/g at 30 days. At 90 days fenoxaprop-p-ethyl, carfentrazone and pinoxaden residue were in wheat soil were found to be <0.001 µg/g. Half life of fenoxaprop-p-ethyl, carfentrazone, and pinoxaden in the soil of wheat field was found 16.61, 9.15 and 8.62 days (Sondhia 2014). Herbicide residues in crop plants at harvest are given in Table 4.

Herbicide residues in pulses: Terminal residues of pendimethalin were monitored in the green field peas (Pisum sativum L.) and chickpea (Cicer arietinum L.) applied as pre-emergence herbicide at 750-185 g/ha rates. Low pendimethalin residues were found in nature pea grains (0.004-BDL µg/g), and straw (0.007-0.001 µg/g) at 750-185 g/ha treatments, respectively (Sondhia 2013). Pendimethalin residues were 0.025, 0.015, <0.001 µg/g in chickpea grains at 750 to 185 g/ha treatments. Much lower pendimethalin residues, viz. 0.015 to <0.001 µg/g were found in straw at 750, 350 and 185 g/ha treatments, respectively (Sondhia 2012). Mandal et al. (2014) and Mukhopadhyay et al. (2012) demonstrated that at harvest, the residues of quizalofop-ethyl on black gram seed, foliage and soil were found to be below the detection limit of 0.01 mg/kg following a single application of the herbicide at 50-100 g/ha for both the periods. In another study persistence and degradation kinetics of trifluralin applied as pre-emergence in black gram at 1.0 to 2.0 kg/ha for the control of broad leaf weeds was conducted. The dissipation at 90 days was found approximately 97% and followed first order kinetics with the half life 23.3 to 26.2 days. Irrespective of any dose, no residues of trifluralin were detected in black gram crop soil and plant samples at harvest (Aktar et al. 2009).

Herbicide residues in oilseed crops: In a three seasons field trial conducted under West Bengal conditions, diclosulam residues were found to be below detectable level (BDL) in soybean plant samples irrespective of the treatment doses and the days in all seasons (Bhattacharya et al. 2012). The residues of imazethapyr 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, applied to soybeans, at 0.25 and 0.50 kg/ha at New Delhi, dissipated to 0.1 mg/kg in 30 days from both the dosages and was below detectable limits (0.08 mg/kg) in 60 days (Singh et al. 1999). 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 application rates. Residues of fluazifop-p-butyl at 0.5 kg/ha rates, application and fluazifop-p-butyl at 0.5 kg/ha rate resulted in the translocation of 0.005 and 0.001 mg/kg residues to soybean grains and cake, respectively (Kulshrestha et al. 1995). The residue level of fluazifop-p in soil was found to be 0.051 to 0.079 µg/g at 125 to 500 g/ha applied rates. Residues of fluazifop-p-butyl were 0.472, 0.554 and 0.702 µg/g in soybean straw and 0.297, 0.300 and 0.312 µg/g in soybean grains at 125,

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Crop</th>
<th>Dose (g/ha)</th>
<th>Residues (µg/g)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethoxy sulfuron</td>
<td>Rice</td>
<td>15-18.7</td>
<td>&lt;0.001</td>
<td>Sondhia and Dixit (2012)</td>
</tr>
<tr>
<td>Butachlor</td>
<td>Rice</td>
<td>1000</td>
<td>0.005</td>
<td>Deka and Gogoi (1993), Reddy et al. (1998), Sondhia et al. (2006)</td>
</tr>
<tr>
<td>Sulfoxuron</td>
<td>Wheat</td>
<td>25</td>
<td>0.010-BDL</td>
<td>Ramesh and Maheshwari (2003), Sondhia et al. (2007)</td>
</tr>
<tr>
<td>Methylsulfuron-methyl</td>
<td>Rice</td>
<td>4-4</td>
<td>BDL</td>
<td>Sondhia (2008)</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>Wheat</td>
<td>1000</td>
<td>0.006-0.332</td>
<td>Sondhia and Singh (2006), Arora et al. (2013)</td>
</tr>
<tr>
<td>Oxyfluorfen</td>
<td>Rice</td>
<td>150-250</td>
<td>BDL</td>
<td>Sondhia (2009)</td>
</tr>
<tr>
<td>Imazethapyr</td>
<td>Soybean</td>
<td>100</td>
<td>0.016</td>
<td>Sondhia (2007, 2008), Patel et al. (2009)</td>
</tr>
<tr>
<td>Imazosulphon</td>
<td>Rice</td>
<td>30-40</td>
<td>BDL</td>
<td>Sondhia (2008)</td>
</tr>
<tr>
<td>Fentiazamide</td>
<td>Rice</td>
<td>240-420</td>
<td>BDL</td>
<td>Mulkerjee and Gopal (2005)</td>
</tr>
<tr>
<td>Fluazifop-p-butyl</td>
<td>Soybean</td>
<td>500</td>
<td>0.012-0.036</td>
<td>Kulshrestha et al. (1995)</td>
</tr>
<tr>
<td>Clodinafop</td>
<td>Wheat</td>
<td>240</td>
<td>0.021-BDL</td>
<td>Singh et al. (2004), Sondhia and Mishra (2005), Arora et al. (2013)</td>
</tr>
<tr>
<td>Tralkoxydim</td>
<td>Wheat</td>
<td>250-800</td>
<td>BDL</td>
<td>Srivastava et al. (1994)</td>
</tr>
</tbody>
</table>

Table 4. Residues of some of the herbicides in the soil, food grain and straw
250 and 500 g/ha, respectively (Sondhia 2007). Patel et al. (2014) evaluated effect of imazethapyr and varying level of fertilizers on soybean grain quality with respect to oil and protein percentage applied in soybean crop under long-term fertilizer experiment. The maximum protein content (39.54 %) and oil content of 19.47 percent was observed in 100% NPK+ FYM+ imazethapyr treatment. While, the lowest value of protein and oil contents we recorded in treatment with no fertilizer + imazethapyr application at recommended dose. The result of the study imply that the use of balance rate of minerals fertilizer in combination with organic manures along with herbicide must form part of soil management practices for the intensively cultivated soil to sustain soil health, productivity and crop quality.

**Herbicide residues in vegetables:** Terminal residues of pendimethalin applied as pre-emergence at 1 kg/ha in tomato, cauliflower, and radishes were studies 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). Terminal residues of oxyfluorfen applied at 150 to 300 g/ha in direct seeded onion crop at 90 days (green onion) and at 130 days (mature onion bulbs) were monitored in green onion, dry onion bulbs and soil samples under field condition at Jabalpur. The residues of oxyfluorfen in the green onion and mature onion bulbs were 0.041- 0.063 and 0.0034-0.0460 µg/g at 150–300/ha rates. Residues of oxyfluorfen applied in mature onion were below the maximum residue limit (0.05 µg/g) (Sondhia and Dixit 2007, Sondhia 2009). A pre-harvest interval of 118 days for onion crop after the herbicide application was suggested (Sondhia 2010). Residues of pendimethalin, fluchloralin, and oxadiazon were found below the maximum residue limit in onion bulbs at harvest (125 days after spraying) at Anand. At harvest, 0.009 and 0.006 mg/kg terminal residues of fluchloralin applied at 0.75 and 1.50 kg/ha, respectively were found in stover and grains (Saikia and Pandey 1999). Sondhia and Dubey (2006) did not find pendimethalin residues 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 (129 days), respectively (Sondhia 2006). Oxyfluorfen residues applied to cabbages at 0.1 to 0.4 kg/ha application rates were not found in soil at harvest (Sundararajan et al. 1993). The half-life of pendimethalin in onion plants and soil varied from 11.8- 15.5 days and 14.9-15.1 days, respectively (Sinha et al. 1996).

Field experiment was conducted to study the persistence of pendimethalin and oxyfluorfen in soil and its residues in edible parts of radish. At harvest in both the seasons more than 98% of initial deposit of pendimethalin was dissipated with half-lives in radish field were 6.45 days and 10.03 days at 0.5 and 0.75 kg/ha applied rates, respectively. More than 60 per cent of the initial deposit of oxyfluorfen was dissipated at the time of harvest of crop and 6.96 days and 12.26 days of half-life was observed at 0.1 and 0.15 kg/ha of oxyfluorfen application, respectively. In radish tubers the residues of pendimethalin and oxyfluorfen were below maximum residue limit (Sirestha et al. 2011). Samples of onion bulbs collected at 30, 60 and 90 days after spray and at up-rooting stage showed no residues of oxyfluorfen and pendimethalin in onion bulbs (Kaur et al. 2010). Dissipation of haloxyfop in onion leaf and soil followed first order kinetics with the DT₅₀ values in onion leaf ranged from 3.24-6.71 days whereas 3.78-6.96 days for soil following application 100-400 g/ha. No residue could be detected in bulb at harvest irrespective of doses (Chakraborty et al. 2005). At harvest the level of pendimethalin, fluchloralin and oxadiazon residue applied pre-emergence at 1.0-0.5 kg/ha in onion bulbs ranged from 0.003 to 0.021, 0.004 to 0.036 and 0.080 to 0.104 µg/g, respectively. Marginal increase in the residue was observed with increased FYM application (Raj et al. 1999).

**Herbicide residues in maize:** 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 2000). The residual effect of atrazine (1.0-2.0 kg/ha) was studied on the succeeding crops of chickpea and Indian mustard, where fluchloralin was applied at 0.75 kg/ha. Atrazine was degraded to undetectable levels at all doses by the time the maize crop was harvested (90 days). The average half-life of atrazine varied from 23 to 25 days in the first year and 26 to 31 days in the second year. In chickpea and Indian mustard, low levels of fluchloralin residues were detected in soil at 150 days (64-85% and 69-82% losses, respectively). However, the magnitude of fluchloralin 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 (2.48 and 1.63 t/ha in 1994 and 1995, respectively, compared to 3.20 and 2.52 t/ha in the hand-weeded treatment). However, atrazine had no significant residual effect on chickpea or Indian mustard yields (Saikia et al. 2000).
Herbicide residues in tea/plantation crops: India is the highest producer of tea in the world. In India tea is being cultivated mainly in north-east. Tea (Camellia sinensis) is a perennial crop grown on wide variety of soil types and climatic conditions. It is the healthiest drinks and second most consumed beverage after water. Napropamide was rapidly dissipated in soil following the first-order kinetics 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 irrespective of any season and doses. At 30 days after application of the herbicide, more than 50% of the residue was dissipated. The residue declined below detectable limit in the tea soil on day 60–90 day in X and 2X doses irrespective of season. The dissipation of napropamide in tea cropped soil followed the first-order kinetics with the half-life values varied from 12.54 to 27.87 days irrespective of doses and seasons in south India. In made tea the initial concentration of napropamide was found in the range of 0.14–0.20 µg/g in recommended dose and 0.35–0.44 µg in double the recommended dose in three seasons (Biswa et al. 2013).

Herbicide residues in non-cropped areas: Glufosinate ammonium at 0.45- 0.90 kg/ha application rates applied as post-emergence to cotton degraded to safe level by 20 day at Ludhiana. At Anand, pendimethalin applied at 0.6-0.9 % to tobacco recorded 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 treated with 0.25% pendimethalin (Parmar et al. 1998). Sushilkumar et al. (2008) 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 soils of Jabalpur.

Herbicide residues in other crops: Pendimethalin residues at 0.5 kg/ha application rate were not detected in the soil of lucerne crop at Anand. 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 conditions at Chennai (Ramesh and Maheshwari 2004). 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, trifluralin and resulted in below detectable limit residues (0.02 mg/kg) in celery seeds (Kaur and Gill 2012). In cucumber, anilophos (ND–0.042 mg/kg) in onion, fluchloralin (0.012–0.065 mg/kg), and anilophos (ND–0.033 mg/kg) were detected (Srivastava et al. 2011). At Anand, pendimethalin applied at 0.6-0.9% to tobacco recorded 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 treated with 0.25% pendimethalin (Parmar et al. 1998).

Herbicide residues in water system: With the increasing use of herbicides for weed control, the applied herbicide may find it way into streams and underground water sources by runoff, drift and leaching mechanism (Sondhi 2008, 2009, 2013). 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 above the prescribed maximum residues limits are 2,4-D, atrazine, cyazine, carbaryl, simazine, bromacil, diuron, diazinon, prometon, metolachlor, dinoseb, pictoram, metribuzin, metsulfuron, glyphosate, metolachlor, propanil, butachlor, pendimethalin, oxyfluorfen etc. Many herbicides are strictly banned or restricted such as butachlor, atrazine, pendimethalin, and paraquat 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. Pyrazosulfuron-ethyl residue level of 0.0154 mg/kg on 21st day and of 0.0023 mg/kg on 35th day were detected in the underground water (Naveen et al. 2012). Persistence and mobility of 2,4-D were found to be dependent on soil water content (Gupta et al. 2012). The water samples collected from Singoora reservoir, Hyderabad were found contaminated with residues of atrazine (BDL-1.056 µg/L). The concentration of atrazine residues in Osmanasagar water was 0.056 µg/L during post-monsoon November 2005 and total pesticide residues together 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 different soils and no residues were detected after 80 days.

The studies conducted at AICRP weed control in water system revealed that butachlor residues were ranged between 0.001 to 0.093 mg/L in the water of rice field (AICRP 2009). Residues of paraquat were not detected after 20 days at 0.80 kg/ha application rates to control Eichhornia but application of 1.8 kg/ha showed 0.069 and 0.028 mg/L residues in pond.
and canal water, respectively. 2,4-D increased pH, EC, carbonates and free CO₂ increased after treatment at 1.0-2.0 mg/kg dose but the dissolved oxygen decreased and the 2,4-D residues become non-detectable after 42 days. 2,4-D residues at lower level than the acceptable daily intake (0.01 mg per kg body weight) were detected in fish samples at Thrissur at recommended rate of application at all the sampling interval and at higher dose, viz. 2.0 or 4.0 kg/ha waiting period of more than 4 months was suggested. Paraquat residues in the fish samples were 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. It is reported that isoproturon residues were not present in the ground water in all the water samples collected from different districts of Hisar.

Leaching results indicated that imazethapyr could leach in clay loam soil up to the depth of 70 cm applied at 100 and 200 g/ha (Sondhia 2013). Sondhia (2009) demonstrated that residues of sulfosulfuron were significantly higher in surface soil at higher dose compared to sub-surface soil at lower dose up to 150 day at 25-100 g/ha in wheat under field conditions. Initial concentration of sulfosulfuron residues in the surface soil (0-15 cm) were 0.229, 0.967 and 1.038 µg/g, which dissipated to 0.003-0.005 µg/g at 25-100 g/ha doses by 100 days. However, at 0 days sulfosulfuron residues in sub-surface soil were 0.136-0.065 µg/g in 25-100 g/ha doses. Sulfosulfuron residues were not detected after 200 days in surface and sub-surface soils in all the doses. Pendimethalin could leach in clay loam soil up to the depth of 55 cm in 200 mm rainfall (Sondhia 2007). High mobility of metsulfuron-methyl was found under continuous saturated moisture conditions (Sondhia 2009).

Khare and Sondhia (2014) demonstrated cyhalofop-p-butyl mobility in a sandy loam soil and subsequent distribution of residues at 0-150 cm depths under field conditions. Cyhalofop-p-butyl application at two rates and subsequent precipitation had a significant impact on soil physico-chemical properties and herbicide mobility. Precipitation caused substantial mobility of cyhalofop-p-butyl in the soil and 1.1 to 7.6 µg/L of cyhalofop-p-butyl was found in leachates. Cyhalofop-p-butyl three transformation products, viz. cyhalofop acid, dicacid, and phenol were also detected.

A laboratory experiment was conducted to study the persistence of pretilachlor in water at acidic, neutral and alkaline pH by incubating for 60 days. Irrespective of pH, pretilachlor residues were detected up to 15 days after application and were below the detectable limit on 30th day. The half-life of pretilachlor 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 40.97 µg/L were recorded as the mean concentration of simazine in groundwater samples collected from Delhi (Aslam et al. 2013).

In fishes: In a study, Yadav et al. (2013) revealed the genotoxic potential of butachlor even at low dose level (1.0 mg/kg) 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. On comparing the effect of different herbicides, it was observed that the fish mortality was more with 2,4-DEE and paraquat than with glyphosate (Muniappa et al. 1995). To evaluate the possible bio-accumulation of sulfosulfuron in the fishes, an experiment was conducted in glass aquarium for 90 days. Sulfosulfuron was applied to the aquaria at 25-100 g/ha. Residues of sulfosulfuron in the fishes were found 1.09-3.52 µg/g after 10 days and by 90 days residues in the fishes were below the MRL (Sondhia 2008, Sondhia 2008). In another indirect effect of herbicides on fishes, mortality was more with butachlor, followed by anilofos and oxyfluorfen (Sondhia 2012). Pretilachlor, penoxsulam and pyrazosulfuron-ethyl residues ranged between 0.0133, 0.0189 and 0.063 µg/g at 30 days and dissipated to <0.001, 0.017 and 0.010, respectively at 60 days respectively in fishes (Sondhia 2012, 2013, 2014). In another study, fishes (Channa punctata) were exposed for 10 days to sub lethal concentration (1/5th of static LC₅₀) of butachlor. Residue of butachlor after 10 days were 0.1255 mg/kg in gills, 0.3515 (bloch) liver and 0.3145 mg/kg in kidney and 0.2350 mg/kg in brain traces muscle of Channa punctata. The results revealed that prolonged exposure to sub lethal concentrations led to increase in the accumulation of residues. The residues are accumulated in different tissue, causing toxicity to the fishes which ultimately resulted in biomagnifications through the food chain (Tilak 2007). The Tilapia mossambica were exposed to sub lethal concentration (66 mg/L) for 24, 48, and 72 hrs respectively to assess toxic effect of the metribuzin on the biochemical aspects such as total protein, carbohydrate and cholesterol in liver, muscle, kidney and gills. All bio chemical parameters were found to be decreased in all tissues in comparison to control (Saradhamani and Selvarani 2009).
Similarly, dissipation of sulfosulfuron in natural water and its bioaccumulation in fish was conducted at two different concentration levels 1 and 2 mg/L. The dissipation data in water showed the DT90 and DT95 values 67-76 and 222-253 days and followed first order kinetics. Bioaccumulation of sulfosulfuron in fish was conducted under static conditions exposing the fish at one-tenth of sub-lethal concentration 9mg/L and at double the concentration 18ml/g, for a period of 56 days. Accumulation of sulfosulfuron in fish in the range 0.009-0.496 µg/g was found. Both in water and fish samples, metabolites of aminopyrimidine, desmethyl sulfosulfuron, guanidine, sulfonamide, ethyl sulfone and rearranged amine were found. One of the metabolite aminopyrimidine was identified at higher concentration levels (0.01-0.1 µg/mL) in comparison to other metabolites (Ramesh et al. 2007, Sondhia 2008). The calculated DT90 and DT95 values for aminopyrimidine dissipation in water were found to be 66-68 days and 218-226 days, respectively with a complete demineralization after three hundred days.

Recently, Sondhia et al. (2014) demonstrated a water quality index (WQI) to see the suitability of water in term of its quality for fishery after application of metsulfuron-methyl. The WQI proposed in the study was composed of eight measurable major environmental parameters, viz. herbicide residue, pH, total dissolve solids (TDS), dissolved oxygen (DO), biological oxygen demand (BOD), free ammonia, chloride and temperature. Concentrations of these eight variables were normalized on a scale from 0 (zero) to 100 and translated into statements of water quality (excel- lent, good, poor, very poor and unsuitable). Based on WQI, water quality of adjacent pond was derived as category I (excellent) to category II (good), and found suitable for fish farming.

**Metabolites / transformation products**

In an experiment, the photo stability of sulfosulfuron was studied after irradiation under sunlight. Under alkaline condition, sulfosulfuron yielded 1-(2-ethylsulfonylimidazo[1,2-a]pyridin-3-yl)-3-(4,6-dimethoxypyrimidin-2-yl) amine, and under acidic condition it degraded to 1-(2-ethylsulfonylimidazo[1,2-a] pyridine)-3-sulfonamide and 4,6-dimethoxy-2-aminopyrimidine. Photodegradation included breaking of a sulfonylurea bridge, as in the case of acidic hydrolysis and contraction of the sulfonylurea bridge was the major pathway of alkaline hydrolysis (Saha and Kulshrestha 2002). The sulifosulfuron degraded within 50 days on topsoil but the residual concentrations were localized at depth 30-45 cm depths this might be due to leaching property of the sulfosulfuron. The absence of sunlight, considerably lesser availability of microbial population and organic carbon content also participates in the stability in subsoil. Desmethyl sulfosulfuron, rearranged amine, sulfonamide and guanidine were identified as breakdown product of sulfosulfuron in the subsurface soil. From the results the calculated DT90 value for sulfisulfuron were around 105 to 147 days and the DT90 values around 349 to 488 days (Ramesh et al. 2007, Sondhia 2008).

Metabolites of pyrazosulfuron were detected from soil and pond water which were identified by LC/MS/MS. Three major transformation products of pyrazosulfuron-ethyl detected from rice field as ethyl5-[(4,6-dimethoxypyrimidin-2-ylcarbamoyl) sulfamoyl]-1-methylpyrazole-4-carboxylic acid; ethyl 1-methyl-5-sulfamyl-1H-pyazole-4-carboxylate and 4,6-dimethoxypyrimidin-2-amine, 1-methyl-5-sulfamyl-1H-pyazole-4-carboxylic acid (Sondhia et al. 2013, Wassem and Sondhia 2014). Penicillium chrysogenum and Aspergillus niger were found as potent pyrazosulfuron-ethyl degrading fungi (Sondhia et al. 2013). Major degradation products of penoxsulam in field soil were identified as 1,2,4 triazolo-[1,5-c] pyrimidine-2 amine, 5,8 dicarboxylic acid; 2-(2,2-difluoroethoxy)-6 (trifluoromethyl) benzencesulfonamide ; 3-[2-(2,2 difluoroethoxy)-N-[1,2,4] triazole [1.5c]-6 trifluromethyl) benzene sulfonamide carbonate (Rajput and Sondhia 2014). Major metabolites of cyhalofop-butyl in soil and leachates were detected by LC/MS/MS as (R)-2-(4-amino-2-fluoro phenoxy) phenoxypropanoic acid (cyhalofop acid) and (R)-2-(4-cabayoxy-2-flurophenoxy) phenoxypropanoic acid (cyhalofop-diacid), and cyhalofop-phenol (Sondhia and Khare 2014). The major photoproducts of metsulfuron methyl were identified as methyl-2-sulf- onyl-amino-benzoate, 2-amino-6-methoxy-4 methyltriazine and saccharin (O-sulfobenzoimide). These metabolites were also identified from metsulfuron methyl treated wheat field soil. Stability test for pinoxaden and its metabolite NOA 407854(8-(2,6-diethyl-4-methyl-phenyl)-tetrahydropryrazol[1,2-d][1,4,5]oxadiazepine-7,9-dione) in wheat for a period of 30 days showed that the compound remained stable and the degradation observed was only 6.5% at the end of storage period. This shows slow dissipation of pinoxaden metabolites at 20±1 °C. Residues of pinoxaden and its metabolites were found below the detectable limit (<0.01 mg/kg) (Dixit et al. 2011).

Seven major degradation products of pretilachlor in field soil were identified by LC/MS/MS as 2,6-diethyl-N-(propoxethyl)acetanilide; 2,6-diethyl-N-(propoxethyl)amline;2,6-diethyl-N-(2-hydrox-ethyl) anline; 2,6-diethyl-N-(ethyl)anline; acetanilide; 2-
Paraquat poisoning is an uncommon entity in India, and is associated with a high mortality rate (Agarwal et al. 2005, Kondele 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). 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 (Dwivedi et al. 2012).

In an experiment, cultured human lymphocytes were exposed to three different concentrations (2.5, 5.0 and 10.0 µg/ml) of fluchloralin for 24 and 48 h to assess chromosomal aberrations. A significant dose-dependent increase of chromatid type aberration was observed in these cells. Multiple aberrations (MA) were scored at all concentrations after 48 h treatment. Higher concentrations of fluchloralin (20, 40 and 50 µg/ml) resulted in a significant dependent increase in number of micronucleated cells and showed genotoxic effects of fluchloralin in human cells (Panneerselvam et al. 1995). Nair et al. (2005) 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). Common symptoms of acute poisoning by some of the herbicides and cases of poisoning are listed in Table 5 and 6.

### Table 5. Some herbicides which caused direct adverse effects on human beings

<table>
<thead>
<tr>
<th>Herbicide</th>
<th>Bioactivity</th>
<th>Adverse effects on human beings</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butachlor</td>
<td>It controls annual grasses and some broad-leaved weeds in transplanted and direct-seeded rice. It is applied as pre-emergence in EC formulations and as early post-emergence in the form of granules.</td>
<td>Weight loss, weight changes in internal organs, reduced brain size together with lesions.</td>
</tr>
<tr>
<td>Isoproturon</td>
<td>It is used to control annual grass weeds in wheat, rye and barley.</td>
<td>Isoproturon appears to be a tumour promoter rather than a complete carcinogen.</td>
</tr>
<tr>
<td>Paraquat</td>
<td>It is used as a plant desiccant effective against grasses.</td>
<td>Parkinson’s and Alzheimer’s diseases.</td>
</tr>
<tr>
<td>Simazine and atrazine</td>
<td>These are persistent soil acting herbicides which in high concentrations acts as total weed killer and in lower concentrations is used for selective control of germinating weeds in a variety of crops - maize, sugarcane, pineapple, sorghum. It is also used for long term control of annual grass and broad-leaved weeds in crops like citrus, coffee, tea and cocoa.</td>
<td>Cancer of testes</td>
</tr>
<tr>
<td>Trifluralin</td>
<td>It is used for the control of annual grasses and broad leaved weeds in a wide range of crops cotton, groundnuts, soybeans, brassica, beans and cereals.</td>
<td>Prolonged or repeated skin contact with trifluralin may cause allergic dermatitis. Other effects include decreased red blood cell counts and increases in methemoglobin, total serum lipids, triglycerides, and cholesterol. It has been shown to cause liver and kidney damage in other studies of chronic oral exposure in animals.</td>
</tr>
</tbody>
</table>
Herbicide residues in soil, water, plants and non-targeted organisms and human health implications: an Indian perspective

Table 6. Cases of intentionally herbicide poisoning in human beings in India

<table>
<thead>
<tr>
<th>Poisoning</th>
<th>Total patients</th>
<th>Death</th>
<th>Amount taken (mL)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Paraquat</td>
<td></td>
<td></td>
<td>Unknown</td>
<td>Attar <em>et al.</em> (2009), Khosya and Gothwal (2012), Kondle <em>et al.</em> (2013)</td>
</tr>
<tr>
<td>Rajasthan and Maharashtra</td>
<td>04</td>
<td>03</td>
<td>10-50</td>
<td></td>
</tr>
<tr>
<td>North India</td>
<td>05</td>
<td>03</td>
<td>Unknown</td>
<td>Agarwal <em>et al.</em> (2006)</td>
</tr>
<tr>
<td>Himachal Pradesh</td>
<td>02</td>
<td>02</td>
<td>Unknown</td>
<td>Raina <em>et al.</em> (2008)</td>
</tr>
<tr>
<td>Karnataka</td>
<td>06</td>
<td>04</td>
<td>Unknown</td>
<td>Saravu <em>et al.</em> (2013)</td>
</tr>
<tr>
<td>Haryana</td>
<td>01</td>
<td>-</td>
<td>Unknown</td>
<td>Ghosh <em>et al.</em> (2012)</td>
</tr>
<tr>
<td>Pendimethalin (Uttar Pradesh)</td>
<td>02</td>
<td>02</td>
<td>20-100</td>
<td>Kumar and Verma (2012)</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>02</td>
<td>-</td>
<td>100-150</td>
<td>Das <em>et al.</em> (2012)</td>
</tr>
<tr>
<td>2,4-D ethyl ester</td>
<td>03</td>
<td>02</td>
<td>100 g</td>
<td>Singh <em>et al.</em> (2008)</td>
</tr>
</tbody>
</table>

Herbicide poisoning: a diagnostic challenge

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. Immunosuppression 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).

**Conclusion**

Herbicide residues after recommended use for control of weeds are relatively high initially; however, the levels are reduced rapidly, and residues are often not detectable after a few days or weeks or at harvest. The soil acts as an important buffer governing the persistence and fate of most herbicides in the environment. As long as soil system remains healthy, possible adverse effect from herbicides in the environment probably can be minimized. Herbicides in most instances when applied at recommended doses have not been detected in food chain or in soil at level that should cause concern. Data on the occurrence of herbicide-related sickness among defined populations in developing countries are scanty. To conclude based on limited data of direct and/or inferential information, the domain of herbicide illustrates a certain ambiguity in situations in which people are undergoing life-long exposure. Further, the persistence and half-life period of many herbicides were found to be less in Indian tropical conditions. This could be one of the reasons for the presence of low level of residues. It can be concluded that in India herbicide contamination of soil, plants and natural waters occurs infrequently and at low levels. With few exceptions aquatic herbicides do not accumulate and persist in fishes. Though some reports of herbicide poisoning are reported though data on the occurrence of herbicide-related illnesses among defined populations in human, the domain of herbicide illustrates a certain ambiguity in situations in which people are undergoing life-long exposure.

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