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Shobha Sondhia · Partha P. Choudhury
A.R. Sharma *Editors*

Herbicide Residue Research in India

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Preface

Herbicides are chemicals used for killing plants which are known as weeds. These are basically organic compounds synthesized after intensive research to block a physiological process by deactivating the enzyme system, leading to complete death or considerable suppression of growth of the plants. A major discovery in the synthesis of such chemicals was achieved in the 1940s when 2,4-dichlorophenoxyacetic acid was found to control broadleaved weeds in certain cereal grain crops. This led to a sort of revolution in chemical weed management as several chemicals were invented during the 1950s and thereafter for killing weed flora in cropped as well as non-cropped situations. Presently, there are about 500 chemicals used as herbicides globally, which have become an important input in the modern agriculture systems.

Herbicides constitute about 60% of the total pesticides consumed globally. In India, the use of herbicides started initially in tea gardens and picked up in the 1970s when the dwarf high-yielding varieties of crops like rice and wheat were introduced. Presently, 60 herbicides are registered in the country for controlling a broad-spectrum of weeds in all the major crops including cereals, pulses, oilseeds, fibre and tuber crops, and also in the non-crop situations. These chemicals are becoming increasingly popular because of efficient weed killing effects and relatively lower cost compared with manual or mechanical weeding operations. Development of low-cost high-potency post-emergence herbicides during the past decade has provided several alternatives to the growers. The contribution of herbicide to total pesticide use, which was only 10–15% during the first decade of twenty-first century, has now increased to about 25%. In fact the annual growth rate of herbicides is 15–20%, which is much higher than insecticides and fungicides. The herbicide consumption is expected to increase further due to labour scarcity in most regions and higher cost of crop production.

Herbicides are chemically designed to kill a specific group of plants. But being biochemically active molecules, herbicides have the potential to also damage beneficial flora and fauna. Harmful effects of these chemicals on non-target organisms and in the foodchain are an issue of serious concern, particularly when these are used indiscriminately and without following required protocols. Toxic concentrations

of such chemicals and their metabolites have been recorded in the soil, water, crop produce, and also in the body parts of humans and animals. These issues are likely to become more important in future with the growing use of herbicides in modern agricultural production systems. This is despite the fact the herbicides are considered relatively safe and less hazardous compared with other pesticides due to high lethal dose (LD_{50}) values, application during the early stages of the crop growth and degradation due to various biotic and abiotic factors.

Research on pesticide residues in India was started during 1970s when such chemicals were introduced on a greater scale along with high-yielding variety seeds, irrigation and fertilizers for increasing crop production. However, the herbicide residue research was not given much emphasis until 1990s because their use was almost negligible (<10% of total pesticides) and sporadic. It was only during the late 1990s that systematic research work on herbicide residues was undertaken at the Indian Council of Agricultural Research (ICAR) – Directorate of Weed Research, some centers of All India Coordinated Research Project on Weed Management, and a few other ICAR Institutes and state agricultural universities. Long-term experiments were also initiated in different cropping systems to determine the cumulative effect of continuous herbicide applications and suggest mitigation measures. Over the last two decades, adequate information has been generated in different states of India on estimation, degradation and mitigation of herbicide residues, which has also been documented through annual reports, bulletins, monographs and published scientific articles. However, there was no consolidated compilation of all the available information providing a critical analysis. Accordingly, an effort has been made in the publication to compile the available information on herbicide residues in India. This is the first report of its kind which presents the findings of herbicide residues and their interactions in the biotic and abiotic environment. There are 16 chapters contributed by the leading herbicide residue scientists, each describing the present status of herbicide use, crops and cropping systems, monitoring, degradation and mitigation, followed by conclusions and future lines of work.

It is hoped that this book will be useful to the weed scientists in general and herbicide residue chemists in particular, besides the policy makers, students and those concerned with the agriculture production in the country.

Jabalpur, Madhya Pradesh, India

Shobha Sondhia
Partha P. Choudhury
A. R. Sharma

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About the Editors

Dr. Shobha Sondhia is a Senior Scientist at the ICAR-Directorate of Weed Research, Jabalpur. With a career spanning over two decades, she has vast research and teaching experience in the field of the environmental impact of herbicides. Dr. Sondhia has received numerous awards, fellowships, and recognition from national and international agencies. She has published over 75 research papers, given more than 100 presentations on national and international platforms and authored two reference books entitled *Herbicides* and *Herbicide Residue Analysis*. She has also organized five national training programs and received several awards and recognitions at national and international level.

Dr. Partha P. Choudhury started his professional career in the pesticide industry after completing doctoral studies at the ICAR-Indian Agricultural Research Institute, New Delhi. He served pesticide industries in various capacities, from research scientist to research manager. He also served as Associate Professor at Uttar Banga Krishi Viswavidyalaya, Coochbehar, West Bengal. Dr. Choudhury served ICAR-Directorate of Weed Research, Jabalpur, where his research work mainly focused on herbicide degradation in the environment and monitoring of their residues and mitigation. Dr. Choudhury is currently a Principal Scientist in the Food Safety Referral Laboratory at ICAR-Indian Institute of Horticultural Research, Bengaluru. His industrial and academic experience spans over 25 years. He has published several research articles, patent, book chapters, and a book.

Dr. A. R. Sharma served as Director, ICAR-Directorate of Weed Research, Jabalpur, Madhya Pradesh, India, from 2012–2017 and made monumental contributions in the field of weed science and conservation agriculture. He has an outstanding record of academic and scientific contributions, and received several awards and recognitions from the ICAR, NAAS, ISCA, IARI, FAI, ISA and others.

He has given new directions to agronomic research and education particularly in the field of weed science. He is currently Director Research, Rani Lakshmi Bai Central Agricultural University, Jhansi, Uttar Pradesh, India.

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Abbreviations

2,4-D	2, 4-Dichlorophenoxy acetic acid
2, 4-D EE	2, 4-Dichlorophenoxy acetic acid ethyl ester
4-CPA	4-Chlorophenoxyacetic acid
ACCase	Acetyl-CoA carboxylase
AHAS	Acetohydroxy acid synthase
AICRP-WC	All India Coordinated Research Project on Weed Control
AICRP-WM	All India Co-ordinated Research Project on Weed Management
AINP-PR	All India Network Project on Pesticide Residues
ALS	Acetolactate synthase
ALS	Amyotrophic lateral sclerosis
AOAC	Association of Official Analytical Chemists
APPMA	Andhra Pradesh Pesticide Manufacturers Association
ASE	Accelerated/Assisted solvent extraction
BDL	Below detection limit
CAC	Codex Alimentarius Commission
CAD	Corona aerosol discharge
CE	Capillary electrophoresis
CD	Critical difference
CDHB	6-Chloro-2,3- dihydrobenzoxazol-2-one
CEC	Cation exchange capacity
CIBRC	Central Insecticides Board and Registration Committee
CODEX	Codex Alimentarius Commission
CP	Clopyralid
DWR	Directorate of Weed Research
CT	Conventional tillage
DH	Dehydrogenase
DAA	Days after application
DAD	Diode array detector
DAHA	Days after herbicide application
DAP	Days after planting
DAS	Days after sowing

DAT	Days after transplanting
DLLME	Dispersive liquid liquid microextraction
DMDA	Dimethyl dodecyl amine
DPX	Disposable pipette extraction
d-SPE	Dispersive solid-phase extraction
DSR	Direct seeded rice
DT_{50}	Dissipation time (50%)
DWSR	Directorate of Weed Science Research
EC	Electrical conductivity
ECD	Electron capture detector
ELSD	Evaporative light scattering detector
EPA	Environmental Protection Agency
ESI	Electron ionization mode
EU	European Union
FYM	Farmyard manure
FICCI	Federation of Indian Chambers of Commerce and Industry
FID	Flame ionization detector
FMOC-Cl	9-Fluorenylmethyl choroformate
FSSAI	Food Safety and Standards Authority of India
GC	Gas chromatograph
GC–ECD	Gas chromatography - electron capture detector
GC-MS	Gas chromatography - tandem mass spectrometry
GPC	Gel permeation chromatography
GUS	Groundwater ubiquity score
H	Henry's law constant
HPLC	High performance liquid chromatography
HPTLC	High performance thin layer chromatography
HS-SPME	Head space - solid phase microextraction
ICAR	Indian Council of Agricultural Research
IGP	Indo-Gangetic plains
IR	Infra red
K_F	Freundlich's constant
kL	kilolitre
K_{OC}	Organic carbon-water partition co-efficient
LC/MS/MS	Liquid chromatography/mass spectroscopy/mass spectroscopy
LC	Liquid chromatography
LC_{50}	Median lethal concentration
LC–MS	Liquid chromatograph mass spectrometer
LD_{50}	Median lethal dose
LOD	Limit of detection
LOQ	Limit of quantification
LLE	Liquid liquid extraction
logP	Octanol-water partition co-efficient
MA	Multiple aberrations
MAE	Microwave-assisted extraction

MCPA	Methyl chlorophenoxy acetic acid
MCPP	Methyl chlorophenoxy propionic acid
MIPs	Molecularly imprinted polymers
MRL	Maximum residue limit
MRM	Multiple reaction monitoring
MS	Mass spectrometry
MSPD	Matrix solid phase dispersion
MWD	Mean weight diameter
MT	Minimum tillage
ND	Not detected
NMR	Nuclear magnetic resonance
NPD	Nitrogen phosphorous detector
NRCWS	National Research Centre for Weed Science
NS	Not significant
OC	Organic carbon
ODS	Octadecylsilane
OM	Organic matter
PCR–DGGE	Polymerase chain reaction-gradient gel electrophoresis
PDA	Photo diode array
PE	Pre-emergence
PFA	Prevention of Food Adulteration
PLE	Pressurized liquid extraction
POE	Post-emergence
ppb	Parts per billion
PSA	Primary secondary amine
PSB	Phosphate solubilizing bacteria
PVC	Polyvinyl chloride
QA	Quality assurance
QC	Quality control
QDa	Quadrupole Dalton
QuEChERS	Quick, Easy, Cheap, Effective, Rugged, and Safe
RF	Reversed phase
RT	Retention time
SALLE	Salting out assisted liquid liquid microextraction
SBSE	Stir bar sorbtive extraction
SFC	Supercritical fluid chromatography
SDME	Single-drop micro-extraction
SFE	Supercritical fluid extraction
SL	Soluble liquid
SOC	Soil organic carbon
SPE	Solid phase extraction
SPME	Solid phase microextraction
TCA	Trichloroacetic acid
TCD	Thermal conductivity detector
TTC	Triphenyl tetrazolium chloride

TPF	Triphenyl formazan
TFAA	Trifluoro aceticanhydride
TFE	Trifluoro ethanol
TLC	Thin layer chromatography
TSD	Thermal sensitive detector
UAE	Ultrasound-assisted extraction
UFLC	Ultra fast liquid chromatography
UPLC-MS/MS	Ultra performance liquid chromatography tandem mass spectrometry
USDA	United States Department of Agriculture
UV	Ultra violet
UV–VIS	Ultraviolet-visible
WHO	World Health Organization
WP	Wettable powder
WTO	World Trade Organization
ZT	Zero tillage

Fate and Persistence of Herbicide Residues in India

S. T. Maheswari and A. Ramesh

Abstract Herbicide usage is continuously increasing in India and is expected to increase at the rate of 15% per year over the next 5 years. This is due to today's labour shortage and rising labour costs. The current scenario of labour shortage has also accelerated the introduction of slow-release formulations in order to avoid multiple sprays. When herbicides are applied to control weeds there are many ways by which herbicides get transported. They may be through runoff, leaching, volatilization and directly/indirectly affect the environment. As a result there are all chances of residual problems, phytotoxicity, and residual effects to the succeeding crops. Leaching of herbicides may cause contamination of ground waters. While spraying the herbicides, there is exposure of the spray man to the toxic chemical. Further, there are all ways of herbicides coming into contact with the non-target organisms (honey bees, earthworms), and pose health hazards to humans. Research on herbicide residues has been done in India to determine the residue levels of various herbicides in crop, soil and water. Currently the research has been extended to find out the effect of herbicide residues in other areas also like the effect on non-target organisms, ground water ubiquity score, and on human and animals. Therefore, future residue research may be focused on these aspects to make a clear picture of safety levels of herbicides in soil, water, non-target organisms, animals and human beings.

1 Introduction

Weeds have been a problem ever since man took the domestication of plants. Therefore, weed management seems to be as old as agriculture itself. There is huge loss of agriculture produce, due to various pests and weeds. Timely control of weeds

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can substantially contribute to the increase in crop yields, which can be achieved effectively using herbicides. Weeding is often done late, causing drastic losses in yield (Rashid et al. 2012). Research has shown that, if enough hand weeding is done at the optimal times, crop yields are not reduced by weed competition (Prasad et al. 2008). Improved weed control with herbicides has the potential to improve crop yields significantly (Masthan et al. 1989). Herbicides are being rapidly adopted in developing countries like India that face shortages of labor and the need to raise crop yields (Zhang 2003).

Herbicides help the crops to grow by destroying the weeds that causes harmful effects which include competition for water, nutrients and light; interference of weeds with crop growth by the release of toxins; modification of soil and air temperatures and the harboring of pests. The herbicides can be safely used as the manual and mechanical removal of weeds can destroy the crop. These chemicals are relatively safe on lands which may erode.

The use of herbicides is increasing day by day. This is because the other alternative control measures do not provide an effective and economic substitute for herbicides in many situations. The efficacy and safety of herbicides are greatly influenced by soil and climate.

Adverse effects of the herbicides are that these chemicals may persist and account for residues in ground and surface water. Some herbicides are non-biodegradable and may prove harmful for a long period of time. Heavy dose of herbicides may affect the microbial population of the soil. The improper use of herbicides may also cause water infiltration into groundwater and then the surface waters, such as ponds, streams, rivers and lakes. Such chemicals may also move deep into the soil and deeper groundwater units polluting them. Most herbicides are specifically poisonous for plants, and are not very toxic to animals. However, by changing the vegetation of treated sites, herbicide use also changes the habitat of birds, mammals, insects, and other animals through changes in the nature of their habitat. Herbivores may eat the plants treated with herbicides and then carnivores eat the herbivores. The toxic herbicide would be passed up the food chain increasing in concentration each time resulting in cancers and even deaths. Anxiety about chemical residues in the environment has increased greatly in the last decade.

Herbicides are classified into two broad categories: (i) inorganic herbicides such as copper sulfate, sodium chlorate, and sodium arsenite; and (ii) organic herbicides such as chlorophenoxy compounds, dinitrophenols, bipyridylliums, carbamates, and amides. Inorganic herbicides were the first available and used before the discovery of organic compounds. There has been a continuous effort over the years to develop effective herbicides that are more selective, meaning that they affect only the weeds as opposed to desirable plants.

Early attempts to control weeds with herbicides were made in Punjab in the year 1937. Sodium arsenite was used for controlling *Carthamus oxycantha*. Herbicide 2, 4-dichlorophenoxy acetic acid (2,4-D) was first tested in India in 1946. From then onwards, a number of herbicides were imported and tested for its efficacy in controlling weeds. In 1952, Indian Council for Agricultural Research (ICAR) initiated schemes for testing the field performance of herbicides in rice, wheat and

sugarcane in different states of India. Recognizing the needs to strengthen the weed research in India, the ICAR set up All India Co-ordinated Research Project on Weed Management (AICRP-WM) in collaboration with United States Department of Agriculture (USDA) in the year 1978. In 1989, the National Research Centre for Weed Science (NRCWS) was established at Jabalpur, which in 2009 was upgraded as Directorate of Weed Science Research (DWSR). This is now being called as the Directorate of Weed Science (DWR) since 2014. Location-specific research is conducted at 23 coordinating units located in different parts of the country. This chapter briefs about the herbicide residue research conducted so far in India and future lines of work.

2 Herbicide Residue Estimation

Modern agriculture depends largely on the use of herbicides for the control of weeds that compete with the crops. In the past, new extraction procedures have been developed to overcome the shortfalls caused by the use of glassware and toxic solvents in the classical liquid extraction procedures. Now-a-days there are various new extraction techniques and chromatographic methods, such as high-performance liquid chromatography (HPLC) and gas-chromatography mass spectrometry (GCMS) used for the assessment of herbicide residue in various matrices.

The main class of herbicides includes substituted chloroacetanilides, such as alachlor, propachlor, clorophenoxy acid derivates such as 2,4-D; triazine derivatives containing three heterocyclic N atoms in the ring structure, such as atrazine, prometryn and metribuzyn; urea derivates; and substituted sulphonylureas, such as amidosulfuron and nicosulfuron. Owing to the use of a wide variety of herbicides with a variety of molecular structures, the development of a considerable number of chromatographic separation methods was necessitated for their analysis. The excellent separation capacity of the various chromatographic techniques has found global acceptance and application of the separation and quantitative determination of residues in different organic and inorganic matrices.

Herbicide residues have to be quantified from various matrices such as soil, water, plant materials. Selection of the most effective extraction method is very important for the quantification of herbicides.

2.1 Liquid Liquid Extraction Method

This method has been frequently used for ennrichment of selected sample constituent. The efficacy of the method is generally high, but requires highly purified and expensive solvents. A considerable number of alternative extraction techniques have been developed and applied in the measurement of herbicides residue.

2.1.1 Accelerated Solvent Extraction Method

This extraction technique speeds the extraction process and reduces the total amount of solvent used. The system uses conventional solvent (ethyl acetate/cyclohexane or dichloromethane/acetone, 1:1 v/v) at elevated temperatures (100 °C) and pressures (10 MPa), which results in improved extraction kinetics. The extraction of the sample requires 1–30 g of sample, 12–17 min of time and 15–50 mL of solvent. The samples are weighed and then are transferred to the extraction cells.

2.1.2 Solid: Phase Extraction Method

In this method a solid sorbent is filled in a short column, where the herbicide residues are retained and selectively eluted with an appropriate solvent systems. The selection of the most effective sorbent depends on the physicochemical characteristics of the herbicide and the components of the accompanying matrix (Pico et al. 2000). Continuous-flow liquid membrane extraction (Chao et al. 2002), class-selective immune extraction using various immune sorbents, and pressurized liquid extraction and microwave-assisted extraction are other extraction methods that are used in herbicide residue research.

Followed by extraction the residues are quantified using High Performance liquid chromatography/Gas Chromatography/Liquid Chromatography- Mass Spectrometry (Table 1).

Table 1 Instrumentation – high performance liquid chromatographic or gas chromatographic separation parameters for certain herbicides

Parameters	Alachlor	Butachlor	Sulfosulfuron	Anilophos
Instrument	GC-17A	GC-17A	HPLC	HPLC
	Electron capture detector	Electron capture detector	Ultra violet detector	Ultra violet detector
Column	DB-5 megabore column (30 m × 0.53 mm i.d;1.0 µm film thickness)	DB-5 megabore column (30 m × 0.53 mm i.d;1.0 µm film thickness)	Phenomenex C18 (25 cm length × 4.6 mm i.d.)	Phenomenex C18 (25 cm length × 4.6 mm i.d.)
Oven	220 °C	220 °C	–	–
Injector	240 °C	240 °C	–	–
Detector	260 °C	260 °C	–	–
Carrier gas/ mobile phase	Nitrogen	Nitrogen	Acetonitrile: water 70: 30	Acetonitrile: water 70: 30
Flow rate	10 ml/min	10 ml/min	1.50 ml/min	1.50 ml/min
Split ratio	1.5	1.5	–	–
Sample volume	0.5 µl	0.5 µl	–	–
Retention time	4.7 min	7.3 min	5.3 min	1.5 min

GC Gas Chromatography, *HPLC* High Performance Liquid Chromatography

3 Effects of Herbicides

3.1 Soil Physico-Chemical and Biological Properties

Herbicides when applied to soil, is subjected to many changes which include the breakdown of herbicides and get transported/stored leading to changes in the soil. This situation occurs when farmers do not follow the recommended doses and application procedures. So it is of prime importance to assess the impact of herbicides on the natural environment, including soil metabolism. Persistence of herbicides in soil depends on their dose as much as on the characteristics of the soil, such as physicochemical properties, structure, temperature and moisture (Haberhauer et al. 2001). The presence of weeds reduces the photosynthetic efficiency, dry matter production and distribution to economical parts, thereby reducing the sink capacity of the crop which results in poor grain yield (Sharma et al. 2000). Degradation of the herbicide 2,4-dichlorophenoxyacetic acid under ultra violet light and the effect of various parameters such as light intensity, solvents, micellar media, wavelength of light, pH, other commonly occurring ions in water were studied by Sanghamitra et al. (2005). Soil organic C content had a positive influence on degradation rates of bispyribac-sodium and the soil pH had negative influence (Rajasekharam and Ramesh 2015). Pre-emergence application of oxadiagryl 225 g/ha at 4 days after sowing of sunflower recorded the higher weed control efficiency and seed yield over untreated control (Ayyappan and Chandrasehar 2012a, b). Also the test herbicide did not show any adverse effect on plant population, branches, head formation and yield of sunflower.

3.2 Non-targeted Organisms

When herbicides are applied to the soil, they not only affect the target organisms, but also microbial communities in soil. These non-target effects may reduce the performance of important soil functions. One of the plausible side-effects of using herbicides involves some disturbance of the biochemical processes occurring in soil. Active substances found in many herbicides may hamper the rate of a series of biochemical processes, interfering with the soil enzymatic activity and microbial growth. Modifications in the count and activity of microorganisms may lead to upsetting the biological equilibrium of soil, which in turn reduces its fertility. All these considerations emphasize the importance of studies on the effect of herbicides on the biological activity of the soil and particularly on soil enzymes, which can serve as a good indicator of the impact of herbicides on soil metabolism.

Soil microbial population plays a crucial role in carbon flow, nutrient cycling and litter decomposition, which in turn affect soil fertility and plant growth (Chauhan et al. 2006; Tripathi et al. 2006; Pandey et al. 2007). A healthy soil microbial population can stabilize the ecological system in soil due to their ability to regenerate

nutrients to support plant growth (Chauhan et al. 2006). When herbicides are applied to soil, there may be initial decrease/increase in soil microbial population depending on the nature of the herbicide. Fungal population (unlike bacteria) usually takes more time to recover from the detrimental effect caused by herbicides (Shukla and Mishra 1997). Application of 2,4-dichlorophenoxy acetic acid increased the fungal population, whereas the bacterial population was depressed initially, and finally 30 days after spraying, the populations in the treated and untreated plots were similar, which were used for weed control (Ayyappan and Chandrasehar 2012a, b). Azimsulfuron was easily biodegraded by a soil bacterial community, both in microcosms and in batch tests, with the formation of intermediates (Valle et al. 2006).

Short-term effects in response to the use of herbicides are related to disturbances of chemical and biological balance in soil, and are known to selectively suppress the activity of soil microorganisms. Little amount of pesticides are adsorbed on the organic matter that masks the effect of these agrochemicals on soil microbial biomass, and subsequently led to lysis of microbial cells thereby causing the decrease in microbial count (Jayamadhuri and Rangaswamy 2005). *Azotobacter* count was found to be less as compared to total bacteria (Barman et al. 2009).

Herbicides pose a risk to the entire ecological system by: (a) changing their biosynthetic mechanism, (b) affecting protein synthesis, (c) affecting cellular membrane, and (d) affecting plant growth regulators (Kalia and Gupta 2004). Fate of herbicides is greatly affected by the presence of soil organic matter by aiding their disappearance (Ali 1990).

Application of herbicides not only affects the soil microbial population, but also reduces the enzyme activity. The reason being that the microbial populations and enzyme activities are recovered after initial inhibition as the microbes gets adapted to these chemicals/herbicides or due to their degradation. The other reason could be due to the microbial multiplication on increased supply of nutrients available in the form of microorganisms killed by the herbicides (Latha and Gopal 2010; Vandana et al. 2012; Sondhia et al. 2013). Increase in soil dehydrogenase activity in herbicide-treated soil from 7th to 28th day of incubation might be due to the increase in microbial community composition with the capability of utilizing the herbicides as C source (Vandana et al. 2012). The protease activity depends on the distribution of proteolytic bacteria (Subrahmanyan et al. 2011). Herbicides used at recommended rate were non-inhibitory on dehydrogenase activity (Rao and Raman 1998). The role of microorganisms in N_2 fixation is given in Fig. 1.

Heavy rainfall after herbicide application may lead to run-off of chemicals, which may enter the water bodies like rivers, lakes and ponds, and there are likely chances for the aquatic organisms to get affected. The serious concern on the danger of butachlor for fish is that it interferes with cellular activities in fishes at genetic level (Yadav et al. 2013). Mortality of fish was high with 2,4-diethyl ester and paraquat than with glyphosate (Muniappa et al. 1995). Further, mortality of fish was high with butachlor, followed by anilofos and oxyflourfen (Sondhia 2012a, b). Residues of sulfosulfuron in the fishes were below the maximum residue level by 90 days (Sondhia 2007b, 2008a, b 2009d, 2010; Sondhia et al. 2007, Sondhia and

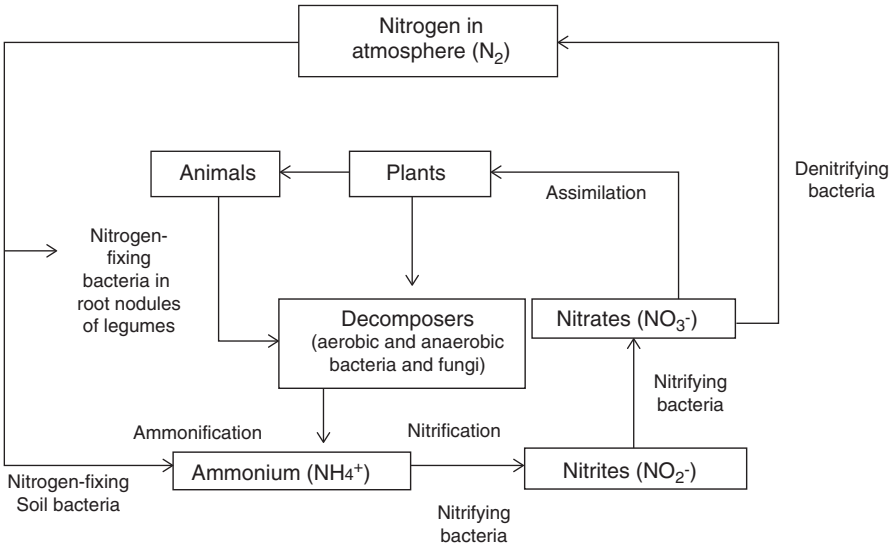

Fig. 1 The role of various microorganisms involved in nitrogen cycle. (Adapted from Wikipedia)

Singhai 2008a, b d, f). Pretilachlor, penoxsulam and pyrazosulfuron-ethyl residues in fishes dissipated to <0.001, 0.017 and 0.010, respectively at 60 days (Sondhia 2012a, b, 2014a, b).

Fishes (*Channa punctata*) exposed for 10 days to sub-lethal concentration (1/5th of static LC_{50}) of butachlor showed residues of butachlor in gills, liver, kidney and brain (Tilak et al. 2007). The prolonged exposure to sub-lethal concentrations led to the accumulation of residues in different tissues, causing toxicity to the fishes and finally led to biomagnifications through the food chain. Fish (*Tilapia mossambica)* exposed to sub-lethal concentration (66 mg/L) of metribuzin for 24, 48, and 72 h revealed that all biochemical parameters were found to be decreased in all tissues in comparison to control (Saradhamani and Selvarani 2009). Sulfosulfuron residues were detected in fishes exposed to sulfosulfuron for a period of 56 days (Ramesh et al. 2007).

Earthworms act as decomposer and are often used as test organisms as they are sensitive towards environmental influences (Edwards and Bohlen 1996). Most of the chemicals which are toxic to birds or mammals are toxic to worms too (Rudd 1964; Bunyan et al. 1981). Earthworms are regarded as reference to observe the soil contaminant bioavailability (Abdul Rida and Bouche 1997). They are useful to assess the contaminant fractions which may act on all organisms getting in touch with soil. Earthworms directly influence the persistence of herbicides in soil by metabolizing a parent compound in their gut (Gilman and Vardanis 1974; Stenersen et al. 1974) by transporting herbicides to depth and increasing the soil bound (non-extractable herbicides) fraction in soil or by absorbing herbicide residues in their tissues.

Increased concentration of butachlor decreased the earthworm biomass (Gobi and Gunasekaran 2010). Cocoon production was also reduced by the increase in butachlor concentration which is due to the increased demand for energy needed for the regulation and detoxification of herbicide. Growth and reproductive parameters of earthworms exposed to pesticides seem to be useful bioindicators of soil pollution (Yasmin and D'Souza 2010). Herbicide 2,4-dichlorophenoxyacetic acid showed toxic effect on the earthworm (*Eutyphoeus waltoni*), and was time and dose dependent. Maximum toxicity was observed in the sandy soil, whereas minimum in the feed material of buffalo dung with gram bran. There was no mortality observed in control (Singh and Singh 2015). The toxicity symptoms due to herbicide application may be lying on the top layer of soil and bleeding (Fig. 2).

3.3 Rotational and Succeeding Crops

Herbicides when applied to crops may also persist in soil and may affect the rotational/succeeding crops also. Herbicide is said to be persistent when it exists in soil for a longer duration such that it affects the succeeding crops. Oxadiargyl when applied 225 g/ha at 4 days after sowing of sunflower did not show any phytotoxicity symptoms, such as crop discoloration, chlorosis, stunting, wilting, deformation and vein clearing on sunflower crop as well as succeeding crops blackgram and maize (Ayyappan and Chandrasehar 2012a, b). Atrazine had no significant residual effect on chickpea or Indian mustard (Saikia et al. 2000). Pendimethalin caused phytotoxicity to the succeeding sensitive sorghum crop at higher dose (Yadav et al. 1995).

The presence of herbicide residues in the soil not only damages the succeeding sensitive crops but also adversely affects human and animal health due to

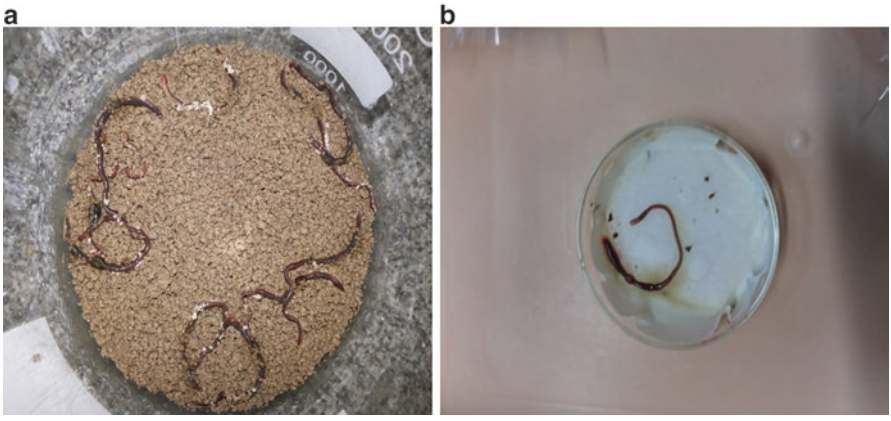

Fig. 2 Toxicity symptoms on earthworm due to herbicide application, such as (**a**) earthworm lying on the top layer of the soil, and (**b**) bleeding by earthworms

bioaccumulation of residues in crop produce (Sondhia and Singhai 2008a, b). Coriander (*Coriandrum sativum*) and edible amaranth (*Amaranthus mangostanus* L.) raised as succeeding crop in cotton field after the application of alachlor did not show any toxic symptoms of alachlor residues in the green leafy vegetable samples (Ramesh and Maheswari 2004). The succeeding crops of coriander and edible amaranth were raised after sulfosulfuron application in the wheat field. The vegetables were analyzed for residues 7 weeks later which revealed that in none of the edible plant leaf samples, detectable concentrations of sulfosulfuron were found. The half-life values for sulfosulfuron in wheat plant ranged from 2.94 to 3.07 days (Ramesh and Maheswari 2003). Succeeding crops of wheat and chickpea sown immediately after the harvest of groundnut were not affected by the residue of post-emergence herbicides at all different doses (Varghasia and Nadiyadhara 2013).

3.4 Metabolites

Herbicides have been successfully used in weed management systems as they harm only the weeds leaving the main crop undamaged. The reason behind the selective action of herbicides against weeds in crops is that crops are able to metabolize the herbicide to a non-toxic form. The process of conversion of herbicides into intermediates with reduced phytotoxicity involves three phases. Phase I involves the initial reactions such as oxidation, reduction or hydrolysis, phase II involves the primary conjugation with endogenous substrates such as sugars, amino acids, or glutathione and phase III involves the secondary conjugation, formation of insoluble residues or sequestration in the vacuole.

Crops are able to biochemically convert herbicides to non-toxic molecules so that the herbicides no longer harm the crop. Many weeds cannot do this and so the weeds die.

Metabolites of certain herbicides are listed below:

Sulfosulfuron metabolites are 1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin-3-yl-3-(4,6-dimethoxypyrimidin-2-yl) amine under alkaline condition; 1-(2-ethylsulfony limidazo[1,2-*a*] pyridine)-3-sulfonamide and 4,6-dimethoxy-2-aminopyrimidine under acidic condition. Major pathway of acidic hydrolysis is breaking of a sulfonylurea bridge whereas the major pathway of alkaline hydrolysis is contraction of the sulfonylurea bridge (Saha and Kulshrestha 2002). Metabolites of sulfosulfuron namely aminopyrimidine, desmethylsulfosulfuron, guanidine, sulfonamide, ethyl sulfone and rearranged amine were found in water and fish samples. One of the metabolite aminopyrimidine was identified at higher concentration levels (0.01–0.1 µg/mL) in comparison to other metabolites. Desmethylsulfosulfuron, rearranged amine, sulfonamide and guanidine were identified as breakdown product of sulfosulfuron in the subsurface soil (Ramesh et al. 2007; Sondhia 2008f, Sondhia 2009a, 2014a,b).

The major metabolite of clodinafop-propargyl ester is acid derivative that is responsible for herbicidal action (Sondhia and Mishra 2005). Ethyl-5-[(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 are the three major transformation products of pyrazosulfuron-ethyl detected from rice field (Sondhia et al. 2013; Wassem and Sondhia 2014). Pyrazosulfuron-ethyl is degraded by *Penicillium chrysogenum* and *Aspergillus niger*. Pyrazosulfuron metabolites were detected from soil and pond water which were identified by LC/MS/MS (Sondhia et al. 2013).

Penoxsulam metabolites in soil are 1,2,4 triazolo-[1,5-c] pyrimidin-2 amine, 5,8 dicarboxylic acid; 2-(2,2-difluoroethoxy) -6 (triflurомethyl) benzenesulfonamide; and 3-[[[2-(2,2- difluoroethoxy)-N-[1,2,4] triazole [1,5c]-6- triflurомethyl) benzene sulfonamide carboxylate (Rajput and Sondhia 2014). Metabolites of cyhalofop-butyl in soil and leachates are (R)-2-4(4-amino 2-fluoro phenoxy) phenoxypropanoic acid (cyhalofop acid) and (R) -2-4(4-caboxyl-2-flurophenoxy) phenoxypropanoic acid (cyhalofop-diacid), and cyhalofop-phenol (Khare and Sondhia 2014).

Metsulfuron methyl metabolites are methyl-2-sulfonyl-amino-benzoate, 2-amino-6-methoxy-4-methyltriazine and saccharin (*O*-sulfobenzoimide) from treated wheat field soil. Pinoxaden and its metabolite NOA 407854(8–(2,6-diethyl-4-methyl-phenyl) -tetrahydropyrazolo[1,2-d][1,4,5]oxadiazepine-7,9-dione) were stable in wheat for a period of 30 days. Pinoxaden metabolites showed slow dissipation at 20 ± 1 °C (Dixit et al. 2011).

Pretilachlor in field soil degraded to seven metabolites namely 2,6-diethyl-N-(propoxyethyl)acetanilide; 2,6-diethyl-N-(propoxyethyl)aniline; 2,6-diethyl-N-(2-hydroxy ethyl)aniline; 2,6-diethyl-N-(ethyl)aniline; acetanilide; 2-chloro-2, (1–hydroxyethyl, 6 -ethyl)-N-(2-propoxyethyl) acetanilide; and 2-chloro-1(-9-ethyl-3-hydroxy-2,3,4,5-tetrahydro-1H-1benzazapin-1-yl) ethanone (Sondhia 2014a, b).

3.5 Herbicide Residues in Soil

When herbicides are applied to soil, a number of processes begin and the herbicide starts moving from the original application site.

The herbicides when taken up by the plants may be washed off due to rainfall to the soil or undergo chemical/microbial or photo-degradation on the plant surface or escape to air in vapour form. The persistence of herbicide in soil is expressed as half-life (time required to degrade 50% of the applied herbicide). Persistence of herbicides depends on many factors like soil type, temperature, concentration of the herbicide, nature of chemical, soil properties and climatic conditions. The herbicide applied to the soil has to persist in soil for a certain time long enough to check the weeds until the end of critical period of weed competition whereas, it should not persist beyond the crop harvest as it is injurious to the sensitive crops grown in rotation (Sondhia 2009a, b, c, d, 2013a, b, c, d, 2014a, b, c, d).

Leaching and runoff of chemicals occur due to heavy rainfall. Leaching potential is high in sandy soil than in clay soil, which is due to larger pore space and lower cation exchange capacity (Sondhia and Yaduraju 2005; Sondhia 2007a, b, c, d, 2008c, d, 2009c). Field application of 2,4-D in wetland paddy soils of Thrissur, Kerala showed that 2,4-D did not persist in the paddy field beyond 30 days after spraying (Durga Devi et al. 2008).

Pyrazosulfuron-ethyl degradation was fast under submergence, followed by maximum water holding capacity and half of maximum water holding capacity in all soils. Half-lives for pyrazosulfuron ethyl in soil under various water holding capacity ranged from 42.9 to 85.5 days (Mukherjee et al. 2010; Kumar et al. 2011; Singh et al. 2012; Sondhia et al. 2013). Degradation of pyrazosulfuron-ethyl residues were not much significantly influenced by the soil organic C and pH (Rajasekharam and Ramesh 2014a, b). Residues of metsulfuron-methyl was detected in surface soil up to 30 days by bioassay method, while the residues were detected only up to 15 days by High Performance Liquid Chromatograph method (Paul et al. 2009). Metsulfuron-methyl applied 2–8 g/ha in rice soil showed a residue of 0.008–0.016 μg/g at 30 days whereas residue in soil, rice grains and straw at harvest were found below 0.001 μg/g (Sondhia 2009b). No residues of metsulfuron-methyl applied at 16 g/ha were detected after 60 days, but at higher application rates (20–24 g/ha), 0.002 and 0.011 mg/kg residues were found (Sushilkumar et al. 2008). However, the residues were below the detection limit at 3–5 g/ha application rates and 0.002 μg/g residues were detected at 8 g/ha, in wheat plants at harvest (Sondhia 2008b, 2009b).

Sondhia and Dixit (2012) found that ethoxysulfuron residues were below <0.001 μg/g in rice soil at harvest at 15–20 g/ha doses. There was gradual degradation with atrazine in soil and no residue was found at harvest, whereas 0.056 mg/kg residue was found in the post-harvest soil at double the recommended dose (Janaki et al. 2012). Triasulfuron in field soil has a half-life of 5.8–6.0 days. Initially the degradation was fast (half-life 3.7 days), followed by a slower dissipation rate at the end (9.4 days). Triasulfuron degradation in soil was influenced by acidic pH and microbial activity (Singh and Kulshrestha 2006). Imazasulfuron residues persisted up to 60 days; however, no residues were found after 90 and 120 days (Sondhia 2008a).

Sulfosulfuron residues were not detected in the soil at harvest under wheat cropping system (Ramesh and Maheswari 2003; Sondhia and Singhai 2008a, b). Sondhia and Singhai (2008a, b) evaluated the persistence of sulfosulfuron residues applied in wheat crop as post-emergence at 25, 50 and 100 g/ha application rates. Initially there was rapid dissipation in surface and subsurface soil. After 150 days, residues were found below 0.001 μg/g in soil samples collected from 25 to 50 g/ha treated plots. However, at 100 g/ha dose, residues were not detected after 200 days in surface and sub-surface soil.

Residues of bromacil persisted in soil even after 8 months (Leela 1984). Atrazine dissipation was more than 95% at the time of crop harvest and had a half-life values of 9.4–21.5 days in soil (Kulshrestha et al. 1977; Sandhu et al. 1994; Sondhia 2001; Nag and Das 2009; Janaki et al. 2012).

Fluazifop-butyl applied at rate 125–500 g/ha in soybean field showed residues of 0.051–0.079 μg/g in the soil (Sondhia 2007c). There was rapid dissipation of butachlor in rice field when compared to laboratory conditions showing a half-life of 18.1–23.0 days at 1.0–2.0 kg/ha (Sondhia et al. 2006). Residues of 2,4-dichlorophenoxyacetic acid persisted up to harvest showing a half-life of 18–22 days (Jayakumar and Ramulu 1993). Sondhia and Mishra (2005) in their study concluded that dissipation of clodinafop was not affected by specific soil pH and soil type. Residue of clodinafop in soil was found 0.093–0.081 μg/g in alluvial, red and black soil.

Application of fentazamide at 240 g/ha resulted in residues to a level of 0.03–0.04 mg/kg in soil; however, the residues were found below the detection limit in rice husk and straw (Tandon et al. 2012). Pretilachlor applied at 0.75–1.50 kg/ha persisted up to 45 days with a half-life of 3.9–10.0 days (Dharumarajan et al. 2008). Metribuzin residues were detected even in the post-harvest soil of potato crop (Sondhia 2005). Fenoxaprop-ethyl or acid residues were not detectable in soil, wheat grain and straw samples at recommended doses (Sondhia 2008e; Singh et al. 2013).

No residues of benthiocarb were detected in soil, grain, straw and husk samples at harvest when applied at 1500–3000 g/ha (Aktar et al. 2007). Persistence was longer at lower temperature and higher concentration (Kumar et al. 1993). Application of alachlor and fluchloralin at 1 kg/ha rate in the soybean field revealed that residues were not detected in the soil at harvest whereas, at 1.2 and 1.5 kg/ha rates, 0.01 and 0.02 μg/g residues were detected at harvest (Sondhia 2002). Alachlor applied at 1.5 kg/ha as pre-emergence in vegetable crops persisted upto 60 days (Leela 1993). Residues of butachlor when applied at 1.0 kg/ha in transplanted rice crop were not detected after 120 days in clay loam soil (Sondhia et al. 2004). Persistence of fluchloralin 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 and 45.6 days (Patel et al. 1996). Imazethapyr 100 g/ha in the soil of soybean crop showed 0.008 μg/g of imazethapyr residues at harvest (Sondhia 2006c).

3.6 Dissipation of Herbicides in Soil

Herbicides when applied to soil to control weeds should not remain in soil for long period. The length of time a herbicide remains active in soil is called “soil persistence,” or “soil residual life” (Fig. 3). Anything that affects the disappearance or breakdown of herbicides affects persistence.

Herbicides that are persistent include triazines, uracils, phenylureas, sulfonylureas, dinitroanilines, isoxazolidiones, imidazolinones, and certain plant growth regulators belonging to the pyridine family.

Persistence of herbicide is influenced by several factors: soil factors, climatic conditions, and herbicidal properties. Soil composition, soil chemistry, and microbial activity are the soil factors affecting herbicide persistence. Soil-herbicide

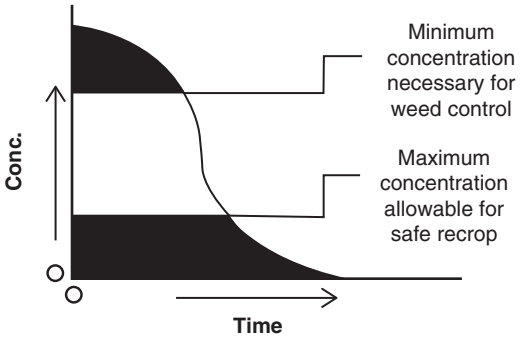

Fig. 3 Herbicide dissipation shown with concentration vs time

binding (adsorption), leaching and vapor loss (volatilization) affects herbicidal activity and persistence. In general the soils high in clay, organic matter or both have a greater potential for the reason that herbicides are strongly bound to soil particles leading to low leachability and loss through volatilization. Persistence of some herbicides, especially the triazines and sulfonylureas is influenced by soil pH.

Degradation of herbicide takes place by chemical degradation or microbial breakdown. The degradation is slower in higher pH soils. The main reason is that in soils with high pH, only less amount of herbicide is bound to soil particles and the major amount is available for plant uptake. There are few herbicides like triazine and sulfonylurea that do not perist and have no carry over effect, regardless of soil pH. Rapid dissipation of these herbicide families is found in soils with pH levels below 6. Atrazine when applied on acidic soils is bound to soil particles and not available for weed control.

In case of imidazolinone herbicides, imazaquin and imazethapyr, low soil pH increases the persistence. Adsorption of these herbicides reduces their availability to soil microorganisms. Inspite of greater adsorption of herbicides in lower-pH soils, the herbicides can still be released several months later for plant uptake thereby potentially injuring the follow crop. Microorganisms play a major role in breakdown of herbicides and the rate of decomposition is determined by the microbial population and the types of microorganisms. *Moisture, temperature,* and *sunlight* are the climatic variables involved in herbicide breakdown. Degradation rate of herbicide increases with increase in temperature and soil moisture.

Sunlight is an important factor in herbicide degradation. Photolysis has been reported for many herbicides, especially in liquid solution (such as water) or on plant leaf surfaces whereas, in case of more persistent soil-applied herbicides loss due to photolysis is small.

Chemical properties of herbicides like water solubility, vapor pressure and the molecule's susceptibility to chemical or microbial alteration or degradation affect its persistence. Yet another mechanism responsible for herbicide dissipation is leaching. Leaching occurs when herbicide is dissolved in water and moves down through the soil profile. Volatile herbicides (those with higher vapor pressures) generally dissipate more rapidly than herbicides with lower vapor pressures. Volatile herbicides include members of the thiocarbamate family, EPTC (Eradicane, Eptam)