Chapter 5
Effects of Herbicides on Soil Enzymes and Their Regulatory Factors in Agroecosystem: A Review

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Abstract Modern agriculture is heavily reliant upon herbicide application to control weeds for increasing crop productivity to meet the need of growing population and for economic benefits. However, such benefits bear high environmental cost including loss of soil fertility. An indispensable role is played by soil enzymes in the decomposition of xenobiotic and mineralization of organic compounds, and they are considered to be the best soil fertility indicators. Therefore, soil fertility sustenance and crop productivity maintenance demand a better understanding of response of soil enzymes to application of herbicides. The present chapter has made an attempt to present a comprehensive account on response of soil enzymes to different classes and types of herbicides under variable soil environment. Efforts were made to address the production and consumption of herbicides, types of regulatory determinants, and fate of herbicide-enzyme interaction. A critical analysis of in situ and controlled experiments suggests that herbicides applied individually or in combinations influence soil enzymes differently. Although the response shows dose dependence, a number of edaphic and climatic factors also play a significant role in regulating herbicide-enzyme cause-and-effect relationships. This has relevance for mechanistic understanding of enzyme-herbicide interaction and exploring strategies of soil management.

Keywords Herbicides · Soil enzymes · Herbicide-enzyme interaction · Soil fertility · Influencing factors

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5.1 Introduction

Agriculture, which had been a major sector in Indian economy, now contributes to only 17% of gross domestic product (GDP) (Economic Survey Report, 2017–2018). Rapidly growing demand of population in developing countries has led to massive intensification of agricultural system. Agricultural weeds are important interspecies competitors of crops, leading to a sharp decline of about 29% and 47% in wheat and rice crops, respectively (Oerke 2005). This has forced the indiscriminate and tremendous application of pesticides mainly herbicides in the agricultural field (Nonga et al. 2011). Herbicides are toxic agrochemicals used against weeds and undesirable vegetation in the agricultural farms and gardens. Herbicide consumption accounts to 47.5%, insecticides 29.5%, fungicides 17.5%, and others only 5.5% on the global scale of pesticide expenditure. In India, insecticides hold 80% utilization, herbicides 15%, fungicide 1.46%, and others below 3%. The herbicide application has descending trend as wheat (44%), followed by rice (31%), plantation crop (10%), soybean (4%), and other crops (11%) (Sondhia 2014). Herbicides are biologically active eco-toxic compounds that may cause unexpected repercussions by influencing microbial populations, soil enzyme activities and therefore, the overall status of the soil because microbial communities are the key determinants of carbon flow, litter decomposition, and nutrient cycling. Such impacts reduce soil fertility and agricultural productivity in the long run (Tripathi et al. 2005; Pandey et al. 2007a, b).

Knowledge about the effect of herbicides, herbicidal efficacy, and consequential yield effects of the herbicide application either alone or amended with other agrochemicals and under organic or inorganic treatments, is important in crop management and long-term sustainable crop production strategies (Borowik et al. 2016). Considering all these issues, several research studies have been already conducted and are continued especially in the context of soil biological system and enzyme activities. The effects of herbicides butachlor, 2,4-D, and oxyfluorfen on dehydrogenase and urease activity have been studied by Baruah and Mishra (1986). The effects of glyphosate and diflufenican applied alone or in combination on soil biological properties have been examined by Tejada (2009). Du et al. (2018) illustrated the dose dependence of mesotrione on soil enzyme activities and microbial communities. A large number of reviews are available focusing on the effect of herbicide contamination on soil quality attributes. Recently, Raj and Syriac (2017) reviewed the dependency of herbicides on soil type, characteristic and concentration of herbicide, vulnerability of nontarget organisms, and climatic conditions in assessing the impact of soil health status. Riah et al. (2014) reviewed the effect of pesticides on soil enzymes. Most of the recent reviews have emphasized the context of weed control strategies. Mauprivez et al. (2019) explored the herbicidal effect on nontarget organisms. Very recently Macías et al. (2019) reviewed the advancement in allelopathy from knowledge to application to overcome the problems of weeds. Least attention has been paid to review the effects of herbicide mixtures in comparison to individual agrochemical on soil biological parameters although it seems to be

more effective in weed killing and nontarget effects. Opportunities and challenges regarding interactions between different categories of herbicides and different classes of soil enzymes and their consequential dose-response relationship have not received sufficient attention so far, irrespective of the fact that soil enzymes quickly response to herbicides and also are the best indicators of soil fertility. The centerpiece of the present review is to precisely enumerate the available scientific literature related to the common soil enzymes, monitored by different herbicidal treatments, in various dose and on discrete soil types in either way as observed in field experiments or laboratory incubation studies, and it is also planned to summarize the knowledge base of factors altering the influence of herbicides on soil enzymes (Table 5.1). Our in-depth analysis of available literature shows that herbicide-soil enzyme interaction follows the "dose-response relationship." At higher doses, herbicides inhibit enzyme activity, while relatively lower concentration acts as stimulator. Further, a complex set of ecological factors like soil moisture, endogenous residues, soil type, herbicide quality, etc. influence the overall interaction between herbicide and soil enzymes. Therefore, extensive investigations to establish a mechanistic link between herbicide and soil enzyme and their regulatory factors, seem to be imperative.

5.2 Overall Production and Consumption of Herbicides

Weeds being the major impediment in crop productivity have caused a phenomenal growth in the application of herbicides for limiting and eliminating the weed population. Herbicide holds the highest position of global pesticide sale which accounts 47% making it a major class of pesticides followed by 29.4% insecticides, 17.5% fungicides, and remaining 5.5% only sold by others (Shea 1985). Herbicides alone share 47.5% of total 2 million tons of global annual pesticide consumption (Gupta 2004). As per the report of Sondhia (2014), herbicides account for 44% of total global annual pesticide consumption (share followed by insecticides (22%), fungicides (27%), and others (7%) at global forum of pesticide consumption). Herbicides consumption is around 60% of total pesticide at global level (Sondhia 2018). The derivatives of chlorophenoxy acid, 2,4-D, triazines having three heterocyclic N atoms in ring structure (atrazines), urea derivatives, substituted chloroacetanilides (propachlor) and sulfonylurea substituted (amidosulfuron and nicosulfuron). Glyphosate undoubtedly holds number one position, whereas paraquat ranks second in terms of worldwide sale (Woodburn 2000). Glyphosate (GP), 2,4-D, atrazine, metolachlor, diuron, imazapyr, pendimethalin, paraquat, and clodinafop propargyl (CF) are the most commonly applied herbicides (Singh and Singh 2014).

Table 5.1 An overview of herbicidal effects on soil enzymes and regulatory determinants

SN	Soil type, crop, study site	Experimental setup (field/incubated), herbicide dose, and mode of application (MA)	Enzymes studied	Observations/findings	References
1	Clay soil	Soil (500 g, 0–20 cm depth) incubated for 10 weeks at 28 °C.	Cellulase	Cellulase activity decreased, and enhancement was recorded once by low or high rates of Brominal, 1 week after soil treatment. Activity of AP inhibited at high dose and stimulated at low doses of herbicide. ALP accelerated with herbicide application low or high	Omar and Abdel-Sater (2001)
	Rice crop	Brominal (bromoxynil, 24%) was added in 1 L per feddan (0.6 g a.i. dws)	Acid phosphatase (AP)		
	Asyut, Egypt	MA: spray	Alkaline phosphatase (ALP)		
2	Fluvo-aquic soil	Soil (5 g, 3–15 cm depth) laboratory incubation for 24 h	Dehydrogenase	DHA increased gradually with increasing dose and showed the highest activity on the 16th Day after application of 22.0 mg g^{-1} dws of butachlor. Hydrogen peroxidase increased on lower dose of butachlor	Min et al. (2001)
	Paddy rice crop China, Hangzhou	Butachlor @ 5.5μg/g, 11.0 mg g^{-1} and 22.0 mg g^{-1} dws	Hydrogen peroxidase		
3	Clay soil (Phaeozem)	Tested soil samples (0–20 cm in depth) preincubated at 25 °C for 7 days.	Urease	The activities of urease ranged from 75.7% to 120% and phosphatase from 41.2% to 136.4% considering control as 100%	Wang et al. (2006)
	Shanghai, China	Butachlor, MA: solution-based application	Phosphatase		
4	Loamy sand	Soil (8 g at 15 cm depth) incubated for 1–3 weeks at 28 °C, atrazine, butylate, ethalfluralin, imazethapyr, linuron, metolachlor, metriburin, and trifluralin (rate 10μg g^{-1} dws)	Dehydrogenase	No effect on amylase activity of all eight herbicidal treatments except ethalfluralin inhibited its activity. All the chemicals significantly inhibited the activity of phosphatase	Tu (1992)
	London, Ontario	MA: spray	Amylase		
5	Clayey texture soil and sandy loam texture soil	Soil (100 g) incubated for 180 days at 25 °C, 0.52 g of glyphosate, 2.08 g of diflufenican, and combination of both	Dehydrogenase	Activity of all the enzymes got inhibited, and more pronounced inhibition was observed in sandy loam soil than clay loam soil	Tejada (2009)

		0.52 g of glyphosate and 2.08 g of diflufenican			
	Seville, Spain	MA: the herbicides were applied using a machine of laboratory treatments equipped with fuzes of flat fan Teejet 80.02 E.VS, to a pressure of 3 kg cm^{-2} and 300 L ha^{-1} of application.	Urease		
		Applied in 1 L water solution	β-glucosidase		
			Phosphatase		
			Arylsulfatase		
6	Cassava farms, woody perennial plants (famine or drought crop)	Topsoil (up to 5 cm depth) treated for a period of 6 weeks, 4 L h^{-1} for paraquat, glyphosate, and primeextra, while recommended rate of 3 kg h^{-1} atrazine powder was used for atrazine treatment.	Dehydrogenase	In the treatment of 6-week period, soil treated with atrazine recorded highest DHA of 14.32μg g^{-1} min^{-1} after fourth week of treatment, while primeextra treatment had the lowest record of DHA 9.02, 12.55, and 16.09μg (g^{-1} min^{-1}) after second, fourth, and sixth week treatment	Sebiomo et al. (2011)
	Nigeria, Ogun State	MA: spray			
7	Sandy clay loam	Field experiment, soil samples (0–15 cm) were collected at 0, 15, 30, and 45 days after spraying of pre-emergent herbicides	Acid phosphatase	During 45-day observations, in lower doses, activity of all the enzymes increased except urease which got inhibited compared to the control	Sireesha et al. (2012)
	Radish crop	Pendimethalin (0.5/0.75 kg a.i. ha^{-1}), oxyfluorfen (0.1/0.15 kg a.i. ha^{-1})	Alkaline phosphatase		
	India, Hyderabad	MA: spraying	Dehydrogenase		
			Urease		
8	Inceptisol (sandy loam)	Field experiment, soil samples (0–10 cm depth) for 2 annual cycles	β-glucosidase	Activities of all the enzymes increased with respect to control	Singh and Ghoshal (2013)
	Rice and wheat	Butachlor (2 kg a.i. ha^{-1})	Alkaline phosphatase		

(continued)

Table 5.1 (continued)

SN	Soil type, crop, study site	Experimental setup (field/incubated), herbicide dose, and mode of application (MA)	Enzymes studied	Observations/findings	References
	India, BHU	MA: spraying	Urease		
9	Clay loam	Field experiment, pre-emergent application of oxyfluorfen @ 0.10 and 0.15 kg ha^{-1}, pretilachlor @ 1.00 and 1.50 kg ha^{-1}, pendimethalin @ 0.675 and 1.00 kg ha^{-1}, atrazine @ 1.25 kg ha^{-1}	Dehydrogenase	Dehydrogenase activity decreased with higher doses of herbicides.	Nadiger et al. (2013)
	Maize crop Dharwad, India	MA: spraying		Enzyme activity was reduced till 20–30 DAS. At 40 DAS, the DHA in the soil was reduced in all the treatments compared to 20 DAS. However, at later stages of the crop growth (60, 80, and 100 DAS), there was a drastic increase in the activity of DHA in the plots treated with pretilachlor, oxyfluorfen, pendimethalin (at both applied doses), and atrazine	
10	Clay and loamy soil	Soil (0–20 cm depth, 80 g) incubated for 60 days at 25 °C, fomesafen (50–-420μg kg^{-1} conc. @ 180–375 g a. i. ha^{-1})	Acid phosphatase (AP)	AP increased with dose. Urease activity inhibited first and then increased. DHA found most sensitive and showed enhanced activity in response to herbicide	Zhang et al. (2014)
	China, Qingdao	MA: spray	Alkaline phosphatase (ALP)		
			Urease		
			Dehydrogenase (DHA)		

11	Sandy loam soil	Pot culture experiment, soil (5 kg), sampling was undertaken at 0, 30, 60, 90, and 120 DAS (days after sowing), Pendimethalin at three different rates (500, 1000, and 1500 g a.i.) were applied.	FDAH (fluorescein diacetate hydrolysis)	Dehydrogenase and FDAH were the least tolerant to the effect of the herbicide, whereas alkaline phosphatase was the most tolerant one. Higher dose was more deleterious than the lower doses of pendimethalin	Singh (2014)
	Aligarh Muslim University, Aligarh, India	(MA): spray	Dehydrogenase		
			Acid and alkaline phosphatase		
12	Sandy loam and loamy soil	Soil (1 kg, 0–10 cm depth) incubated for 30 min at 20 °C, nicosulfuron @ 0.3,0.6, 3.0, and 30.0 mg a.i. kg^{-1} of soil	β-glucosidase	The herbicide was found to stimulate β-glucosidase and protease activity in both types of the soil. Enzyme activity increased after treatment with nicosulfuron. Protease activity stimulated in both soil types on herbicide application	Santric et al. (2014)
	Belgrade, Serbia	MA: spray	Protease		
13	Clay loam	A field experiment was conducted for 2 years in randomized complete block design pattern. Buctril super (bromoxynil) herbicide was applied at 375, 750, 1500, and 22,500 mL ha^{-1}.	Dehydrogenase (DHA)	Dehydrogenase activity declined	Abbas et al. (2015)
	Wheat (variety Chakwal-50)	MA: spray	Urease	The highest dehydrogenase activity was found in control, followed by in 375 mL ha^{-1} treatment and least in 2250 mL ha^{-1} treatment. The highest urease activity in 375 mL ha^{-1} and lowest in 2250 mL ha^{-1} treatment were reported.	
	Rawalpindi, Pakistan		Alkaline phosphatase	30% and 31% reduction in urease activity, 36% inhibition in dehydrogenase activity, and 34% and 31% decline in alkaline phosphatase activity were recorded in two seasons	

(continued)

Table 5.1 (continued)

SN	Soil type, crop, study site	Experimental setup (field/incubated), herbicide dose, and mode of application (MA)	Enzymes studied	Observations/findings	References
14	Sandy clay loam	Soil (4 kg), incubated for 0 (before spray), 5, 10, 15, 20, 25, 30, and 45 days	Dehydrogenase	DHA at 20 days after pretilachlor application was inhibited by 27%, 28%, and 40% compared to initial values for RD, 2 RD, and 10 RD treatments, respectively. DHA was found elevated in control sample.	Sahoo et al. (2016)
	Rice crop (var. Naveen, Indica-type)	Pretilachlor @ recommended dose (RD), 600 g a.i. ha^{-1} @ 1200 g a.i. ha^{-1} (2 RD), and @ 6000 g a.i. ha^{-1} (10 RD) and control with no herbicide.	Fluorescein diacetate (FDA)	FDA activity was reported with an increase of 29%, 36%, 10%, and 36% for RD, 2 RD, 10 RD, and control treatments after 25 days of pretilachlor application, respectively.	
	Cuttack, India	MA: spray as pre-emergent herbicide	β-glucosidase	There was an increase of 29%, 36%, 10%, and 36% FDA activity from initial values for RD, 2 RD, 10 RD, and control treatments after 25 days of pretilachlor application, respectively. β-glucosidase and urease activity inhibited, compared to control, 5 days after herbicide application	
			Urease		
15	Eutric Cambisols	Soil (3 kg, 0–20 cm depth) incubated for 60 days	Dehydrogenase (DHA)	0.73 mg P + T kg^{-1} destabilized activity of all enzymes, and 14.63–-468.16 mg P + T kg^{-1} strongly inhibited all the enzymes' activity. Inhibition trend was recorded as DHA > AP > U > Al. P > βG > ArS > C	Wyszkowska et al. (2016)
	Maize crop Tomaszkowo, Poland	Enzyme assay on Day 30 and 60 of the experiment, pethoxamid (P) (300 g dm^{-3}), terbuthylazine (T) (250 g dm^{-3})	Catalase (C)		
			Urease (U)		
			Alkaline phosphatase (ALP)		
			Acid phosphatase (AP)		
			Arylsulfatase (ArS)		
			β-glucosidase (βG)		

16	Silty clay loam	Field exp., soil samples were collected continued with an interval of 20 days till harvest. Tembotrione (110 g ha^{-1}), atrazine (1500 g ha^{-1} as pre-emergent)	Dehydrogenase	Enzyme activity decreased at higher doses from 2 to 60 days after sowing and increased 60–100 days in all treatments	Kumar et al. (2017)
	Maize	MA: spray fitted			
	Palampur, India				
17	Haplic Luvisol	Field experiment, soil (0–20 cm) collected in the end of May, each year. Azoprim (atrazine) @ 3 kg ha^{-1}, Roundup Ultra (glyphosate) 4 dm^{-3} ha^{-1} plus Chwastox Extra (MC PA) 2 dm^{-3} ha^{-1}, Azotop (simazine) 4 kg ha^{-1}, Roundup 3 dm^{-3} ha^{-1} plus ammonium sulfate approximately 12 kg ha^{-1}, and Dual 720 EC (metolachlorine) 1 dm^{-3} ha^{-1}	Dehydrogenases	Among the enzymes analyzed, the activity of phosphatases was the most sensitive indicator for soil contamination with triazine herbicides. The application of herbicide-triggered fallow land and a high level of mineral fertilization effected in the lowering of the enzymatic activity of the soil over the years. DHA reduced by 44.8%, phosphatase by 58%, urease by 46%, and protease by 43%	Bielińska and Pranagal (1994)
	Lublin, Poland		Phosphatase		
			Urease		
			Protease		
18	Soil Endocalcaric Cambisols, with sandy loam texture	Soil (1.5 g cm^{-3}, from 0 to 20 cm depth terbuthylazine (T), mesotrione (M), and S-metolachlor (S)). One cubic decimeter of the herbicide contains 187.5 g of T, 37.5 g of M, and 312.5 g of S.	Dehydrogenase	Activity decreased strongly dependent to dose in response to mixture of three Hbs.	Borowik et al. (2016)
	Maize crop	MA: applied to the soil in the form of aqueous suspension	Catalase (C)	AP 27%, C by 43%, ArS by 52%, ALP by 57%, DHA by 83%, U by 89%, and βG by 92%	
	Olsztyn, Poland		Urease (U)		
			Arylsulfatase		
			B-glucosidase (βG)		
			Acid and alkaline phosphatase (AP and ALP)		

(continued)

Table 5.1 (continued)

SN	Soil type, crop, study site	Experimental setup (field/incubated), herbicide dose, and mode of application (MA)	Enzymes studied	Observations/findings	References
19	Sandy loam	Field experiment, pre-emergent herbicides (atrazine 50% WP @ 1.0 kg a.i. ha^{-1}, pendimethalin 30% EC @ 1.0 kg a.i. ha^{-1})	Urease	Activity decreased in pendimethalin-treated soil more than atrazine	Kumari et al. (2018)
	Maize	Post-emergent herbicides (pendimethalin 30% EC @ 1.0 kg a.i ha^{-1}, topramezone 42% SC @ 105 g a.i. ha^{-1}, tembotrione 42% SC @ 105 g a.i. ha^{-1})			
	India	Topramezone + atrazine @ 25.2 + 250 g a.i. ha^{-1} and tembotrione + atrazine @ 105 + 250 g kg a.i. ha^{-1}			
		MA: the pre-emergent herbicides were sprayed at zero days after sowing where post-emergent herbicides were sprayed after 15 days after sowing			
20	Taian brunisolic soil	Soil (50 g, 0–20 cm) incubated for 2 weeks at 25 °C, mesotrione exposure at doses of 0.1, 1.0, and 5.0 mg kg^{-1}	B-glucosidase (βG)	U and AP activity is found relatively stable in mesotrione-treated soil compared to control, while βG activity was reduced in the 5.0 mg kg^{-1} treatment of mesotrione application	Du et al. (2018)
	China, Taian	MA: solution-based application	Urease (U)		
			Acid phosphatase (AP)		

5.3 Classification of Herbicides

The understanding and management of herbicide resistance equally demand the classification of herbicides in order to overcome the continuous problems in sustainable agricultural management (Sherwani et al. 2015). Herbicides are categorized into diverse groups based on their chemical families, method of application, mode of action, target site, timing of application, target specificity, selectivity, and translocation (Sherwani et al. 2015; Vats 2014).

5.3.1 Based on Mode of Application

Singh and Singh (2014) have described the herbicide application methodologies. This includes foliar spray, soil application, and broadcasting, either covering complete regime or spot spray masking the specified area. Sherwani et al. (2015) have advocated that herbicide mixing with soil is a traditional approach, while weed-specialized eco-friendly herbicide spraying is a modern practice followed in advanced agricultural sector. The soil-applied herbicides such as fluchloralin in contrast to the foliar spray-applied herbicides such as glyphosate and paraquat, act primarily on the plant foliage. Soil-applied herbicides often leave a greater amount of residual herbicide (Sopeña et al. 2009). Along with the weed specificity, planned emplacement of herbicides at an appropriate rate is pivotal. The higher the rate of absorption and retention, the lesser will be the volume of herbicides required, and the lesser will be the potency compared to their counterparts (Sherwani et al. 2015).

5.3.2 Based on Formulation

Herbicides are generally not applied in the form they get synthesized. The basic idea of different types of herbicide formulations with their pros and cons is to make their handling easier in terms of effectiveness, safety, adverse impact minimization on non-target organisms, stability, management, and application.

Herbicide formulations are usually prepared for commercial purpose in which active ingredients are supplemented with the adjuvants and surfactants to meet regulatory standards without compromising the potency of the active ingredients (Sopeña et al. 2009).

5.3.3 Based on Translocation

Based on translocation, the herbicides can broadly be classified into three major classes:

- Symplastically translocated (source to sink capable of downward movement), e.g., glyphosate, 2,4-D, sulfonylureas
- Apoplastically translocated (capable of only upward movement), e.g., glyphosate
- Contact herbicide, those which do not move appreciably (kill very quickly), e.g., paraquat

5.3.4 Based on Application Time

Preplant herbicides are mechanically incorporated into the soil before planting is done. Pre-emergent herbicides such as dithiopyr and pendimethalin are introduced into the soil prior to weed seedling emergence. Post-emergent herbicides are subjected to the soil only after emergence of weed seedlings through the soil and require multiple applications. For example, 2,4-D is a selective, systemic, foliar-absorbed post-emergent herbicide (Vats 2014).

5.3.5 Based on Mode of Action

Herbicides belonging to the same chemical family, tend to share similar mode of actions, although a few, assigned to different chemical class, depict the same mode of actions. Some of the common groups of herbicide and their mode of action are described below (Sherwani et al. 2015):

1. Group 1. Lipid biosynthesis inhibitors (fluazifop-*p*-butyl and sethoxydim) inhibit acetyl-CoA carboxylase, the enzyme required for biosynthesis of phospholipid bilayer which results into disruption of structural and functional integrity of the cell membrane.
2. Group 2. Amino acid biosynthesis inhibitors or acetolactate synthase (ALS), the largest group of inhibitors (imidazolinones, pyrimidinyl thiobenzoates, sulfonyl glyphosate, imazapyr, and imazapic), which prevent protein synthesis by inhibiting branch chain amino acids, causing plant wilting and ultimately death.
3. Group 3: Root growth inhibitors (benzamide, benzoic acid, dinitroaniline, phosphoramidate, and pyridine), which inhibit the cell division and ultimately check the root extension and growth.
4. Group 4. Synthetic auxins or plant growth regulators (2,4-D, clopyralid, picloram, and triclopyr) which mimic indole acetic acid (IAA), thus increasing the transcription, translation, and protein biosynthesis within the cell leading to

uncontrolled disorganized vascular growth, causing cell bursts and ultimately cell and plant death.
5. Group 5, 6, and 7. Photosynthesis inhibitors (hexazinone, triazine, triazinone, nitriles, benzothiadiazinones, paraquat, phenyl urea, and amides), which cause disruption of photosynthetic pathway, especially PSII.

5.4 Fate of Herbicides After Application in the Soil

Apart from the very small fraction of herbicides reaching the target organisms (Pimentel 1995), a large proportion of residual herbicides end up into the soil, water, and atmosphere or in the harvested produce, posing a potential threat to nontarget organisms, including crop produce and health of consumers (Kudsk and Streibig 2003; Singh and Singh 2014; Zabaloy et al. 2011). Once introduced into the soil, herbicides simultaneously dissipate and degrade, resulting into redistribution or transformation into other metabolites. Dissipation mechanism comprises of multiple complex processes such as volatilization, soil adsorption, runoff, and downward leaching. On the other hand, degradation constitutes three main processes, photodegradation, chemical degradation, and microbial degradation leading to partial or total degradation of herbicide (Gianfreda and Rao 2008; Rana et al. 2016). Large and repeated dose of herbicide application in modern agricultural practices is a major concern. It may cause risk to soil microbial diversity, alter soil enzymes and overall performance of soil microflora (Kumari et al. 2018).

5.5 Soil Enzymes

5.5.1 An Indicator of Soil Health

Soil quality is evaluated in terms of microbial diversity, activity, bulk density, porosity, stability, texture, infiltration, governing water and solute flow, buffering capacity, and carbon and nutrient cycling (Dexter 2004; USDA 2015).

Soil enzymes are among the most important soil biological indicators driving mineralization of organic matter and release of nutrients for plant and microbial growth (Jimenez De la Paz et al. 2002; Kızılkaya et al. 2004; Khan et al. 2009; Buturugă et al. 2016). Quick response to soil management changes and environmental factors also high sensitivity towards agrochemicals especially herbicides, make soil enzymes as healthy indicators. They can be measured using cost-effective simple methods based on short-term laboratory incubations. These attributes make soil enzymes more suitable soil health detector and indicator compared to other determinants (Nannipieri et al. 2002, 2012; Gianfreda and Ruggiero 2006).

5.5.2 Sources and Status of Enzymes in the Soil

Living and dead microorganisms are primary source of soil enzymes. Additionally, plant roots also contribute a small share to overall enzyme pool (Infinita Biotech 2019). Enzymes occur either accompanying viable microbes or soil fauna, the *biotic* form or as excreted enzymes, linked to nonviable cells or amalgamated with mineral colloids in *abiotic* manner. The latter class is also known as "soil-bound enzymes" or "naturally immobilized enzymes" (Dick et al. 2011; Gianfreda and Bollag 1996).

5.5.3 Indispensable Soil Enzymes

Soil is a dynamic resource with unprecedented treasures of enzymes such as oxidoreductases, hydrolases, isomerases, lyases, and ligases, catalyzing enumerable reactions related to energy and material conversion (Gu et al. 2009).

5.5.3.1 Oxidoreductase

The class comprises a cluster of enzymes (dehydrogenase, catalase, and peroxidase) involved in catalyzing oxidation reaction in the cell with the help of cofactors NAD^+/NADH and flavins ($FAD/FADH_2$).

Dehydrogenase (EC 1.1.1.). It is the most important enzyme found in all living microorganisms intracellularly (Moeskops et al. 2010; Zhao et al. 2010; Yuan and Yue 2012), and is used to assess the overall microbial activity in the soil (Quilchano and Marañón 2002; Gu et al. 2009; Salazar et al. 2011; Dotaniya et al. 2019). These enzymes transfer H^+ ions and electron on either the nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide phosphate (Gianfreda and Rao 2014) and thus play a major role in biological oxidation of soil organic matter (Sebiomo et al. 2011). Assessment of immediate soil microbial metabolic activities can easily be represented by measuring dehydrogenase activity (Nannipieri et al. 2002).

Catalase (EC1.11.1.6). An enzymatic antioxidant, capable of breaking down H_2O_2 into water and O_2 without generating free radical. These enzymes play a key role in soil fertility (Shiyin et al. 2004; Trasar-Cepeda et al. 2008).

Peroxidases (EC 1.11.1). Act as biological catalysts, mediated by free radical species generated while using H_2O_2 as an electron acceptor (Passardi et al. 2007). These serve as an important factor in biogeochemical processes, lignin degradation, H_2O_2 removal, oxidation of toxic substances, carbon mineralization sequestrations, and dissolved organic C export (Erman and Vitello 2002; Bach et al. 2013).

5.5.3.2 Hydrolases

A dominant class of extracellular enzymes (cellulases, glucosidases, phosphoesterases, sulfatases, amidases, urease, etc.) which mediate hydrolytic cleavage of complex macromolecules such as cellobiose, urea, and organophosphorus to provide smaller utilizable forms. *Cellulase* (endocellulase and exocellulase) hydrolyzes the glycosidic bonds of cellulose into simple, reasonable, and soluble sugar (Alvarez et al. 2013; Dotaniya et al. 2019).

β-glucosidase (EC 3.2.1.21). Catalyzes cellulose degradation, commenced with the breakdown of complex cellulose chain into smaller units involving endo-1,4-ß-glucanase (EC 3.1.2.4), followed by cellobiohydrolase (EC 3.1.2.91). The hydrolytic process is accomplished by the enzymatic action of β-glucosidase where 2 mol of glucose are extracted per mole of cellobiose (Turner et al. 2002). Thus it plays a vital role in C-cycle.

Urease (EC 3.5.1.5). Urease is produced by all the groups of microorganisms (Follmer 2008) that exist both as extracellular and intracellular forms (Mobley and Hausinger 1989). This enzyme hydrolyzes urea into ammonium and carbon dioxide (Byrnes and Amberger 1989; Mohammadi 2011; Fazekasova 2012; Zhang et al. 2014). This enzyme regulates N-cycle.

Phosphatase *alkaline* (EC 3.1.3.1) and acid phosphatase (EC3.1.3.2) hydrolyze ester-phosphate bonds of organic phosphorus and anhydrides of phosphoric acid into inorganic phosphorus accessible to plant and microbes and necessary for P cycling in P-deficient soil (Mohammadi 2011; Quiquampoix and Mousain 2005). It plays a major role in P-cycle.

5.6 Soil Enzyme and Herbicide Interaction

Floch et al. (2011) proposed soil enzyme activity as a sustainable indicator of pesticide effects on the soil. Herbicides are applied in agro-ecosystems to hit the target weeds and increase the harvest of desired crop but pose simultaneously a great threat to soil microbial community which eventually leads to the decline of the fertility of soils in agroecosystems. Herbicides may modify the interrelationships between different groups of organisms, thus making an impact on the amount and type of enzymes produced (Tripathi et al. 2005; Pandey et al. 2007a, b). Latha and Gopal (2010) reported a decline in the activity of enzymes when treated with substituted urea herbicides. While studying the dose response, Sireesha et al. (2012) examined increased enzyme activity at lower dose of herbicide application. Singh (2014) observed that overdose of pendimethalin was detrimental for soil enzymes as compared to low or medium dosages. Phenomenal changes in both qualitative and quantitative attributes of soil enzymes in response to herbicidal effects have been observed by many investigators (Sebiomo et al. 2011; Xia et al.

2011; Nikoloff et al. 2013). A number of similar studies consolidated that herbicides behave as enzyme inhibitors (Tejada 2009; Sofo et al. 2012; Vlădoiu et al. 2015).

5.6.1 Dehydrogenase

Baruah and Mishra (1986) conducted incubation studies to examine the influence of three post-emergent herbicides, namely, 2,4-D, butachlor, and oxyfluorfen on dehydrogenase activity with recommended doses in paddy field that constitutes sandy loam soil. They observed that peak rate of dehydrogenase activity followed a trend as follows: 2,4-D > oxyfluorfen > butachlor. Dehydrogenase activity increased with time for the first 7 days and then decreased in subsequent days. Abbas et al. (2015) noted 36% decline in dehydrogenase activity subjected to bromoxynil. Baboo et al. (2013) studied transitory impacts on types and rate of herbicides such as butachlor, pyrazosulfuron, paraquat, and glyphosate on microbial populations and dehydrogenase. Sireesha et al. (2012) conducted a field study for two seasons and found strong link between herbicide treatments and period of their interaction influencing soil enzymes. They reported that with the application of pendimethalin and oxyfluorfen, dehydrogenase activities increased and attained their peak at 30 DAA. They also noted that lower doses of herbicides enhanced the dehydrogenase activity. Tu (1992) conducted laboratory experiment using atrazine, butylate, ethalfluralin, imazethapyr, linuron, metolachlor, metribuzin, and trifluralin, applied to a loamy sand at a rate of 10μg g^{-1}, and reported that the soil dehydrogenase activities were lowered by ethalfluralin application for 1 week. Min et al. (2001) observed gradual increase in dehydrogenase activity in butachlor-treated fluvo-aquic paddy soil, and the enzyme activity showed linearity and attained the maxima on Day 16th following exposure to 22.0 mg g^{-1} butachlor. Zhang et al. (2014) in 60-days incubation experiment with clay and loamy soils showed dehydrogenase activity to be more sensitive to fomesafen compared to acid and alkaline phosphatase and urease. Dehydrogenase activity increased appreciably on Day 10th after herbicide application. Juan et al. (2015) measured the response of soil microbial biomass and enzyme activity to mesotrione, a triketone herbicide. When applied at 50 mg/kg, it escalated soil biomass but reduced the dehydrogenase activity. Dehydrogenases which generally do not accumulate in the extracellular environment received more attention of researchers in response to mesotrione. The activity drops initially but get stimulated in due course of time. Hang et al. (2001), Crouzet et al. (2010), Kaczynska et al. (2015), P. Juan et al. (2015), and Kaczynski et al. (2016) observed dose dependence of dehydrogenase and butachlor. Vandana et al. (2012) in a field experiment reported that butachlor and cyhalofop-butyl when applied at the rate of 1 kg ha^{-1} at 30, 45, and 60 days after transplanting (DAT) enhanced the dehydrogenase activity. Nadiger et al. (2013) also showed dehydrogenase activity at 20 and 40 days after sowing (DAS) in response to pendimethalin and oxyfluorfen when applied at the rate of 0.1 kg ha^{-1}, respectively. Borowik et al. (2016) performed a pot culture experiment using a mixture of three active ingredients of herbicide, Lumax 537.5 SE:

terbuthylazine (T), mesotrione (M), and S-metolachlor (S), using 2,3,5-triphenyltetrazolium chloride (TTC) as a substrate for dehydrogenase. The mixture did show largest variability (83%) in dehydrogenase activity on Day 60. Baćmaga et al. (2014) reported that metazachlor negatively influences dehydrogenases, catalase, urease, acid and alkaline phosphatase, arylsulfatase, and β-glucosidase. Similarly Muñoz-Leoz et al. (2011) found β-glucosidase activity to be negatively influenced by tebuconazole. Contrary to this, stimulating effect on β-glucosidase activity in response to chloroacetanilide herbicides (alachlor, butachlor, and pretilachlor) has been observed by Saha et al. (2012). Wyszkowska et al. (2016), using Eutric Cambisols-filled pot culture experiment, demonstrated dose dependence and persistence effect of pethoxamid (P) and terbuthylazine (T) mixture, with the half-life of 6.1–14.2 days and 5–116 days, respectively, on dehydrogenase activity. Even the smallest dose (0.73 mg P + T kg^{-1}) of soil destabilized enzyme. Higher doses (14.63–468.16 mg P + T kg^{-1}) inhibited the activity by 90.56%. Sebiomo et al. (2011) conducted incubation studies for dehydrogenase responses to four herbicides (atrazine, primeextra, paraquat, and glyphosate). A significant decrease in DHA was observed with values being lowest at 9.02μg (g^{-1} min^{-1}), 12.55μg (g^{-1} min^{-1}), and 16.09μg (g^{-1} min^{-1}) in response to primeextra after second, fourth, and sixth week of treatment, respectively. The highest DHA of 14.32μg (g^{-1} min^{-1}) was recorded after fourth week compared to other treatments. The enzyme exposed to glyphosate was found to be the highest 20.16μg (g^{-1} min^{-1}) after sixth week. A. Kumar et al. (2017) explained the effect of post-emergent herbicide tembotrione soil dehydrogenase. They observed a decrease in DHA at higher doses from 20 to 60 DAS. This was followed by a drastic increase on 60th to 100th Day in all the treatments. Tejada (2009) studied the effects of glyphosate, diflufenican, and a combination of these on dehydrogenase activity. He observed that all the three treatments declined the enzyme activity. The highest decline (37.3%) was recorded in respect of herbicide mixture followed by 35.7% for diflufenican and 32.2% for glyphosate.

5.6.2 Urease

Baruah and Mishra (1986), in an incubation study, examined the influence of recommended doses of three post-emergent herbicides, namely, 2,4-D, butachlor, and oxyfluorfen on urease activity and found no significant effect. Abbas et al. (2015) noticed a 30% decline in urease activity subjected to bromoxynil exposure. Baboo et al. (2013) established a transient effect of types and dose of herbicides butachlor, pyrazosulfuron, paraquat, and glyphosate on microbial populations and urease activity. Kumari et al. (2018) remarked a decline in urease activity on treatment with pre-emergent herbicides atrazine and pendimethalin. The effect was more severe due to pendimethalin in a 60-day incubation experiment. Zhang et al. (2014), unlike positive response on phosphatase and dehydrogenase, showed a remarkable decline in urease activity on Day 10th in response to fomesafen. Du

et al. (2018), in another incubation experiment to study the effect of mesotrione exposure, found no effect on urease activity except a mild initial increase. Borowik et al. (2016) observed the largest variability (89%) in urease activity on Day 60 under exposure of herbicide mixture. They reported over 50% decrease in urease activity at 53.768 mg T + M + S. Wyszkowska et al. (2016) showed adverse effect of a mixture of pethoxamid (P) and terbuthylazine (T) on urease activity. They found that even small dose 0.73 mg P + T kg^{-1} could influence the enzyme activity and higher doses (14.63–468.16 mg P + T kg^{-1}) significantly inhibited the activity. Tejada (2009) noted 83.4%, 67.1%, and 58.2% decline in urease activity in response to glyphosate + diflufenican, diflufenican, and glyphosate.

5.6.3 Phosphatase

Bromoxynil application causes a decline in microbial population and consequently 34% reduction in alkaline phosphatase activity (Abbas et al. 2015). Sireesha et al. (2012) used reddish crop to establish connections between herbicide treatments and period of their interaction. They observed that application of pendimethalin and oxyfluorfen causes a decline in acid and alkaline phosphatase activities. Zhang et al. (2014), to show the response of acid and alkaline phosphatase against fomesafen (a diphenyl ether herbicide), conducted a laboratory experiment using clay and loamy soil. Both acid and alkaline phosphatase activities increased significantly on Day 10th after fomesafen treatments although the effect on alkaline phosphatase was relatively mild. Du et al. (2018) in their 20-day laboratory experiment determined the impact of mesotrione on acid phosphatase. They did not observe significant effect at experimental concentrations. Similarly, Aurora 40 WG (carfentrazone-ethyl) did not show negative effect on acid phosphatase (Baćmaga et al. 2014). Rao et al. (2012) showed the response of phosphatase to oxadiargyl, the activity being highest at 0.75 kg ha^{-1} and lowest at 1.5 kg ha^{-1}. Some investigators (Sukul 2006; Yu et al. 2006) unanimously believe a decline of acid phosphatase activity on herbicide application. Majumdar et al. (2010) showed that manual weed control promotes acid phosphatase activity. Borowik et al. (2016) in their pot culture experiment used 4-nitrophenyl phosphate disodium PNPP as a substrate for phosphatase to assess the effect in response to soil contamination with a mixture of three active ingredients of the herbicide Lumax 537.5 SE: terbuthylazine (T), mesotrione (M), and S-metolachlor (S). On Day 30, they observed highest decrease in alkaline phosphatase and acid phosphatase. In another pot culture experiment, the activities of alkaline and acid phosphatase declined by the P + T mixture where the duration of persistence brought 0.54% and 25.99% variability in alkaline and acid phosphatase activity, respectively (Wyszkowska et al. 2016).

5.6.4 β-glucosidase

β-glucosidase activity in the soil is sensitive to herbicide and varies with concentration and incubation period and soil status prior to, during, and post-application period (Hussain et al. 2009). Saha et al. (2012) noted higher β-glucosidase activity in the soil treated with pre-emergent herbicides, butachlor and pretilachlor. Latha and Gopal (2010) observed that soil application of pyrazosulfuron, butachlor, and pretilachlor at a rate 100 times the field rate inhibited β-glucosidase by 16.21%, 21.32%, and 10.09%, respectively. At the field rate, the respective decline was only 5.64%, 7.47%, and 3.59%. On the contrary, Sofo et al. (2012) found increased activity of β-glucosidase in response to triasulfuron applied at tenfold higher than the field rate. Santric et al. (2014) observed 5.6–29.4% rise in the response of β-glucosidase activity to nicosulfuron, a sulfonyl urea herbicide, at two elevated doses (3.0 and 30.0 mg) after 7–14 days of exposure. Borowik et al. (2016) conducted a pot culture experiment using *p*-nitrophenyl-β-D-glucopyranoside (PNG) as a substrate to find β-glucosidase activity. The activity reduced by 92% in response to terbuthylazine (T), mesotrione (M), and S-metolachlor (S). Kucharski et al. (2016) showed that dehydrogenase, catalase, urease, arylsulfatase, and β-glucosidase activities declined with soil application of Boreal 58 WG 40 mg kg^{-1}. In a pot culture experiment, Wyszkowska et al. (2016) used Cambisols soil and concluded that the sensitivity of enzymes can be ranked as dehydrogenases > acid phosphatase > urease > alkaline phosphatase > β-glucosidase > arylsulfatase > catalase. Tejada (2009) used two soil types (Vertic Chromoxerert and Typic Haploxeralf with 575 g kg^{-1} and 161 g kg^{-1} clay content, respectively) to study the effect of herbicides on enzyme activity. Soil treatments with glyphosate + diflufenican, diflufenican, and glyphosate reduced enzyme activity by 7.2%, 5.8%, and 4.6%, respectively.

5.6.5 Catalase

Wyszkowska et al. (2016) noted a 21% decrease in catalase activity in response to 468.16 mg kg^{-1} dose of a mixture of pethoxamid (P) and terbuthylazine (T). Borowik et al. (2016) tested the effect of three active ingredients of herbicide Lumax 537.5 SE on the activity of catalase in maize crop and found that the mixture inhibited the activity strongly. About 43% variability in the activity was observed depending on the dose of mixture applied.

Perucci and Scarponi (1994) investigated the effects of imazethapyr, an imidazolinone derivative, on catalase where they observed no adverse effect in the activity at field rate (50 g a.i. ha^{-1}) for soybean weeding. The laboratory treatment at 10-fold and 100-fold higher than the field rates, catalase activity increased.

5.6.6 *Arylsulfatase*

This enzyme hydrolyzes sulfate ester bonds in the extracellular soil environment (Kertesz and Mirleau 2004). Wyszkowska et al. (2016) reported 14.95% decline in arylsulfatase which is relatively less compared to 90.56% decline in urease activity in response to pethoxamid (P) and terbuthylazine (T). Tejada (2009) observed a decreasing trend in the inhibition of arylsulfatase in response to glyphosate + diflufenican followed by diflufenican and glyphosate.

5.7 Factors Affecting Soil Enzyme-Herbicide Interactions

Soil microbial community, soil enzyme activity, and many soil physical chemical properties are influenced by the concentrations and toxicological response variability of herbicides and factors such as climatic variables, soil organic matter, soil texture, temperature, available soil moisture, and pH (Haney et al. 2000; Schreffler and Sharpe 2003). Management practices such as crop type, cultivation system and fertilization, or pesticide application also influence enzyme-herbicide interactions.

5.7.1 *Temperature*

Response of soil dehydrogenase activity (DHA) to temperature has been explored by a large number of researchers. Wolińska and Stępniewska (2012) have reported that dehydrogenase activity increases with increase in temperature unless it reaches to the level of denaturation. Brzezińska et al. (1998) propounded similar results about soil DHA stating that the enzyme activity can be optimized at 28–30 °C under laboratory conditions. Kumari et al. (2018) using Alfisols and Vertisols, incubated at different temperatures ranging from 20 to 70 °C, demonstrated temperature maxima of 70 °C for urease activity. They further studied Alfisols and Vertisols, in temperature ranging from 20 to 90 °C, and observed that acid phosphatase activity increased in temperature range of 20–70 °C and thereafter declined on further rise in temperature. Steinweg et al. (2012) found that β-glucosidase activity remained stable at 15, 25, and 35 °C. Herbicide application with highest efficacy and appropriate temperature and timing favorably influence absorption, translocation, and metabolic degradation of herbicides. Thus a combination of optimum temperature ranges and weed size synergistically influences the herbicide performance. Studies show very obvious effect of growth temperature before, during, and after herbicide application. Ganie et al. (2017) have illustrated that 2,4-D and glyphosate should be applied during warmer days ($>$20 or $\approx$29 °C) for better efficiency. According to "Leaders in Farming Technology (2020)," temperature drop is an important issue for weeds to absorb herbicides, very similar to plants facing difficulty in nutrient mobilization at

low temperature. Atienza et al. (2001) reported that with a rise in temperature from 5 to 25 °C, the extent of triallate, a pre-emergent selective herbicide dissipation, increases from 14% to 60% in sandy soil and 5–25 °C in loamy soil. Thus, temperature is an important regulator of condition that determines herbicide sensitivity of soil enzymes.

5.7.2 Soil Moisture

Baldrian et al. (2011) observed strong correlation between acid phosphatase activity and soil moisture in horizons L and H both during spring and late summer. However, for other extracellular enzymes such as laccase, Mn-peroxidase, endo-1,4-ß-glucanase, endo-1,4-ß-xylanase, cellobiohydrolase, ß-glucosidase, ß-xylosidase, and chitinase. The correlations were case specific. Sardans and Penuelas (2005) found diminished soil enzyme activities together with fewer microbial biomasses during dry periods in forest soils. Criquet et al. (2000) and Criquet et al. (2004) observed that phenoloxidase, glucosidase, acid phosphatase, urease, and protease activities declined in dry seasons, and that was later endorsed by Sardans and Penuelas (2005). Criquet et al. (2000) found Mn-peroxidase activity in evergreen oak litter during moist season only. Steinweg et al. (2012) observed increased sensitivity of soil moisture to β-glucosidase in drought-treated plot. Zhang et al. (2001) have shown that efficiency of preplant-incorporated (PPI) imazethapyr (a broad-spectrum herbicide) on barnyard grass and red rice was reduced in response to high soil moisture condition, although post-emergent imazethapyr efficacy remained unaltered. Upchurch (1957) analyzed the response of cotton to diuron, DNBP, and CIPC herbicides under variable soil moisture conditions. He concluded that soil moisture had no absolute effect but a large relative effect on phytotoxic properties of diuron. Geisseler et al. (2011) reported that enzyme activity declines on reduction of soil moisture potential. Quilchano and Marañón (2002) did show that soil moisture content is positively correlated with dehydrogenase activity.

5.7.3 Soil Organic Matter

There exists very intimate relationship among soil enzyme activities, microbial population, and soil organic matter content. Bhavya et al. (2017) experimented with different cropping systems, namely, mango, cashew, vegetables, rose, and medicinal and aromatic plants at varying soil depths (0–15, 15–30, 30–50, 50–100 cm) in sandy loam setup. The highest organic carbon content (OCC) was found to be 6500.00 mg kg^{-1} at 0–15 cm, and with the increase in depth, OCCs decreased by 6316.00 mg kg^{-1}, 5846.00 mg kg^{-1}, and 4611.00 mg kg^{-1} at 15–30 cm, 30–50 cm, and 50–100 cm, respectively, obtained in mango orchard followed by cashew orchard. Medicinal and aromatic plant soil held less OCC as

4300.00 mg kg^{-1}, 3916.00 mg kg^{-1}, 3834.00 mg kg^{-1}, and 3786.00 mg kg^{-1} at 0–15 cm, 15–30 cm, 30–50 cm, and 50–100 cm, respectively. The highest dehydrogenase and urease activity 650.84μg g^{-1} soil triphenyl formazan (TPF) and 1230μg g^{-1} soil *p*-nitrophenol (PNP), respectively, was recorded in mango orchard, followed by cashew orchard (9624.64μg TPF g^{-1} soil and 1246μg PNP g^{-1} soil), rose (426.48μg TPF g^{-1} soil and 840.34μg PNP g^{-1} soil), vegetables (421.44μg TPF g^{-1} soil and 821μg PNP g^{-1} soil), and medicinal and aromatic block (418.14μg TPF g^{-1} soil and 800μg PNP g^{-1} soil). Dehydrogenase and urease activity varied with soil depth. The topsoil layer (0–15 cm) was richest in dehydrogenase and urease enzyme activity with the increase in depths; enzyme activities declined irrespective of crop systems. Sondhia (2005) elucidated that butachlor with half-life of 18.1–23.0 days rapidly dissipated under field condition under the influence of soil organic matter and moisture. Sondhia (2014) showed that physical, chemical, and biological properties of soil are influenced by organic manuring, which, in turn, determines the fate of herbicides.

5.7.4 Soil pH

Martínez and Tabatabai (2000) observed a proportional increase in all the 13 study enzymes with a rise in soil pH except acid phosphatase which showed a declining trend. The sensitivity of enzymes to soil pH did appear in the following order: L-glutaminase > alkaline phosphatase > phosphodiesterase > β-glucosidase > acid phosphatase > L-asparaginase > amidase > arylsulfatase > arylamidase > -β-galactosidase > urease > α-galactosidase > α-glucosidase > L-aspartate. Shuler and Kargi (2010) conceptualized that pH influences soil enzymes either by modifying their 3-D shape, altering substrate-enzyme affinity, or by changing active sites. Quilchano and Marañón (2002) and Moeskops et al. (2010) contemplated pH as an important factor influencing soil enzymes. Włodarczyk et al. (2002) observed pH 6.6–7.2 to be the optimum range for dehydrogenase activity.

5.7.5 Soil Texture, Type, and Depth Profile

Stotzky (1985) affirmed that soil textural property can be a key determinant of microbial ecology. Microbial biomass and activity regulating soil moisture content, nutrient translocation, and soil pH are affected by soil texture (Gorres et al. 1998; Leirós et al. 2000). Roy and Singh (2006) described residue retention of clodinafop (0.093–0.081μg g^{-1}) in alluvial, red, and black soil. Martínez et al. (2003) studied the effect of texture of Amarillo soil, Estacado loam, Acuff soil, and Patricia soil containing different ratios of clay, silt, and sand at various soil depth on activities of arylsulfatase, β-glucosidase, β-glucosaminidase, phosphodiesterase, arylamidase, and acid and alkaline phosphatase. The lowest enzyme activity was recorded in

Patricia soil, containing 85% sand and 10% clay, whereas the highest activity was recorded in Estacado loam containing 21% clay and 59% sand. In general, the enzyme activities declined with depth, and the effect was more pronounced in β-glucosidase and arylamidase. Landgraf and Klose (2002) stated that enzyme activities were 1.5-fold higher at 0.5 cm depth than those at 15–30 cm. Quilchano and Marañón (2002) did show positive correlation of clay content with DHA. Clay is fine microporous textured soil that harbors and protects mineralizing microbes from grazers. Therefore, it supports high microbial biomass and higher enzyme activity. Wolińska and Stępniewska (2012) incubated soil samples enriched with glyphosate to see the effect of Mollic Gleysol, Eutric Fluvisol, and Terric Histosol on DHA. The enzyme activity declined in response to pesticides in both the soil samples. At 10μg g^{-1} of glyphosate, the enzyme activity declined by 33–47% in Eutric Fluvisol and Terric Histosol. Tejada (2009) studied dehydrogenase, urease, phosphatase, β-glucosidase, and arylsulfatase in response to glyphosate, diflufenican, and in combination of these. All the enzymes responded negatively to these treatments, and the effects were severe in Typic Haploxeralf soil relative to Vertic Chromoxerert having 161 g kg^{-1} and 575 g kg^{-1} clay content, respectively.

5.7.6 *Heavy Metal Amendment*

Chemical contaminants pollute soil in complex mixtures rather than as an individual. The abundance, diversity, and distribution of soil organisms are affected by heavy metals. Earthworms in the soil are more sensitive to heavy metals compared to other terrestrial organisms. Uwizeyimana et al. (2017) studied the response of earthworms to pesticides and heavy metals. Pesticides such as atrazine exaggerated the toxic effects of Cd on earthworm. It is supposed that soil fertility is reduced with the decreased number of earthworms as they are assumed to be the key determinant of soil fertility. More than 50% surveyed literatures show synergistic effects of pesticides and heavy metals at higher concentrations.

5.7.7 *Cultivation System*

Martínez et al. (2003) evaluated the response of acid and alkaline phosphatase activities under four cultivation practices, namely, conservation reserve program (CRP), native rangeland (NR), cotton-cotton conventional tillage (Cv), and cotton-wheat conservation tillage (Cs). The authors observed three to five times higher microbial biomass and enzyme activities under CRP and NR compared to Cv probably due to scarcity of residues during spring and winter season. Other studies reveals that crop rotation promotes enzyme activity under CPR and NR much higher than conventional tillage (Ekenler and Tabatabi 2002; Martínez et al. 2003). Reduced tillage cultivated under various crop and rotation systems consolidate

greater diversity of aerobic microbes, facultative anaerobes, and denitrifiers (Franzluebbers 1996; Angers et al. 1997). This probably supports greater microbial biomass responsible for increased soil enzyme activity.

5.7.8 *Fertilizer and Pesticide Treatment*

Martínez and Tabatabai (2000) explored the impact of lime application on soil pH and enzyme activities. The activity of all the 14 enzymes (α- and β-glucosidases, α- and β-galactosidases, amidase, arylamidase, urease, L-glutaminase, L-asparaginase, L-aspartate, acid and alkaline phosphatases, phosphodiesterase, and arylsulfatase.) increased from 4.9- to 6.9-fold after 7 years of lime application on Kenyon loam soil. Geisseler et al. (2011) concluded that organic residues play important role in regulating extracellular enzymes. Mohammadi (2011) monitored changes in the activities of soil dehydrogenase, acid and alkaline phosphatase, and urease in response to different farmyard manure (N1), compost (N2), and chemical fertilizers (N3);[(N4) = N1 + N2]; [(N5) = N1 + N2 + N3]. All the treatments enhanced the enzyme activities with values being the highest in N4 treatment and lowest in the N1-treated cropland. Singh and Ghoshal (2013) in 2 years of study evaluated the effect of butachlor independently or in combination with soil amendments on β-glucosidase, alkaline phosphatase, and urease in a rice-wheat summer unplowed crop-rotated agroecosystem. β-glucosidase and phosphatase activities were recorded highest under a combination of HC + wheat straw, followed by HC + FYM, HC + sesbania shoot, HC + chemical fertilizer, and HC + control. The urease activity declined under all the treatment mixtures excluding herbicide + wheat straw.

5.8 Conclusions

Soil application of herbicides has dramatically increased the crop yields by eliminating the weeds. However, it has levied a high environmental cost in terms of damages to water and soil environment. Soil enzymes, the major drivers of soil fertility, despite being a nontarget group, are invariably influenced by soil-herbicide interactions. A critical analysis of available literatures shows that although herbicides' interaction with certain enzymes may render stimulatory effects, most of the soil enzymes respond negatively. Here, we identify soil dehydrogenases and urease with strong negative effect of herbicides at higher dose. Enzymes such as acid and alkaline phosphatase, protease, and catalase are least affected due to herbicides' application. The magnitude of these responses, however, differs subject to edaphic and climatic variables that influence microbial communities in the soil. Here, we conclude that because the enzymes are intrinsic attributes of soil fertility, there is need to minimize the negative influence of herbicides on soil enzymes. Therefore, further studies need to be oriented to explore herbicide-specific changes in microbial

community structure and function in the soil. This will help screening novel agronomic practices that can support desired microbial communities for maintaining soil fertility under case-specific herbicidal treatments.

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