Effects of Agrochemicals on Soil Microbial Enzymes

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Abstract This chapter considers the effects of agrochemicals (pesticides and fertilizers) on microbial enzymes (fluorescein diacetate hydrolases, acid phosphatases, alkaline phosphatases, phosphatases, β-glucosidases, cellulases, ureases, and arylsulfatases). The pesticides considered include fungicides, insecticides, and herbicides. Soil is not a mass of dead debris, arising from physical and chemical processes of soil formation, but is a mixture of decomposed plant and animal remains. Microbial enzymes in the soil aid in the recycling of carbon and nutrient assimilation. The cell control mechanisms of nutrients, coupled with carbon, nitrogen (N), and phosphorous (P) uptake, trigger biomass growth and increase the rate of enzyme synthesis and secretion. The impacts of agrochemicals on microbes and their extracellular enzymes are generally known to be unpleasant. These impacts include, but are not limited to, destruction of microbial habitats, ecological succession, reduction of microbial communities, development of new strains, and multiple drug-resistant microbes. These effects may result in increased pathogenic activities, reduction in soil fertility, high soil acidity, eradication or reduction of the natural flora of a particular ecology (both flora and fauna), low crop yield, etc.

1 Introduction to Agrochemicals

Agrochemicals, in general are referred to as products that include fertilizers, fungicides, insecticides, nematicides, etc., which enhances plant growth (Biswas et al., 2014). Over the last few decades, a large amount of chemicals have been used in agriculture to increase the production of crops in both developed and developing

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countries (Tan et al., 2020). Crops tend to grow, slowing with inadequate provision of the right nutrient. Hence, to overcome these problems, agrochemicals are applied with their best modified and oriented results. These are chemicals used mainly in agriculture to aid crop growth and safety. They are applied in various practices of the farming sector such as crop shifting, poultry, dairy farming, commercial farming, horticulture, etc. (Princy & Prabagaran, 2020).

Agrochemicals are produced to protect agricultural crops from pests and for increasing crop yields. They are inorganic fertilizers and pesticides that provide benefits and manage the agricultural ecosystem. The continuous use of pesticides has affected the entire ecosystem and also the microorganisms in soil (Onder et al., 2011). Weeds and insects are the main reducing biotic factors in agriculture; they reduce crop yield, resource use efficiency, and productivity (Oliveira et al., 2014). Agrochemicals are usually harmful and may cause major environmental risks.

Different researchers have proven the adverse effects of agrochemicals on soils and ecosystems at large and consider them a matter of major concern that needs attention especially because of their studied impacts on pathogens, fertility, microorganisms, and enzymes (Mergel et al., 1998; Nannipieri et al., 2008; Steinauer et al., 2016; de Vries et al., 2019; Perucci et al., 2000; Vischetti et al., 2000, 2002; Puglisi et al., 2005, 2012; Nannipieri et al., 2012; Sofo et al., 2012; Suciu et al., 2019). Although the results varied in some aspects, the major negative impacts were clearly stated and explained. According to Boivin and Poulsen (2017), it has become mandatory that in most countries any pesticide must be authorized before use, in which case, before authorization, a risk assessment procedure must have been conducted to ascertain its safety for nontarget organisms. The reason for the risk assessment comes from the high rate of the adverse effects of pesticides and other agrochemicals on the ecosystem, which is quantifiably related to different concentrations of their use in a particular environment (Desneux et al., 2007; Beketov et al., 2013; Brühl et al., 2013; Wood & Goulson, 2017).

2 Types of Agrochemicals

Agrochemicals are widely used in farming activities; they are known as pesticides, which include herbicides, insecticides, fungicides, nematicides, rodenticides, and molluscicides. Agrochemicals also include fertilizers and soil conditioners.

2.1 Pesticides

Pesticides are substances used for preventing, repelling, destroying, reducing, or eliminating damages caused by pests (Eldridge, 2008). They are used to control some types of organisms known as pests, which are harmful to cultivated plants and animals. They mostly work through poisoning of pests. Pests can be insects, plant pathogens, weeds, and microbes that compete with humans for food, destroy properties, and carry or help spread diseases. Most commonly, they are used in health sectors and for agricultural crops (Yadav et al., 2015). Naturally, pesticides may generally become harmful to other nontarget organisms, including humans. Therefore, it is important to be careful when handling them and they must be safely disposed.

2.2 *Insecticides*

Insecticides are commonly used to protect households, restaurants, hospitals, farms, forest plantations, etc. from insects. These substances offer protection from harmful insect-borne diseases, insect pests in warehouses, and agricultural and forest pests (Cardoso & Alves, 2012). In general, they are used to destroy insects. Insecticides can be ovicides that kill eggs or larvicides that kill larvae. They are categorized based on their mode of action and structure. Many insecticides act on the insects' nervous system (e.g., cholinesterase inhibition), whereas others act as growth regulators or endotoxins (Relyea, 2005).

2.3 *Herbicides*

Weeds have been known to affect human activities, especially in agriculture, since ages. The growth of these weeds can be controlled with the use of pesticides. Herbicides are chemicals used to manipulate or control undesirable vegetation (Belden & Lydy, 2000). They are generally applied to control or kill plants, weeds, and herbs. Their application occurs more frequently in row crop farming where they are applied before or during planting to maximize crop productivity by minimizing other vegetation. Herbicides can act by inhibiting cell division, photosynthesis, or amino acid production by mimicking natural plant growth hormones that cause deformities (Ross & Childs, 1996).

2.4 *Fertilizers*

Fertilizers are materials of synthetic or natural origin that are applied to plant tissues or soil with the aim of supplying the needed nutrients. Many sources of fertilizers exist naturally or are industrially produced (Scherer et al., 2009). These are compounds used for enhancing plant development; they add the needed nutrients to the soil and eliminate nutrient deficiency. For most modern agricultural practices, fertilization focuses on three major macronutrients, namely, nitrogen, phosphorous, and potassium, with the occasional addition of supplements for micronutrients (Scherer et al., 2009). Fertilizers can be categorized into two types: organic and

Table 1 Agrochemicals and active ingredients (Lamberth et al., 2013; Jeschke 2016; Hamilton 2001)

Agrochemicals	Active ingredients
Insecticides	Abamectin, cyfluthrin, fipronil, deltamethrin, permethrin, bifenthrin, and pyrethrum
Herbicides	Atrazine, butachlor, dithiopyr, flufenacet, isoproturon, and chlorimuron
Fungicides	Captan, dinocap, pyrimethanil, quinoxyfen, iprodione, fenarimol, and azoxystrobin
Nematicides	Chloropicrin, 1,3-dichloropropene, dimethyl disulfide, allyl isothiocyanate, and oxamyl
Fertilizers	Nitrogen, phosphorus, potassium, magnesium, and calcium

inorganic fertilizers. Organic fertilizers are naturally existing substances prepared through natural processes. Inorganic fertilizers, also called synthetic fertilizers, are manufactured artificially using chemical processes (Table 1).

2.5 Soil Conditioners

To keep all soils in good conditions, the best thing to do is to add things that help keep it in good conditions. These good things are called soil conditioners that include manures, composts, peats, livestock manures, and leaves. Conditioners are products applied to the soil to improve soil properties and to control erosion (Baumhardt & Blanco Canqui, 2014). Soil conditioners boost the water holding capacity and aeration of the soil. Some of the conditioners used to reduce water erosion include polyacrylamide (PAM), phosphogypsum, flue gas desulfurization (FGD) gypsum, etc.; all these conditioners are laid on the soil and then mixed. Conditioners are not a substitute to soil conservation practices, but they should be used as companions to other practices (Baumhardt & Blanco Canqui, 2014).

3 Importance of Agrochemicals

If agrochemicals are handled with care, they will produce fruitful results. Crop protection solutions allow growers in crop production processes to increase output and crop yield. As weeds, pests, and diseases have an impact of up to 30% on the future crop production worldwide, food production will deteriorate without crop protection chemicals (Princy & Prabagaran, 2020). The benefits of agrochemicals are not limited to growing crop yields. Agrochemicals are also used to prevent the negative impacts caused to society in many ways; for example, trees and weeds growing under power lines when left unchecked would result in power outages (Sharma et al., 2019). Herbicides are also widely used to control unwanted vegetation along national highways, roadsides, in parks, and in other public areas to ensure public safety and convenience. In food processing, insecticides are used in permissible levels to protect raw commodities and packaged groceries from insects infesting during the processing, manufacturing, and packaging stages. Pesticides are also used in homes for controlling insects and pests (Sharma et al., 2019).

4 Environmental Impacts of Agrochemicals

Along with having positive impacts, the negative impacts of agrochemicals are becoming clear. The uses of agrochemicals pose threats and cause harm to the ecological balance and environment. These agrochemicals cause pollution; they enter water bodies and kill many fishes (Aktar et al., 2009). During many uses of pesticides in agriculture, their exposure to other organisms, including humans, is not well controlled, which then causes several problems. Pesticides keep accumulating in soil residues and cause biomagnification in plant and animal tissues; this is dangerous to humans and can cause health problems (Hans & Faroq, 2000). Microorganisms become resistant to pesticides, which is a serious issue. In general, the effects of pesticides will vary depending on the chemical dosage, various environmental factors, and the properties of the soil.

Agricultural runoffs often contain developed levels of heavy metals from fertilizers and other agricultural chemicals applied to the fields. These chemicals are washed away with rainfall runoffs into rivers, streams, and reservoirs, thus polluting water bodies and modifying aquatic habitats (Ogbodo & Onwa, 2013). There could be potential damage to soil organisms from high concentrations of agrochemicals. The effects of agrochemicals can be either direct (immediate or short-term impacts), due to the harm to organisms that come in contact with the chemicals, or indirect due to changes caused by the chemicals to the environment or food source of the organisms (Ogbodo & Onwa, 2013). The direct effects of these chemicals can be short, obvious in the first season after application of the fertilizer or in the long term if repeated addition has taken place. The indirect effects may be long term; they may take up to one season or more to build up due to soil organic matter levels, changes in productivity or pH, and residue inputs (Bunneman & McNeil, 2004). Nitrate pollution has been reported to be a result of excessive use of fertilizers. Nitrate is a chemical compound that is toxic to animals and humans if exposed to high concentrations (Princy & Prabagaran, 2020).

5 Soil Microbial Enzymes

Soils home a vast majority of microbes that are accountable for the disintegration of organic matter and the mobilization of nutrients. Microbes in soil have the highest genetic diversity, and they participate in maintaining the functionality of plant diversity and other various important processes in the ecosystem (Zhang et al., 2018). Living organisms in the soil are grouped into two types, viz. soil and soil fauna. Soil is not an inert stable material but is a medium that supports life. Soil is dynamic in nature; it is composed of a mass of dead debris of plant and animal remains. Soil structure and fertility are aided by soil microorganisms; this is one of the major microbial activities that take place in the formation of soil. Microorganisms in soil can be grouped as bacteria, actinomycetes, fungi, algae, and protozoa. Each of these groups possesses characteristics and functions that determine the group they belong to in soil.

5.1 Soil Faunas

These include invertebrates that contribute to the breaking of organic matter and the presupplying of nutrients to microorganisms by reducing the size of the organic matter in the process of feeding. Apart from increasing the surface area, faunas promote bioturbation of litters and also enhance formation of soil enzymes (Rao et al., 2017). Microbial communities in soil correspond to soil biogeochemical processes and play a vital role in soil nutrient cycles and turnover (Zeng et al., 2016). Biochemical processes contribute to direct changes in the soil microbial community structure, which may affect microbial functions and population (Sekaran et al., 2019b).

5.2 Soil Enzymes

These are responsible for the biochemical activities of organic matter transformation in the soil processes, such as soil physical properties, microbial activity, and nature of biomass. Enzymes can be extracellular or intracellular. Intracellular enzymes are bound to the cell walls of living and metabolically viable cells, such as spores. Extracellular enzymes are discharged into the soil and "permanently" stick to clay and humic colloids through ionic interplay, hydrogen bonding, and covalent bond immobilization. Soil enzymes aid in catalytic decomposition of organic matter and production of nutrients and vehemently enhance transformation of energy, environmental quality, and agronomic productivity. Nonetheless, tillage, monoculture, and removal of residues adversely affect the enzymatic processes and availability of nutrients to plants. Enzymatic activity reduces due to an increase in soil depth. Moreover, soil enzymes reveal early changes in soil health due to quick response to changes in soil management and environmental factors such as soil quality. Meanwhile, understanding the relationship between various forms of enzymes in relation to biotic and abiotic factors will be a panacea for determining the potential effects of soil management, functionality and productivity of an ecosystem, and changes in the environment (Rao et al., 2017).

6 Production of Soil Enzymes

Microbial enzyme secretion in the soil is favored by natural selection processes, which control the intake of carbon and nutrients to the cell. Production of enzymes requires cellular management of the available minerals to produce enzymes with the advantage of increasing assimilation of nutrients, energy production, and low molecular mass of organic compounds. Carbon, nitrogen, phosphorous, and nutrients are needed for energy in the form of adenosine triphosphate (ATP), enzyme (protein) synthesis and secretion, production and arrangement of membrane transporters for the uptake of nutrients to enhance formation, and discovery of efficient surfaces for microbial interaction. For instance, enzyme production by *Bacillus licheniformis* requires approximately 1–5% of carbon and nitrogen intake. In addition, the *Escherichia coli* synthesis of ATP costs of protein per unit mass of the enzymes that are secreted is significantly reduced compared to protein retained within the cell (Fig. 1) (Burns et al., 2013).

Clearly, extracellular enzymes are responsible for the microbial recycling of energy and carbon. Elevated concentrations of N and P in plants trigger production of enzymes, leading to decomposition and recycling of nutrients. An increase in enzyme activity in response to the available resource contributes to excess release of product reaction; hence, a possible synergy between enzyme activity and resource availability is envisioned. Normally, enzyme synthesis and secretion is aided by substrate availability, but the substrate may not be the main facilitator of enzymes. More so, adequate density with the right aggregate microbial degraders is a factor for successful catalysis and subsequent microbial proliferation (Franklin et al., 2011).

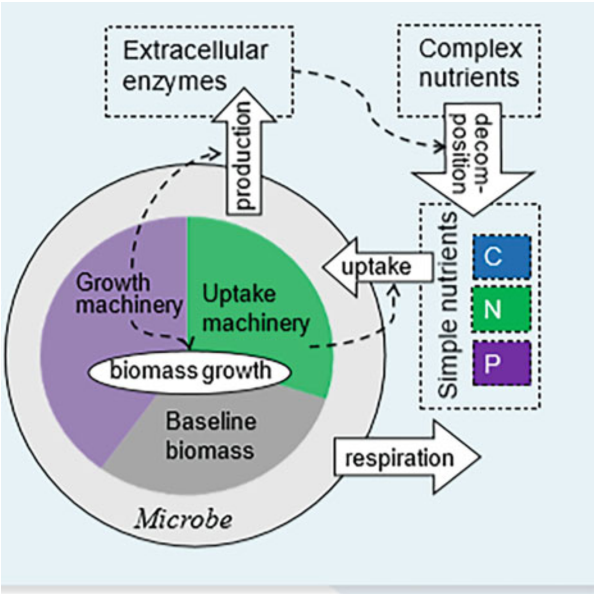

Fig. 1 Extracellular production of enzymes (Franklin et al., 2011)

7 Groups of Cellular Enzymes and Their Activities

7.1 Mobile Extracellular Enzymes

Nearly all extracellular enzymes move (diffuse) away from their parent cells because they are more active than intracellular enzymes due to possession of disulfide bonds and they are glycosylated. Extracellular enzymes have modified structures, which make them stable, with the ability to resist proteases and modulate cell adhesion. An increase in the gap between extracellular enzymes and a cell, leads to a reduction reaction on the sum of products trapped by the cell per unit of enzyme yield due to loss in product reaction, concentration of the substrate and enzymes, and diffusional environment (Burns et al., 2013).

7.2 Immobile Extracellular Enzymes

Some of the extracellular enzymes are immobilized; they stick to clay, humic acids, and particulate organic matter, which make them comfortable, active, and persistent for a longer time. The activity of static enzymes is low compared to that of their diffusible counterparts; they are confined to a position and so are unable to access the substrate oftentimes. Soil entrapment of enzymes serves as housing for the enzymes toward effective catalytic process in soils and also, provide energy for microbes when they are stressed out or during low accessibility of biomass (Feketeová et al., 2021; Quiquampoix & Burns, 2007).

7.3 Competition

Enzymes compete for products once they are available in different forms. Among these responses are the action of fungal and bacterial celluloses engulfing moieties holding enzymes to substrates in a manner that permits the catalytic site to cleave the β-1,4 linkages. Sometimes, cellulose-holding moieties may split from the substrate, which will trigger the sliding of enzymes across the surface of fibrillary cellulose. By this, the catalytic site will be shifted and hydrolysis of the substrate will occur. In the presence of adequate catalytic processes, diffusible dissolved products are emitted, and the molecules are taken up by some active microbes before the enzyme-producing cells can benefit. Microbes that keep their extracellular enzymes intact suffer less, whereas those relying on the secreted enzymes are affected. An opportunistic microbe that does not contribute to extracellular enzyme production benefits more from the diffusion and dilution of the available resources (Allison, 2005).

7.4 Cells Engulfed by Extracellular Enzymes

Diffusional losses are minimal in enzymes secreted from the cytoplasmic membrane. The enzyme is structured in a manner that its viable site is exposed, which makes it vulnerable to microbial attacks, but the proteases are protected. Proteases give protection to enzymes, provide strength to scavenge, prompt responses to the substrate distal to the cell, and aid in unavoidable reductions in freely diffusible enzymes. Apart from substrate diffusion and convection, cell possession of the enzyme holds onto the principle of Brownian motion, which aids in the collection of substrates through signals and chemical gradients to initiate and control movement toward efficient energy sources. This is possible due to the chemotaxis process, which empowers microorganisms to find gradients and enhance migration to elevated concentrations of the substrate (Centler et al., 2011). Possession of extracellular enzymes within the periplasm of some Gram-negative bacteria accounts for the survival of periplasmic enzymes through metabolic synthesis of protein as a result of shut down of cells due to starvation. The adhesive nature of the polymeric material (biofilm) enhances the attachment of microbes, thus producing enzymes to directly bind to insoluble substrates. Dissolution of substrates by extracellular enzymes betides at the interface of reaction products entering the biofilm, leading to reduction of diffusional and convective effects associated with the unavailability of the biofilm (Van Horn et al., 2011). Polysomes are associated with the anaerobic thermophile *Clostridium thermocellum*. A large number of extracellular enzymes secreted by *C. thermocellum* are polygalacturonate hydrolases, endoglucanases, exoglucanases, β-glucosidases, lichenases, laminarinases, xylosidases, galactosidases, mannosidases, pectin lyases, pectin methylesterases, cellobiose phosphorylases, cellodextrin phosphorylases, and xylenes (Burns et al., 2013) (Table 2).

8 Significance of Microbial Enzymes in Soil

Soils are the naturally occurring physical covering of Earth's surface and represent the interface of the three material states, namely, solids, liquids, and gases. Soil is an excellent culture medium for the growth and development of various microorganisms. Soil is not an inert static material; it is a medium pulsating with life (Eilers et al., 2012).

Soils are the foundation of all terrestrial ecosystems and are home to a vast diversity of bacteria, archaea, fungi, insects, annelids, and other invertebrates as well as plants and algae. These soil dwellers are referred to as microbes, and they play a major role in the human society. We depend on soils for the basis on which we and our buildings stand and for the production of food and other materials. Indeed, soils influence most ecosystem services on which we depend (Dominati et al., 2010).

Soil microbes, bacteria, archaea, fungi, and all others play diverse and often critical roles in these ecosystem services. The vast metabolic diversity of soil

Table 2 Some soil enzymes, their sources, and their functions (Rao et al., 2017)

Enzymes	Sources	Functions	Influencing agents	Catalytic reactions	Products
Arylsulfatase	Secreted by plants, animals, and microorganisms	Cycling of sulfur	pH, organic matter composition, heavy metal pollution, and the presence of organic sulfate esters	Hydrolysis of sulfate esters	Sulfate (SO_4^{2-})
Phenol oxidase	Plants and microorganisms	Carbon cycling	Soil pH, rainfall, temperature, excess nitrogen, and soil organic materials	Hydrolysis of lignin	Humic materials
Urease	Invertebrates, plants, and microorganisms	Nitrogen cycling	Organic matter content, management practices, soil depth, heavy metals, temperature, pH, and cropping history	Urea hydrolysis	Ammonia (NH_3) and CO_2
α-Amylase	Plants and microorganisms	Carbon cycling	Environment, soil and vegetation types, and management practices	Starch hydrolysis	Glucose
Dehydrogenase	Microorganisms	Microbial oxidative actions and carbon cycling	Content of water in the soil, temperature, pesticides, trace elements, and pollution	Organic compound oxidation	Hydrogen transfer to NAD
β-Amylase	Plants	Carbon cycling	Vegetation types and management practices	Starch hydrolysis	Maltose
Protease	Microorganisms and plants	Nitrogen cycling	Humic acid concentration and excess of carbon and nitrogen	Mineralization of nitrogen	Nitrogen availability in plants
Alkaline phosphatase	Bacteria	Phosphorus cycling	Organic content, pH, management practices, pollution, and crop species	Hydrolysis of esters and anhydrides of phosphoric acid	Phosphate (PO_4)
Chitinase	Microorganisms and plants	Carbon and nitrogen cycling	Level of atmospheric CO_2 and soil depth	Degradation and hydrolysis of chitin	Carbohydrates and inorganic nitrogen

Endo-1,4-β-glucanase	Microorganisms, protozoa, and termites	Cellulose endohydrolysis	Temperature, pH, water, oxygen contents, quality of organic matter, fungicides, and mineral elements	Cellulose endohydrolysis	Oligosaccharides
Xylanase	Plant cell	Degradation of the linear polysaccharide xylan	Temperature and mineral content	Breaking of hemicellulose	Xylose

microbes means that their activities drive or contribute to the cycling of all major elements and this cycling affects the structure and the functions of soil ecosystems as well as the ability of soils to provide services to people. Collectively, soil microbes play an essential role in nutrient cycling, recycling of wastes and detoxification, decomposing organic matter, and biogenic element circulation, which makes nutrients available to plants; they are also important for the development of healthy soil structures (Di et al., 2010).

Microbes are the smallest organisms (<0.1 mm in diameter) and are extremely abundant and diverse. They include protozoa, bacteria, nematodes, fungi, and actinomycetes. Most of them are able to decompose almost any existing natural material. Microorganisms transform organic matter into plant nutrients that are assimilated by plants. Soil microbes represent a large fraction of the global terrestrial biodiversity. Microbes include:

1. Bacteria: Bacteria are the crucial workforce of soils. They are the final stage of breaking down nutrients and releasing them into the root zone of a plant. In fact, the Food and Agriculture Organization once stated "Bacteria may well be the most valuable of life forms in the soil" (Hobbie, 2006).
2. Actinomycetes: Actinomycetes were once classified as fungi and act similarly in the soil. However, some actinomycetes are predators and will harm the plants, whereas others living in the soil can act as antibiotics for the plants.
3. Fungi: Like bacteria, fungi also live in the root zone and help make nutrients available to plants. For example, mycorrhizae, which is the association between roots and fungi, facilitates water and nutrient uptake by the roots and plants to provide sugars, amino acids, and other nutrients (Hibbett et al., 2007).
4. Protozoa: Protozoa are larger microbes that ingest bacteria and are surrounded by them. In fact, nutrients that are consumed by bacteria are released when protozoa, in turn, ingest the bacteria.
5. Nematodes: Nematodes are microscopic worms that live around or inside plants. Some nematodes are predators, whereas others are beneficial as they consume pathogenic nematodes and secrete nutrients to the plants.

Although there are several other soil microbes, the ones listed above are the most abundant. Microbes play a pivotal role in the cycling of nutrients essential for life; they exclusively mediate nitrogen fixation, denitrification, and nitrification. For example, soil microbes play major roles in cycling carbon, nitrogen, and phosphorus, which are essential for producing biomolecules such as amino acid, proteins, DNA, and RNA—the fundamental compounds of life. Many plant nutrients are ultimately derived from weathering of minerals. Mineral weathering by soil bacteria and fungi plays a significant role in ion cycling and plant nutrition (Philippot et al., 2007).

Carbon Cycling Microbes play major roles in the cycling of carbon—the key constituents of all living organisms. Primary producers fix carbon dioxide and convert it into organic materials. In terrestrial ecosystems, the primary producers of organic materials are plants, although surface-dwelling algae and cyanobacteria, both free-living and symbiotic as lichens, can significantly contribute to carbon fixation in some ecosystems. Within soil, autotrophic microbes can also fix carbon dioxide (Eilers et al., 2010).

Nitrogen Cycling All organisms require nitrogen because it is an essential element in protein and nucleic acids. Animals derive nitrogen from organic sources, whereas plants require inorganic nitrogen sources such as ammonium and nitrate or relatively depolymerized nitrogen sources such as single amino acids. Microbes play an important role in the nitrogen cycle; they carry out processes not carried out by other organisms, namely, nitrogen fixation, dissimilatory nitrate reduction to ammonia (DNRA), anaerobic ammonium oxidation (anammox), etc. Because nitrogen is the major limiting nutrient for plant biomass production in terrestrial habitats, the rates of this microbial process often limit ecosystem productivity (Philippot et al., 2007).

Biodegradation Many years of laboratory studies have provided a wealth of information about how microbes biodegrade or detoxify organic contaminants. It describes the establishment of enrichment cultures for detection of biotransformation of contaminants under a range of environmental conditions, for example, pH or nutrient or oxygen availability. The source of microbes for the enrichment cultures are typically soils contaminated with the compound of interest. Where possible, pure cultures that can degrade the contaminants are obtained and have been used for biochemical and molecular characterization of the degradation pathways (Dominati et al., 2010).

Heterotrophic bacteria in soil—for example, *Pseudomonas*, *Sphingomonas*, and *Mycobacterium*—have often been implicated in oil degradation. *Pseudomonas*, for example, has been well studied, and the genes and enzymes responsible for degrading alkanes, monoaromatics, naphthalene, and phenanthrene as a sole carbon source under aerobic conditions are well understood. Knowledge of the mechanisms that microbes use to degrade oil has been applied in situ. For example, enhancing oil degradation in soil typically involves addition of nutrients (N and P) and sometimes oxygen and water (Fierer et al., 2007).

There is usually no need to add hydrocarbon-degrading bacteria to oil-contaminated sites because they are ubiquitous in soil, and, when oil is spilled, they increase in numbers. However, high concentrations of hydrocarbons can deplete the available nitrogen and phosphorus because these elements are assimilated during biodegradation; consequently, the activity of the hydrocarbon degraders may become limited by these nutrients. They are also responsible for the chemical degradation of pesticides; examples include bacteria and fungi (Philippot et al., 2007).

Soil microbes are responsible for maintaining soil quality and health; they are also involved in disease transmission and control and increase soil aeration and penetrability (Dominati et al., 2010).

Generally, microbes play the foremost role in soil formation and ecology because they, as "natural soil engineers," regulate the flux of nutrients to plants and pop up nitrogen fixation and detoxification and ultimately promote detoxification of naturally occurring inorganic and organic pollutants in soil (Fierer et al., 2007).

The quantitative composition of the population and its qualitative nature depend largely on the origin and nature of the soil and the relative composition of its inorganic and organic constituents. The prevailing climate and growing vegetation also greatly influence the nature and abundance of microbes that inhabit the particular soil. Soil microbes play a crucial role in returning nutrients to their mineral forms, which plants can take up again (Hobbie, 2006).

This process is known as mineralization. Biological nitrogen fixation contributes about 60% of the nitrogen fixed on Earth. Some soil microbes yield numerous substances that boost plant growth. They break down organic matter, create humus, and also promote plant growth (Dominati et al., 2010).

Furthermore, soil microbes produce antimicrobial agents and enzymes used for biotechnological purposes. They also mobilize nutrients from insoluble minerals to support plant growth. Macropores are formed by plant roots, earthworms, and other soil biota, which may depend on soil microbes as food or for nutrients. In concert with the organic matter and clay content of soils, microbial products add to both the wettability and the hydrophobicity of soils, impacting the property of the soil to filter contaminants (Hobbie, 2006).

Soil bacteria, fungi, and archaea comprise the vast majority of the biological variety on Earth. They also make up the foundation of soil food networks, thereby sustaining the variety of higher trophic intensities. Interactions between plants and soil microbes often decide plant biodiversity. Beneficial species include fungi, archaea, and bacteria that promote plant development by outcompeting invading pathogens and increasing nutrient availability (Eilers et al., 2012). By mineralizing soil carbon and nutrients, microbes are major determinants of the carbon storage capacity of soils.

9 Effects of Herbicides, Fungicides, and Insecticides on Microbial Enzymes

9.1 Effects on Dehydrogenase Activity

Dehydrogenase occurs in all living microbial cells, and it is linked to microbial respiratory processes (Bolton et al., 1985). Author findings showed that all fungicides except Prochloraz at a recommended field application dose between pH 4.4 and 7.5 have both negative and positive effects on dehydrogenase enzyme activities and population (Chen et al., 2001; Burrows & Edwards, 2004; Bending et al., 2007; Bello et al., 2008; Rasool & Reshi, 2010; Ataikiru et al., 2019; Małgorzata et al., 2021). Most insecticides have no effects or a slight inhibition effect (Caceres et al., 2009; Beulke & Malkomes, 2001; Kalam et al., 2004; Yao et al., 2006; Jastrzebska, 2011; Gangan et al., 2015; Nataraj et al., 2017; Madhavi et al., 2019). Similarly, herbicides also cause inhibition of the activity of dehydrogenase enzymes not minding the application dose or pH (Sebiomo et al., 2012; Filimon et al., 2021), except butachlor (Min et al., 2002; Xia et al., 2011). In summary, pesticides (fungicides, herbicides, and insecticides) may have no effect, inhibitory effects, or sometimes enhance the activities depending on the pesticide and conditions involved in their applications.

9.2 *Fluorescein Diacetate Hydrolase*

The influence of insecticides on fluorescein diacetate hydrolase is not much; however, Das et al. (2007) and Bishnu et al. (2012) conducted some research on it explaining that its activities could be enhanced by the imidazolines (Imazethapyr) and organochlorines (endosulfan) families (Perucci et al., 2000; Kalyani et al., 2010; Riah et al., 2014; Mariane et al., 2020). Authors noted that application doses have similar or same effects on its activities (Bishnu et al., 2012). Fluorescein diacetate hydrolase activity in soil is poorly influenced by herbicide or insecticide applications, except endosulfan applications, which seem to stimulate this activity (Wassila et al., 2014).

9.3 *Cellulase and β-Glucosidase*

The effects of fungicides and herbicides were tested by different authors and they were discovered to have no solid impact on the activity of cellulase (Bishnu et al., 2012; Tejada et al., 2011; Niemi et al., 2009; Gundi et al., 2007; Omar & Abdel-Sater, 2001). However, Gundi et al. (2007) went further to show that there is a valid relationship between some insecticides (monocrotophos, quinalphos, and profenofos) and cellulolytic bacteria population growth. Similarly, Tejada (2009) noted the inhibition of the β-glucosidase activity by glyphosate and diflufenican combination. Among the various insecticides, Defo et al. (2011) observed an enhancement of β-glucosidase activity by endosulfan at high concentrations above the normal dose. Wassila et al. (2014) were able to support the claim that the effects of the endosulfan insecticide may be related to the strong functional redundancy of β-glucosidase activity.

9.4 *Effects on Phosphomonoesterase Enzymes*

The effects of pesticides on enzymes have been studied by many researchers who have come to the conclusion that pesticides either decrease enzyme activity or, in some cases, have no effect on them (Schneider et al., 2001. Kalam et al., 2004; Yan et al., 2011; Dick et al., 2000), depending on some conditions like doses, soil pH, and other physiochemical properties of soil (Min et al., 2002; Tejada, 2009). For the sake of differentiation, Rasool and Reshi (2010) noted an inhibition of the activity of the alkaline form of the enzyme when fungicides are used, which was also confirmed by Sharma et al. (2010), but an enhancement of the activity of the acid phosphatase. The different responses between the alkaline and acidic forms of the enzyme can be attributed to their sensitivity (Klose et al., 2006) Monkiedje et al. (2002) furthered this research and discovered that fungicides at basic pH will inhibit alkaline phosphate activity; this was also confirmed by other authors (Bello et al., 2008; Tejada et al., 2011; Yan et al., 2011). Studies by Perucci et al. (2000), Omar and Abdel-Sater (2001), and Bacmaga et al. (2012) showed that the type of insecticide has to do with their reaction to it. For example, Xia et al. (2011) discovered that butachlor enhances the activity of the enzyme, especially the alkaline type. Similar to the responses with herbicides, insecticides may inhibit acid phosphatase and enhance alkaline phosphatase activity, and vice versa (Omar & Abdel-Sater, 2001; Cycoń et al., 2010; Defo et al., 2011; Jastrzebska, 2011; Madhuri & Rangaswamy, 2002; Yao et al., 2006).

9.5 Nitrogen Cycle and Enzymatic Activity of Urease

Antonious (2003) explained that urease is generally beneficial because it helps maintain nitrogen availability to plants. The study summaries of certain authors observe that herbicides and fungicides do not have any effects on urease activities (Cycoń et al., 2010; Romero et al., 2010; Tejada et al., 2011; Yan et al., 2011; Bacmaga et al., 2012), but some studies have recorded a decrease in urease activity, e.g., carbendazim and validamycin (Sukul, 2006; Caceres et al., 2009; Tejada, 2009). Generally, pesticides do not seem to affect the activity of this enzyme (Niemi et al., 2009; Tejada, 2009; Vavoulidou et al., 2009). It is difficult to identify a clear response of the activity of this enzyme to pesticides as it has received only a few mentions in the literature in past years.

10 Effects of Application of Fertilizers on Enzymatic Activities

Wang et al. (2020) used organic fertilizers on four types of soil enzymes (ureases, sucrases, alkaline phosphatases, and catalases), which did not significantly respond to the addition of vermicompost and mushroom residue fertilizers. Urease activities declined as a result of vermicompost and mushroom residue applications. However, sucrase, alkaline phosphatase, and catalase activities increased to varying degrees under the different levels of treatment of vermicompost and mushroom residue fertilizers. Sawicka et al. (2020), using nitrogen fertilizers, observed that the activity of dehydrogenases, phosphatases, and ureases changed as the nitrogen dose increased. The polynomial regression analysis enabled a better understanding of those dependences. However, soil acidity did not have a significant influence on either the enzymatic activity or the physicochemical characteristics of soil under the cultivation of sweet potatoes. Ye and Peng (2019) discovered that NPK fertilizers improve soil enzyme activity. The long-term effects of fertilizers were considered by Chew et al. (2019), using a combination of inorganic and organic fertilizers, who discovered that they enhanced dehydrogenase, urease, alkaline phosphatase, invertase, and glomalin enzymes. From different authors and the literature, it was discovered that factors including time, type of fertilizer (inorganic or organic), dose of application, and soil parameters are responsible for the response of soil enzymes (Gostkowska et al., 1998; Lü et al., 2018; Sekaran et al., 2019a).

11 Relationships Between Pesticide Mechanisms of Action and Enzymatic Responses

11.1 Pesticides

Gianfreda and Rao (2008) noted that the relationships between pesticide action and enzymatic responses have been known to be direct and indirect, which could include active site binding or a nutrition source for the enzymes (Tabatabai, 1994); the former could cause a change in the catalytic reaction, and the latter could cause a biosynthesis of the enzymes by induction (Cycoń et al., 2006; Tejada, 2009; Zabaloy et al., 2012; Chishti et al., 2013). The relationships are strongly related to the functionality power or resistance of the target (Chaer et al., 2009; Griffiths & Philippot, 2013; Puglisi et al., 2012) and to the physicochemical properties of soil, pH, humus, clay content, or organic matter, which have been known to affect the expression and proper function of the pesticide in soil (Chen et al., 2001; Gundi et al., 2007; Defo et al., 2011; Muñoz-Leoz et al., 2013).

11.2 Fungicides

It has been noted that the high application of fungicides has destructive effects on the fungal population but enhances the bacterial population (Monkiedje & Spiteller, 2002; Moharram et al., 2004; Cycoń et al., 2006; Bending et al., 2007; Cycoń et al., 2010), which explains why bacteria use dead fungi as a source of nutrients and energy for their population increase (Cycoń et al., 2006; Tejada et al., 2011). According to Muñoz-Leoz et al. (2013), microbial biomass decrease is parallel to the decrease in enzymatic activities after the use of fungicides, which may lead to a global unpleasant response within 28–50 days of incubation. The effect on the field is not far apart because even at a recommended standard of application, the field is still found to be under the negative influence even after 3 years (Niewiadomska, 2004; Niewiadomska & Klama, 2005).

11.3 Insecticides

Endosulfan (one of the commonly used insecticides in the world) has been noted to cause an increase in microbial biomass carbon (Kalyani et al., 2010; Joseph et al., 2010; Xie et al., 2011), but the opposite action has been noted for organophosphate. This claim has been affirmed using chlorpyrifos and monocrotophos, which are two major molecules in that class; it showed that they caused a decrease in microbial biomass carbon in soil and also have adverse effects on soil bacterial and fungal counts (Shan et al., 2006; Vischetti et al., 2007; Zayed et al., 2008). This does not enable all molecules of organophosphate to function similarly (Martinez-Toledo et al., 1992; Tejada, 2009).

11.4 Herbicides

Herbicides that inhibit the acetolactate synthase enzyme and photosynthesis process have predominately neutral effects on soil enzymatic activities. Radivojevic et al. (2008) noted that the addition of atrazine had no effect on soil microbial activity, bacterial density, and functional richness, whereas metsulfuron-methyl herbicides had a little effect (Zabaloy et al., 2008). Researchers have noted that the recommended field rate of glyphosate had a benign effect (Barriuso & Mellado, 2012; Hart et al., 2009), whereas above the concentration, enhancement of bacteria was discovered (Ratcliff et al., 2006; Weaver et al., 2007).

12 Conclusions

Adequate secretion of microbial enzymes is a significant factor in enriching soil for profitable agricultural practices. Soil enzymes improve the soil biogeochemical processes, soil health, and quality. Soil enzymes are influenced by the physical, chemical, and biological properties of soil, which are the functions of biomass content and nutrient quality, resulting in the synthesis and secretion of enzymes in the soil. Unfortunately, modern-day agricultural practices coupled with other factors pose threats to the microbial community, most especially application of chemicals, soil management practices, and environmental factors. Agrochemical application reduces microbial community and ecological niche and hampers the response of microbes toward nutrients. For mediating the effects of agrochemicals on the microbial community for effective secretion of soil enzymes, natural attenuation of soil will be the leading option. In addition, the use of harmful agrochemicals such weed killers should be stopped. It is a known fact that the total stoppage of agrochemicals is not possible, but the mode of action can be selective, most especially when dealing with pests. Culturing and multiplication of bacteria-producing enzymes for desired purposes will also serve as a meditative approach through biotechnological means.

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