Chapter 11
Agrochemicals and Soil Microbes: Interaction for Soil Health

Zaffar Malik, Maqshoof Ahmad, Ghulam Hassan Abassi, Muhammad Dawood, Azhar Hussain, and Moazzam Jamil

11.1 Introduction

Soil is a complex and heterogeneous system consisting of both living and nonliving components. The nonliving components of soil include soil texture (sand, salt, and clay) and organic matter, while soil living components are composed of soil flora (algae, fungi, and bacteria) and fauna (nematodes, arthropods, earthworm, and mollusks). Soils have a large number of bacteria, fungi, and animal species. It is reported that one cm^3 of fertile soil may have up to 10^{10} bacteria belonging to an estimated 10^4 species (Anderson and Weigel 2003). Soil microbes are important biological components of soil and perform functions in soil fertility through nutrient cycling and organic matter degradation (Tejada et al. 2014). Plant species get nutritional benefits from association with soil microbial mutualism and often provide sugars to these microbes, e.g., legumes and ectomycorrhizal tree species respond positively to rhizobia and fungi, respectively, compared to nonlegumes and non-ectomycorrhizal plants (Abbott et al. 2015). Soil microbes have a critical role in the functioning of terrestrial ecosystems and act as drivers of plant diversity (Van Der Heijden et al. 2008). Free-living soil microbes promote plant diversity by increasing the nutrient pool and alter the plant dominance due to symbiotic and pathogenic interactions (Prober et al. 2015). Similarly, plant diversity promotes soil microbes by providing food resources (exudates and litter), physical microhabitats, and environmental conditions (Millard and Singh 2010; Prober et al. 2015). Ecologists are well aware of the significance of microbes in soil functions, but it is due to

Z. Malik (✉) • M. Ahmad • G.H. Abassi • A. Hussain • M. Jamil
Department of Soil Science, University College of Agriculture and Environmental Sciences, The Islamia University of Bahawalpur, Bahawalpur 63100, Pakistan
e-mail: zafar_agrarian@yahoo.com

M. Dawood
Department of Environmental Sciences, Bahauddin Zakriya University, Multan, Pakistan

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advancements in the technology that enabled scientists to extract and characterize microbial communities to assess their functions in the soil (Bardgett et al. 2005).

The interactions between plant and microbe in the rhizospheric soil determine many processes including plant growth, pollutant degradation, and nutrient mobilization through atmospheric nitrogen fixation, solubilization of nutrients and control movements, and availability of pollutants to plants by the production of chelating agents, biosurfactants, acidification, redox changes, and phosphate solubilization (Glick 2010; Rajkumar et al. 2013). Bacteria and fungi transform and degrade different types of pollutants including pollutants from agriculture origin. The term degradation describes a variety of processes undertaken by the microbe: for example, the pollutant substances may either be completely mineralized, or it may undergo the partial transformation before a nontoxic metabolite excreted in the soil and become immobilized by bonding to matrix component like humic acid (Kiel and Engesser 2015; Murphy 2016).

Agrochemical is a generic term for the chemical products used in agriculture which may include pesticides (herbicides, insecticides, and fungicides), synthetic fertilizers, growth agents, and raw manures. Balanced application of fertilizers can promote soil organic matter and soil microbial diversity and hence improve soil functions and ultimately increases the soil resistance against environmental stresses. The use of these agrochemicals may increase the yield of crops, but their excessive use poses a great threat to environment, especially soil biology. Long-term and excessive uses of synthetic fertilizers (N, P, and K) along with organic fertilizers (manures) were reported to seriously affect soil microbial and soil enzymatic activities (Zhang et al. 2015b). Pesticides when entering into soil can cause environmental hazards and greatly alter the soil biochemical and microbial aspects. Soil microbes on the other hand overcome the toxic effects of these chemicals by performing different functions in the soils and make them less toxic for the environment.

The soil enzymatic activities are used as indicator for soil fertility and quality. These activities are important to predict microbiological and biochemical processes involved in organic matter synthesis and decomposition, nutrient cycling and availability, and biodegradation of toxic organic pollutants especially pesticide utilization in agriculture (Raiesi and Beheshti 2014). Enzymes are also important to monitor sudden changes in the soil environment because of their rapid response to any change within the soil. Studies showed that long-term supply of P and N can affect the soil microbial activities, and absolute and specific acid phosphate activities decreased as mineral P application rates and ratios increase (Zhang et al. 2015b). Apart from the degradation of agrochemicals, soil enzymatic activities also inhibited due to exposure to external pollutants like heavy metals, pesticides, and certain antibiotics used in agriculture. Soil enzymes like urease, alkaline phosphatase, and invertase are considered to be the indicators of soil disruption under stress (Jin et al. 2015). Certain microbial enzymes (urease and protease) are involved in the organic matter decomposition and N dynamics by participating in the hydrolysis of peptide bonds and release of NH^{+4} (Wang et al. 2008).

11.2 Agrochemical and Soil Microbes

Soil microbes perform crucial functions for the restoration of polluted soils and therefore are considered important component of ecosystem restoration (Harris-Hellal et al. 2009; Liu et al. 2016). Soil microorganisms are closely associated with plant roots, contributing to nutrient cycling, and show resistance and tolerance to pests, diseases, drought, and heavy metals and improve the soil structure. In this regard, soil microbial diversity and community composition are important indicators of soil health (Liu et al. 2016). The biodiversity and composition of soil microbes are influenced by many factors like pH, organic matter, and the additives such as pesticides and fertilizers. *Actinobacteria* and *Proteobacteria* were reported to be most abundant phyla in relation to soil containing agrochemicals and had a positive relationship with atrazine in soil (Liu et al. 2016). Similarly, *Arthrobacter* communities found in contaminated soils showed atrazine-degrading capabilities by having trzN, atzB, and atzC genes (Zhang et al. 2015b). Soil management practices such as type of rotation, proportion of organic material, and intensity of tillage can alter the physicochemical characteristics of the soil. These practices can manage the biogeochemical cycles and the dynamics of the microbiota, including colonization of arbuscular mycorrhizal fungi. The conventional tillage practices where crop residues are removed along with the synthetic inputs of herbicides exaggerate the negative effect of herbicides on the microbial population. Synthetic fertilizers and herbicides along with the type of organic material had greatly affected the enzymatic activities and mycorrhizal colonization in the soil (Mariela et al. 2016). Addition of soil organic matter in the form of compost provides several microorganisms and nutrients to indigenous degraders. Pentachlorophenol (PCP) is used in the wood treatment and persists in the environment and classified as priority contaminant. Many fungi such as *Phanerochaete chrysosporium*, *Antracophyllum discolor*, *Trametes versicolor*, *Ganoderma lucidum*, *Armillaria mellea*, and *Gloeophyllum striatum* showed potential to degrade and mineralize PCP (Bosso et al. 2015a, b). Bosso et al. (2015a) also found that compost and fungal strains had a synergistic effect on the reduction of more than 95 % of the extractable PCP. The use of organic fertilizers can enhance the microbial diversity and soil health. Long-term use of organic fertilizer contributed to the improvement of soil C and N contents and most enzyme activities (Zhang et al. 2015a) (Table 11.1).

11.3 Effect of Agrochemicals on Soil Biological Process in Soil

Agrochemicals are used to enhance or protect the agricultural crops, vegetables, and livestock through the world. Agrochemicals include all chemical products which are manufactured or processed for use in the agriculture sector and allied industries. According to The American Heritage Science Dictionary,

Table 11.1 Relationship of agrochemical/manures and soil microbes on the health of soil

Reference and location	Agrochemicals/manures	Microbial species	Effects
Liu et al. (2016) China	Atrazine	*Actinobacteria*, β-*Proteobacteria*, *Firmicutes*, *Acidobacteria*, *Verrucomicrobia*	To convert atrazine-polluted farmland to secondary forest. *Actinobacteria*, *Firmicutes*, and β-*Proteobacteria* species remain unchanged, while community structure of *Acidobacteria* and *Verrucomicrobia* decreased
Bosso et al. (2015b) Switzerland	Pentachlorophenol (PCP)	*Byssochlamys nivea*, *Scopulariopsis brumptii*	The compost and the fungal strains, *B. nivea* and *S. brumptii*, showed good capability to tolerate and degrade PCP
Zhang et al. (2015a) China	Organic fertilizers	Microbial community structure like G^{+} and G^{-} bacteria and fungal communities	Improvement in enzyme activities and diverse community composition
Li et al. (2015) China	Compost manures, antibiotics (tylosin and vancomycin), and Cu	Soil microorganisms	Inhibited enzymatic activities. Selective pressures on both the microbial tolerance to Cu and the co-tolerance to antibiotics including tylosin and vancomycin. Greater risk for ecology due to animal wastes contaminated by the heavy metal Cu
Postma and Schilder (2015) Netherlands	Organic amendments (yeast and chitin)	*Lysobacter* populations	Suppression of *Rhizoctonia* disease by *Lysobacter* populations in soil
Guo et al. (2015) China	Azoxystrobin	Cultivable bacteria, fungi, and actinomycetes	Azoxystrobin showed significant negative effect on cultivable bacteria, fungi, and actinomycetes and enzymes assays (urease, protease, and dehydrogenase)

(continued)

Table 11.1 (continued)

Reference and location	Agrochemicals/manures	Microbial species	Effects
Sabale et al. (2015) India	Kresoxim methyl	Soil microbes	Dissipation kinetics of kresoxim methyl and its residual effect on soil extracellular (acid phosphatase, alkaline phosphatase, and β-glucosidase), and intracellular (dehydrogenase) enzyme activities
Malhotra et al. (2015) India	Fertilizers and pesticides	*Actinobacteria* Ammonifiers Rhizobium 16S rRNA	Adverse effect on soil microbial diversity and function was found at high fertilizer and pesticide usage. Diversity of nitrogen fixers was changed. Reduction in rhizobial *nifH* sequences
Majumder and Das (2016) India	Organophosphate insecticides (monocrotophos, profenophos, quinalphos, and triazophos)	Phosphate solubilizing microorganisms	Phosphate activities (acid phosphatase and alkaline phosphatase) significantly increased in the soil
Taheri et al. (2015) Canada	Chlorothalonil, pyraclostrobin, and boscalid	*Fusarium*, *Olpidium*, *Alternaria*, and *Cryptococcus*	Relative abundance of *Fusarium* increased after the application of fungicides
Zhang et al. (2015b) China	Swine manures and NPK fertilizers	Actinomycetes and G^{+} bacterium enzymatic activities	Enzyme activities were positively correlated with actinomycetes and G+ bacterium. To improve microbial activity, P fertilizer should be applied with inorganic and organic forms

"agrochemicals" are defined as a chemical, such as a hormone, a fungicide, or an insecticide, that improves the production of crops. Pesticides are used to protect the crops from insects and diseases, and fertilizers are used to fulfill the deficiency of nutrients.

Agrochemical (fertilizer, pesticides, and insecticide) application is considerably increased in the developing world. Agrochemicals perform an important role in intensive agriculture. The use of these agrochemicals is a low-cost method of increasing production and gives the farmer a high economic return for his labor and investment. In our agricultural systems, pesticides and insecticides are introduced to protect crops against insects, pests, and weeds to minimize harmful effects and to get maximum yield (Yang et al. 2007). The ultimate objective of using fertilizer and pesticides is to enhance the crop yield for maximum benefit.

Agrochemicals are very important component of an agricultural industry for increasing crop yield from viewpoint of economic; therefore, their continued use is essential (Yang et al. 2007). Insecticides and pesticides are part of insect and pest control strategies which help in improving public health.

No doubt, agrochemicals (fertilizer, pesticide, and insecticides) have tremendous role in the increase of crop production (Blain 1989; Hashmi et al. 2004); on the other hand, these agrochemicals have generated many environmental and health issues. Agrochemicals directly affect the soil microbes which ultimately deteriorate the soil health. Pesticides may drastically affect the proliferation of beneficial soil microorganisms and their associated biotransformation in the soil. The best pesticide is the one, which only toxic to targeted organism and degrade it and not contaminate the soil environment. When nontarget organism is exposed to the applied pesticide, the pesticide may have harmful effects on that nontarget organism. (Odenkirchen and Eisler 1988; Bretaud et al. 2000; Galloway and Handy 2003).

Total amount of applied pesticide which reaches to targeted organism is about 0.1%, while remaining 99.9% contaminates soil environment. (Pimentel 1995; Ardley 1999; Chenseng et al. 2006; Carriger et al. 2006). Hence, these harmful compounds enter the food chain through food crops and soil and cause toxicity to the biodiversity (Araújo et al. 2003; CFTRI 2003). The use of pesticides is increasing day by day in agriculture sector; toxic chemicals in agrochemical directly affect the soil microorganisms (Baxter and Cummings 2008). A pesticide (Simethoate) applied to the agriculture crops also has negative effects on the microbial diversity and the soil enzyme activity in soil (Begum and Rajesh 2015). The indigenous microorganisms are affected by the application of an herbicide Bromoxynil (Baxter and Cummings 2008).

Pesticide application caused reduction in microorganisms present in the soil (Ubuoh et al. 2012). Some pesticides disturbed molecular interactions between plants and nitrogen-fixing rhizobia and consequently reduced the vital process of biological nitrogen fixation. Inactivation of phosphorus-solubilizing and nitrogen-fixing microorganisms is observed in pesticide-contaminated soils (Hussain et al. 2009a, b). A great difference has been observed between microbial population in pesticide-treated and nontreated soil confirming the effects of microbial deduction and extinction due to indiscriminate ways of applying pesticide in the soil (Ubuoh et al. 2012). Pesticides also influence soil biochemical processes driven by microbial and enzymatic reactions (Demanou et al. 2004). Nitrogenous fertilizers decrease the mycorrhizal fungus spore number and root colonization. Application of fertilizer adversely affects soil microorganisms. Negative effect of pesticide on the symbiotic efficiency and nitrogenase activities was observed on *Rhizobium leguminosarum* bv, Trifolii KGL, *Sinorhizobium meliloti* Bp, *Bradyrhizobium sp.*, and *Ornithopus B* bacteria (Demanou et al. 2004). Pesticides have adversely affected the microbial mineralization of organic compounds and related biotransformation like nutrient dynamics and their bioavailability to plants.

In general, fungi, actinomycetes, and the phosphorus-solubilizing microbes were more affected by the agrochemicals (fertilizers, pesticides, insecticide, etc.) with reductions in their abundance. Microorganisms presented varying behavior depending on the agrochemical and the nitrogen fixers were stimulated. Chemicals may affect in different ways the microorganisms that are responsible for the decomposition of organic matter in the rhizospheric soil.

11.4 Effect of Agrochemicals on Soil Enzymes

The living microbial fractions of soil are the governing bodies of a soil ecosystem, and their diversity dictates the potential of a soil to support life. These soil microbes exudate several enzymes performing many fundamental processes in soils. The activities of these enzymes in soil are keenly important for sustainable use of a soil as natural resource. These enzymes are involved in geochemical cycling of all chemical elements, which continue the flow of nutrients in ecosystem not only in soil but, in fact, of the whole planet Earth. However, the emergence of industrial era and the use of chemicals in crop production severely deteriorated the soil health, especially the biological conditions (Trasar-Cepeda et al. 2000; Chu et al. 2003).

In a modern agriculture system, a huge amount of agrochemicals are being incorporated in soil as amendments, fertilizers, and pesticides during the production of a crop. The residual and hazardous effect of these chemicals on living beings is well documented. From a soil microbiologist's point of view, these chemicals are also equally harmful for the microbial populations of the soil resulting in severe destruction of soil enzymatic activity (Dong et al. 2005; Qiu et al. 2006). These chemicals eradicate the beneficial soil microbes which ultimately remove important enzymatic components from a chain of reactions that play vital role in synchronizing important chemical processes in soil (Hernandez-Rodriguez et al. 2006).

There are numerous enzymes that are present in a soil ecosystem. The most important microbial enzymes are dehydrogenase, fluorescein diacetate hydrolase, and enzymes involved in biochemical cycles of nutrients, i.e., enzymes involved in C cycle, P cycle, N cycle, and S cycle (Ronhede et al. 2007). These microbial enzymes are the indicators of soil biological health, fertility, as well as the chemical status of the soil (Trasar-Cepeda et al. 2000; Chu et al. 2003). Consequently, the assessment of a particular enzyme activity plays an important part in understanding the biogeochemical cycles of nutrients. The effect of agrochemicals on soil microbes is assessed by determining several functional attributes that mainly includes the monitoring of enzymes related to the mineralization of nutrients (N, P, S, etc.). These parameters are important as the biogeochemical cycling and transformation of nutrients require microbial enzymes (Antonious 2003; Bending et al. 2004). Agrochemicals incorporated in the soil interrupt the metabolism or enzymatic activities (Hussain et al. 2009a, b). Adverse influences of agrochemicals on soil microbial enzymatic, e.g., hydrolases, oxidoreductases, and dehydrogenase, activities have been reported in the literature (Gianfreda and Bollag 1994; Kalam et al. 2004; Menon et al. 2005; Gil-Sotres et al. 2005; Hussain et al. 2009a, b).

Dehydrogenases are important enzymes synthesized by almost all living cells. These are involved in the respiration reactions in organisms. In soil, its presence regulates the decomposition of organic matter. This microbial enzyme is the indicator of inclusive activity of soil microbial population. The literature showed that agrochemicals significantly reduce the activity of dehydrogenase enzyme (Sebiomo et al. 2012). Several insecticides, fungicides, and herbicides are reported to suppress the activity of this enzyme (Burrows and Edwards 2004; Bending et al. 2007; Rasool and Reshi 2010; Sebiomo et al. 2012). However, the impact of these chemicals on soil microbes is regulated by the physiochemical properties of agrochemicals as well as by the nature of the soil and prevalent environmental circumstances (Monkiedje and Spiteller 2002). In general, the activity of dehydrogenase is severely affected by fungicides that are formulated to act on metabolic machinery of pathogen (Dick et al. 2000; Bello et al. 2008).

The fluorescein diacetate hydrolase (FDH) is also an important functional enzyme in soil ecosystem. It is an important enzymatic parameter to measure the activity of microbial enzymatic activities. These enzymes are related to hydrolyze fluorescein diacetate compounds present in soil and take part in nutrient cycling. Measuring the FDH activity has the potential to roughly denote soil enzymatic activities and collected biological impacts (Janvier et al. 2007; Bishnu et al. 2012). Fluorescein diacetate compounds are hydrolyzed by several FDH enzymes including protease, esterase, amylase, etc. The studies showed that FDH activity is stimulated by the application of imidazolines, organophosphate, and organochlorines (Kalyani et al. 2010; Riah et al. 2014).

The literature showed that microbes involved in the cycling of C, P, N, and S had a variety of response toward pesticide application. The enzymes involved in C cycling, i.e., cellulase and b-glucosidase, are not widely reported to be affected by agrochemicals. Most of the pesticides have neutral effect on their activity (Deng and Tabatabai 1994; Niemi et al. 2009). Omar and Abdel-Sater (2001) reported that even ten times higher doses of herbicides have no pronounced effect on cellulase and b-glucosidase activities. However, some fungicides from amide group are reported to have inhibitory effect on cellulase and b-glucosidase activities (Monkiedje and Spiteller 2002; Niemi and Vepsalainen 2005). Phosphorus cycle enzymes are grouped into five major classes, i.e., the phosphomonoesterases (PME), the phosphodiesterases (PDE), the phosphotriesterases (PTE), the pyrophosphatases (PP), and the phosphoamidases (Riah et al. 2014). Acid phosphatase and alkaline phosphatase function in low and high pH, respectively, are key enzymes involved in P cycling in soil, and are included in PME. These are diverse enzymes adapted to catalyze hydrolysis organic phosphoric acid (Monkiedje and Spiteller 2002; Riah et al. 2014). The activity of phosphatase enzymes are negatively affected by the higher concentrations of pesticides which hamper the velocity of P cycle in the ecosystem (Schneider et al. 2001). Studies showed that this decrease in phosphatases directly related to P stress and plant growth (Dick et al. 2000; Sharma et al. 2010; Monkiedje and Spiteller 2002). Urease is an important enzyme involved in N cycling by catalyzing the hydrolysis of organic urea. This enzyme is integral N transformation in soil, and it is mainly derived from plant and soil microbes (Riah et al. 2014). It is reported that agrochemicals have negative impact on urease activity (Sukul 2006; Caceres et al. 2009; Tejada 2009). On the other hand, the activities of enzymes involved in S cycling are positively affected by most of the agrochemicals, and literature shows that the enzymes show accelerated activities under high concentration of pesticides (Ganeshamurthy and Takkar 1997; Kertesz and Mirleau 2004; Riah et al. 2014).

The incorporation of high concentrations of chemicals in soil severely disturbs the natural equilibrium of soil enzymes that affect the natural cycles otherwise going on a constant speed. The literature showed that these chemicals, in most cases, may speed up or inhibit the activities of soil enzymes that alter the nature of soil processes. However, there is a huge gap present in literature for understanding the chemical, physical, and biological nature of effected processes and enzymatic activities.

11.5 Role of Soil Microbes for Detoxification of Agrochemicals

The use of living organisms for the removal of agrochemical pollutant from the soil is a common process for the remediation of soil because of its low cost and environment-friendly approach (Mackay and Frasar 2000). Biotic degradation is the use of microorganisms, plants, or their enzymes to detoxify contaminants in the soil and water environments (Lu et al. 2006). Most living organisms are capable of directly degrading the agrochemical pollutants, and some of the microbes have the ability of metabolizing even very complex compounds. Biotic degradation is divided in to two different types: microbes and plants.

Microorganisms present in the soil also degrade the agrochemicals. Degradation of a persistent organochlorine pesticide like endosulfan by the soil microbes is an effective approach. Three bacterial strains, *Pseudomonas spinosa*, *P. aeruginosa*, and *Burkholderia cepacia*, were reported as efficient degraders of endosulfan (Hussain et al. 2007). Microbial technology (using plant growth-promoting bacteria) has received increasing attention to detoxify the hazardous waste from the environment (Radhika et al. 2006).

Different bacterial species, including members of the genera *Flavobacterium*, *Alcaligenes*, *Rhodococcus*, and *Pseudomonas*, metabolize toxic compound which is found in pesticide and insecticides (Aislabie and Lloyd-Jones 1995; Richins et al. 1997; Mulchandani et al. 1999). Soil microorganisms have the ability to degrade the toxic compounds of pesticides in the soil (Hussain et al. 2007). The use of bacteria for the degradation and detoxification of toxic chemicals released from agrochemicals (pesticides and fertilizers) is an effective and environment-friendly tool to decontaminate the polluted areas. Indigenous bacteria are capable of metabolizing toxic compounds of pesticides and provide environmentally friendly means of on-site detoxification. Environmental factors such as temperature, pH, water potential, nutrient, amount of pesticides and fertilizer directly influence the rate of biodegradations. Presences of inductive enzyme are also necessary for the degradation of toxic compounds (Singh et al. 2009).

Best suitable pathway of degradation is the most important factor for the remediation of the agrochemical-contaminated soil. Degradation of toxic agrochemical compounds affected by different physical, chemical, and biological factors to a variable extent in the soil environment is a highly complex process (Lu et al. 2006).

Remaining products of pesticides after fully degradation by soil microbial assimilation result to enhance soil microorganisms population and their activities (Das and Mukherjee 2000). Different insecticides with different doses affected the chemical and microbiological properties of rhizospheric soil in rice field. Carbofuran strongly stimulated the mineralization of organic carbon. Microorganisms have similar herbicide-degraded processes and an intrinsic nature for rapid genetic adaptation to chemicals in the environment. Pollutants of diverse chemical nature could be remediated from soil and water with the use of potential microorganisms in the soil.

11.6 Conclusions and Future Perspectives

The interaction of plants and microbes in rhizospheric soil controlled many process like plant growth, nutrient mobilization, nitrogen fixation, pollutant degradation, and control movement and availability of pollutants through chelating agents, biosurfactants, and acidification. Agrochemicals such as fertilizers, herbicides, and pesticides contributed a lot in the production of food and fiber but had profound effects on the soil fertility and health. Extensive use of these chemicals caused a stress over natural resources along with the increase in water and air pollution. Soil microbes are under great threat by the application of diverse nature of agrochemicals which interrupt large biochemical reactions performed by the soil microbes. Many functions like C, P, S, and N cycle, metabolism, and enzymatic activities performed by soil microbes are disrupted by the application of agrochemicals. The use of organic/natural resources should be promoted against agrochemicals which enhance the microbial activities in soil and hence can improve soil health. Moreover, soil microbes have the potential to remediate the agrochemical-contaminated soils thus improving soil fertility. Therefore, researchers and scientists should develop and follow technologies for sustainable use of natural resources.

References

Abbott KC, Karst J, Biederman LA, Borrett SR, Hastings A, Walsh V, Bever JD (2015) Spatial heterogeneity in soil microbes alters outcomes of plant competition. PLoS One 10 (5):e0125788

Aislabie J, Lloyd-Jones G (1995) A review of bacterial-degradation of pesticides. Soil Res 33(6): 925–942

Anderson T, Weigel H (2003) On the current debate about soil biodiversity. Landbauforschung Volkenrode 53(4):223–234

Antonious GF (2003) Impact of soil management and two botanical insecticides on urease and invertase activity. J Environ Sci Health B 38(4):479–488

Araújo AD, Monteiro RTR, Abarkeli RB (2003) Effect of glyphosate on the microbial activity of two Brazilian soils. Chemosphere 52:799–804
Ardley JH (1999) Pesticide considerations: an environmental concern. Agric Sci 12:21–24
Bardgett RD, Bowman WD, Kaufmann R, Schmidt SK (2005) A temporal approach to linking aboveground and belowground ecology. Trends Ecol Evol 20:634–641
Baxter J, Cummings SP (2008) The degradation of the herbicide bromoxynil and its impact on bacterial diversity in a top soil. J Appl Microbiol 104(6):1605–1616
Begum SM, Rajesh G (2015) Impact of microbial diversity and soil enzymatic activity in dimethoate amended soils series of Tamil Nadu
Bello D, Trasar-Cepeda C, Leiros MC, Gil-Sotres F (2008) Evaluation of various tests for the diagnosis of soil contamination by 2,4,5-trichlorophenol (2,4,5-TCP). Environ Pollut 156(3): 611–617
Bending GD, Turner MK, Rayns F, Marx MC, Wood M (2004) Microbial and biochemical soil quality indicators and their potential for differentiating areas under contrasting agricultural management regimes. Soil Biol Biochem 36:1785–1792
Bending GD, Rodriguez-Cruz MS, Lincoln SD (2007) Fungicide impacts on microbial communities in soils with contrasting management histories. Chemosphere 69:82–88
Bishnu A, Chakraborty A, Chakrabarti K, Saha T (2012) Ethion degradation and its correlation with microbial and biochemical parameters of tea soils. Biol Fertil Soils 48:19–29
Blain PG (1989) Aspects of pesticide toxicology. Adverse Drug React Acute Poisoning Rev 9(1): 37–68
Bosso A, Salmaso D, De Faveri E, Guaita M, Franceschi D (2015a) The use of carboxymethylcellulose for the tartaric stabilization of white wines, in comparison with other oenological additives. VITIS-J Grapevine Res 49(2):95
Bosso L, Scelza R, Testa A, Cristinzio G, Rao MA (2015b) Depletion of pentachlorophenol contamination in an agricultural soil treated with byssochlamys nivea, scopulariopsis brumptii and urban waste compost: a laboratory microcosm study. Water Air Soil Pollut 226(6):1–9
Bretaud S, Toutant JP, Saglio P (2000) Effects of carbofuran, diuron and nicosulfuronon acetyl cholinesterase activity in goldfish (*Carassius auratus*). Ecotoxicol Environ Saf 47:17–124
Burrows LA, Edwards CA (2004) The use of integrated soil microcosms to assess the impact of carbendazim on soil ecosystems. Ecotoxicology 13(1):143–161
Caceres TP, He WX, Megharaj M, Naidu R (2009) Effect of insecticide fenamiphos on soil microbial activities in Australian and Ecuadorean soils. J Environ Sci Health B 44:13–17
Carriger JF, Rand GM, Gardinali PR, Perry WB, Tompkins MS, Fernandez AM (2006) Pesticides of potential ecological concern in sediment from south Florida canals: an ecological risk prioritization for aquatic arthropods. Soil Sediment Contam 15(1):21–45
Central Food Technological Research Institute (CFTRI) (2003) Report of analysis of pesticide residue in soft drink samples, Mysore
Chenseng L, Toepel K, Irish R, Richard AF, Dana BB, Bravo R (2006) Organic diets significantly lower children's dietary exposure to organophosphorous pesticides. Environ Health Perspect 114(2):260–263
Chu HY, Zhu JG, Xie ZB, Zhang HY, Cao ZH, Li ZG (2003) Effects of lanthanum on dehydrogenase activity and carbon dioxide evolution in a haplic acrisol. J Soil Res 41:731–739
Das A, Mukherjee D (2000) Soil application of insecticides influences microorganisms and plant nutrients. Appl Soil Ecol 14(1):55–62
Demanou J, Monkiédjé A, Njiné T, Foto SM, Nola M, Zebaze Togouet SH, Kemka N (2004) Changes in soil chemical properties and microbial activities in response to the fungicide Ridomil Gold plus copper. Int J Environ Res Public Health 1(1):26–34
Deng SP, Tabatabai MA (1994) Cellulase activity of soils. Soil Biol Biochem 26:1347–1354
Dick WA, Cheng L, Wang P (2000) Soil acid and alkaline phosphatase activity as pH adjustment indicators. Soil Biol Biochem 32:1915–1919

Dong YJ, Bartlam M, Sun L, Zhou YF, Zhang ZP, Zhang CG, Rao ZH, Zhang XE (2005) Crystal structure of methyl parathion hydrolase from *Pseudomonas* sp. WBC-3. J Mol Biol 353: 655–663

Galloway T, Handy R (2003) Immunotoxicity of organophosphorus pesticides. Ecotoxicology 12: 345–363

Ganeshamurthy AN, Takkar PN (1997) Residual management of sulfur applied to soybean or wheat in a soybean-wheat system on vertisols. J Soil Res 35:199–208

Gianfreda L, Bollag JM (1994) Effect of soils on the behavior of immobilized enzymes. Soil Sci Soc Am J 58:1672–1681

Gil-Sotres F, Trasar-Cepeda C, Leirós MC, Seoane S (2005) Different approaches to evaluating soil quality using biochemical properties. Soil Biol Biochem 37:877

Glick BR (2010) Using soil bacteria to facilitate phytoremediation. Biotechnol Adv 28(3): 367–374

Guo P, Zhu L, Wang J, Wang J, Xie H, Lv D (2015) Enzymatic activities and microbial biomass in black soil as affected by azoxystrobin. Environ Earth Sci 74(2):1353–1361

Harris-Hellal J, Vallaeys T, Garnier-Zarli E, Bousserrhine N (2009) Effects of mercury on soil microbial communities in tropical soils of French Guyana. Appl Soil Ecol 41:59–68

Hashmi I, Khan MA, Kim JG (2004) Malathion degradation by *Pseudomonas* using activated sludge treatment system (biosimulator). Biotechnology 3:82–89

Hernandez-Rodriguez D, Sanchez JE, Nieto MG, Marquez-Rocha FJ (2006) Degradation of endosulfan during substrate preparation and cultivation of *Pleurotus pulmonarius*. World J Microbiol Biotechnol 22:753–760

Hussain S, Arshad M, Saleem M, Khalid A (2007) Biodegradation of α-and β-endosulfan by soil bacteria. Biodegradation 18(6):731–740

Hussain S, Siddique T, Saleem M, Arshad M, Khalid A (2009a) Impact of pesticides on soil microbial diversity, enzymes, and biochemical reactions. Adv Agron 102:159–200

Hussain S, Siddique T, Arshad M, Saleem M (2009b) Bioremediation and phytoremediation of pesticides: recent advances. Crit Rev Environ Sci Technol 39:843–907

Janvier C, Villeneuve F, Alabouvette C, Edel-Hermann V, Mateille T, Steinberg C (2007) Soil health through soil disease suppression: which strategy from descriptors to indicators? Soil Biol Biochem 39:1–23

Jin Z, Li Z, Li Q, Hu Q, Yang R, Tang H, Li M, Huang B, Zhang J, Li G (2015) Canonical correspondence analysis of soil heavy metal pollution, microflora and enzyme activities in the Pb–Zn mine tailing dam collapse area of Sidi village, SW China. Environ Earth Sci 73: 267–274

Kalam A, Tah J, Mukherjee AK (2004) Pesticide effects on microbial population and soil enzyme activities during vermicomposting of agricultural waste. J Environ Biol 25:201–208

Kalyani SS, Sharma J, Dureja P, Singh S, Lata (2010) Influence of endosulfan on microbial biomass and soil enzymatic activities of a tropical alfisol. Bull Environ Contam Toxicol 84: 351–356

Kertesz MA, Mirleau P (2004) The role of soil microbes in plant sulphur nutrition. J Exp Bot 55: 1939–1945

Kiel M, Engesser KH (2015) The biodegradation vs. biotransformation of fluorosubstituted aromatics. Appl Microbiol Biotechnol 99:7433–7464

Li Y, Liu B, Zhang X, Gao M, Wang J (2015) Effects of Cu exposure on enzyme activities and selection for microbial tolerances during swine-manure composting. J Hazard Mater 283: 512–518

Liu X, Hui C, Bi L, Romantschuk M, Kontro M, Strömmer R, Hui N (2016) Bacterial community structure in atrazine treated reforested farmland in Wuying China. Appl Soil Ecol 98:39–46

Lu C, Barr DB, Pearson M, Bartell S, Bravo R (2006) A longitudinal approach to assessing urban and suburban children's exposure to pyrethroid pesticides. Environ Health Perspect 1: 1419–1423

Mackay D, Frasar A (2000) Bioaccumulation of persistent organic chemicals: mechanisms and models. Environ Pollut 110:375–391

Majumder SP, Das AC (2016) Phosphate-solubility and phosphatase activity in Gangetic alluvial soil as influenced by organophosphate insecticide residues. Ecotoxicol Environ Saf 126:56–61

Malhotra J, Aparna K, Dua A, Sangwan N, Trimurtulu N, Rao DL, Lal R (2015) Microbial and genetic ecology of tropical Vertisols under intensive chemical farming. Environ Monit Assess 187(1):1–7

Mariela FP, Pável MEI, Manuel SRL, Jesús FGM, Reyes LO (2016) Dehydrogenase and mycorrhizal colonization: tools for monitoring agrosystem soil quality. Appl Soil Ecol 100:144–153

Menon P, Gopal M, Parsad R (2005) Effects of chlorpyrifos and quinalphos on dehydrogenase activities and reduction of Fe^{3+} in the soils of two semi-arid fields of tropical India. Agric Ecosyst Environ 108:73–83

Millard P, Singh B (2010) Does grassland vegetation drive soil microbial diversity? Nutr Cycl Agroecosyst 88:147–158

Monkiedje A, Spiteller M (2002) Effects of the phenylamide fungicides, mefenoxam and metalaxyl on the microbiological properties of a sandy loam and a sandy clay soil. Biol Fertil Soils 35:393–398

Mulchandani P, Mulchandani A, Kaneva L, Chen W (1999) Biosensor for direct determination of organophosphate nerve agents. 1. Potentiometric enzyme electrode. Biosens Bioelectron 14(1): 77–81

Murphy CD (2016) Microbial degradation of fluorinated drugs: biochemical pathways, impacts on the environment and potential applications. Appl Microbiol Biotechnol 100(6):2617–2627

Niemi RM, Vepsalainen M (2005) Stability of the fluorogenic enzyme substrates and pH optima of enzyme activities in different Finnish soils. J Microbiol Methods 60:195–205

Niemi RM, Heiskanen I, Ahtiainen JH, Rahkonen A, Mäntykoski K, Welling L, Laitinen P, Ruuttunen P (2009) Microbial toxicity and impacts on soil enzyme activities of pesticides used in potato cultivation. Appl Soil Ecol 41:293–304

Odenkirchen EW, Eisler R (1988) Chlorpyrifos hazards to fish, wildlife and invertebrates: a synoptic review. Report no. 85(1.13) U.S. fish and wildlife services. Biological report of chlorpyrifos in pure culture and in soil. Bull Environ Contam Toxicol 62:48–55

Omar SA, Abdel-Sater MA (2001) Microbial populations and enzyme activities in soil treated with pesticides. Water Air Soil Pollut 127:49–63

Pimentel D (1995) Amounts of pesticides reaching target pests: environmental impacts and ethics. J Agric Environ Ethics 8(1):17–29

Postma J, Schilder MT (2015) Enhancement of soil suppressiveness against *Rhizoctoniasolani* in sugar beet by organic amendments. Appl Soil Ecol 94:72–79

Prober SM, Leff JW, Bates ST, Borer ET, Firn J, Harpole WS, Lind EM, Seabloom EW, Adler PB, Bakker JD (2015) Plant diversity predicts beta but not alpha diversity of soil microbes across grasslands worldwide. Ecol Lett 18:85–95

Qiu XH, Bai WQ, Zhong QZ, Li M, He FQ, Li BT (2006) Isolation and characterization of a bacterial strain of the genus *Ochrobactrum* with methyl parathion mineralizing activity. J Appl Microbiol 101:986–994

Radhika V, Subramanian S, Natarajan KA (2006) Bioremediation of zinc using *Desulfotomaculum* nigrificans: bioprecipitation and characterization studies. Water Res 40:3628–3636

Raiesi F, Beheshti A (2014) Soil specific enzyme activity shows more clearly soil responses to paddy rice cultivation than absolute enzyme activity in primary forests of northwest Iran. Appl Soil Ecol 75:63–70

Rajkumar M, Prasad MNV, Swaminathan S, Freitas H (2013) Climate change driven plant–metal–microbe interactions. Environ Int 53:74–86

Rasool N, Reshi ZA (2010) Effect of the fungicide Mancozeb at different application rates on enzyme activities in a silt loam soil of the Kashmir Himalaya, India. Trop Ecol 51:199–205

Riah W, Laval K, Laroche-Ajzenberg E, Mougin C, Latour X, Trinsoutrot-Gattin I (2014) Effects of pesticides on soil enzymes: a review. Environ Chem Lett. doi:10.1007/s10311-014-0458-2

Richins RD, Kaneva I, Mulchandani A, Chen W (1997) Biodegradation of organophosphorus pesticides by surface-expressed organophosphorus hydrolase. Nat Biotechnol 15:984–987

Ronhede S, Sorensen SR, Jensen B, Aamand J (2007) Mineralization of hydroxylatedisoproturon metabolites produced by fungi. Soil Biol Biochem 39:1751–1758

Sabale RP, Shabeer TPA, Utture SC, Banerjee K, Oulkar DP, Adsule PG, Deshmukh MB (2015) Kresoxim methyl dissipation kinetics and its residue effect on soil extra-cellular and intra-cellular enzymatic activity in four different soils of India. J Environ Sci Health B 50(2):90–98

Schneider K, Turrion MB, Grierson PF, Gallardo JF (2001) Phosphatase activity, microbial phosphorus and fine root growth in forest soils in the Sierra de Gata, western central Spain. Biol Fertil Soils 34:151–155

Sebiomo A, Ogundero VW, Bankole SA (2012) Effect of four herbicides on microbial population, soil organic matter and dehydrogenase activity. Afr J Biotechnol 10:770–778

Sharma ID, Chandel RS, Kaushal R, Patyal SK, Sharma PL (2010) Effect of pesticides on biochemical properties of tomato (*Solanum lycopersicon*) cropped soil. Indian J Agric Sci 80:640–644

Singh PB, Sharma S, Saini HS, Chadha BS (2009) Biosurfactant production by *Pseudomonas* sp. and its role in aqueous phase partitioning and biodegradation of chlorpyrifos. Lett Appl Microbiol 49(3):378–383

Sukul P (2006) Enzymatic activities and microbial biomass in soil as influenced by metalaxyl residues. Soil Biol Biochem 28:320–326

Taheri AE, Hamel C, Gan Y (2015) Pyrosequencing reveals the impact of foliar fungicide application to chickpea on root fungal communities of durum wheat in subsequent year. Fungal Ecol 15:73–81

Tejada M (2009) Evolution of soil biological properties after addition of glyphosate, diflufenican and glyphosate + diflufenican herbicides. Chemosphere 76:365–373

Tejada M, Rodríguez-Morgado B, Gómez I, Parrado J (2014) Degradation of chlorpyrifos using different biostimulants/biofertilizers: Effects on soil biochemical properties and microbial community. Appl Soil Ecol 84:158–165

Trasar-Cepeda C, Leiros MC, Seoane S, Gil-Sotres F (2000) Limitations of soil enzymes as indicators of soil pollution. Soil Biol Biochem 32:1867–1875

Ubuoh EA, Akhionbare SMO, Akhionbare WN (2012) Effects of pesticide application on soil microbial spectrum: case study-fecolart demonstration farm, Owerri-West, Imo state, Nigeria. Int J Multidisc Sci Eng 3(2):34

Van Der Heijden MG, Bardgett RD, Van Straalen NM (2008) The unseen majority: soil microbes as drivers of plant diversity and productivity in terrestrial ecosystems. Ecol Lett 11:296–310

Wang SL, Wang CY, Huang TY (2008) Microbial reclamation of squid pen for the production of a novel extracellular serine protease by *Lactobacillus* paracasei subsp paracasei TKU012. Bioresour Technol 99:3411–3417

Yang CL, Sun TH, He WX, Zhou QX, Chen S (2007) Single and joint effects of pesticides and mercury on soil urease. J Environ Sci 19(2):210–216

Zhang Q, Zhou W, Liang G, Sun J, Wang X, He P (2015a) Distribution of soil nutrients, extracellular enzyme activities and microbial communities across particle-size fractions in a long-term fertilizer experiment. Appl Soil Ecol 94:59–71

Zhang X, Dong W, Dai X, Schaeffer S, Yang F, Radosevich M, Xu L, Liu X, Sun X (2015b) Responses of absolute and specific soil enzyme activities to long term additions of organic and mineral fertilizer. Sci Total Environ 536:59–67