Pesticides Pollution in Agricultural Soils of Pakistan

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Abstract Pesticides are widely used worldwide to control a range of pests infesting the agricultural crops. Increased use of pesticides has threaten human and viroenmnetal health. In this book chapter, we have compiled data regarding pesticide use, soil and water contamination, and human poining in Pakistan. Pesticide utilization in Pakistan started in 1954 and is currently on the rise. Of the total pesticides used in Pakistan, insecticides shared major portion, followed by herbicides, acaricides, and fumigants. High percentage of pesticides is being applied in the Punjab province, followed by Sindh, Khyber Pakhtoonkhaw and Balochistan. In Pakistan, the pesticide uses are mostly focused on cotton crop (almost 70–85 % of total pesticides use) and other crops such as wheat, sugarcane, maize, rice and tobacco as well as for vegetables and fruits. Different groups of pesticides, especially the residues of organochlorine, have been reported in soils and waters in different areas of Pakistan. The fate and charactiristics of pesticides in soils and percolation to deep soil depends vary with soil physico-chemical properties. Over 500,000 Pakistanis suffered annually from poisoning due to agro-chemicals, out of which 10,000 died. Regulations have also been developed for safe use of pesticides in Pakistan such as Farmer Field School led Integrated Pest Management model.

Keywords Pesticide pollution • Soil health • Pakistan • Integrated pest management • Pesticide use

1 Introduction

Increased crop production has appeared an inevitable component of modern agricultural system in order to support the increasing population pressure (Omer et al. 2010; Sabir et al. 2013; Pierart et al. 2015; Hakeem 2015). Pesticides are widely used to control a range of pests infesting the agricultural crops. In the context of current farming practices, if pesticide use is banned, the crop production will decrease significantly and food prices would soar drastically. Under such circumstances, it would become impossible to feed the ever increasing population of the world on sustainable basis. Therefore, use of pesticides has become imminent for increased crop protection and production. Application of pesticides is considered a cheap and efficient defence against the attack of pests which contributes to increased crop productivity. The use and development of pesticides to protect crops against insects, pests and diseases increased steadily during the last three to four decades. Nowadays, the development in pesticide sector has given rise to entirely new ways of production and protection of crops, as well as preservation of stored grains and their products in the godowns and warehouses.

The risks associated with the pesticides use are serious as well (Kouser and Qaim 2011; Lee et al. 2014). From environmental and health perspectives, the use of pesticides in contemporary agriculture has enhanced the impact of these chemicals on environment (Debenest et al. 2009, 2010; Kouser and Qaim 2011). Pesticide-induced chronic poisoning causes health hazards to farming community who are at high risk of being poisoned upon pesticides exposure (Lekei et al. 2014). Almost three million people have been poisoned and over 200,000 are reported to die each year around the globe as a result of pesticide poisoning (Sheikh 2011). The situation might be even worse in Pakistan, but for the moment there is very rare data available regarding pesticide contamination of air, water, soil, plants, animals and human beings.

In addition to human poisoning, use of pesticide also contaminate the different parts of an environment i.e., soil, water and air. Soil being the basic and most essential part of the ecological system is heavily contaminated by organic and inorganic pollutants including the pesticides throughout the world (Farlin et al. 2013; Shahid et al. 2013, 2015; Sultana et al. 2014; Mombo et al. 2015). Soil contamination with pesticides illustrates great attention owing to their potential risk to environmental and food safety. Pesticides pollution in agricultural soils may lead to the functional disorder of soil (Niemi et al. 2009; Karpouzas et al. 2014). For example, pesticides disturb enzymatic activity, which is considered as an indicator of soil tolerance to hazardous pollutants (Niemi et al. 2009). Pesticides interfere with soil properties and nutrient behaviour (Hussain et al. 2009; Hakeem 2015). Soil ecosystem may be disturbed by extensive use of pesticides by by harming soil microorganisms. Several previous studies have reported the harmful effects of pesticides on soil microbial diversity and activities (Hussain et al. 2009; Karpouzas et al. 2014). Pesticides also influence the microbial assisted breakdown of organic matter and nutrient dynamics and availability in soil (Kinney et al. 2005). However, the environmental and health hazards of pesticides depend on their persistence in the soil environment. Several pesticides have been banned worldwide owing to their long environmental persistence and acute toxicity.

Inside the soil, pesticides have several fates including retention or degradation, uptake by animals, plants (bioavailability) and leaching to groundwater (Fenoll et al. 2014; Paszko 2014a, b). The fate and behaviour of pesticides in soils and percolation to deep soil depends on a variety of complex biological, chemical and physical processes, including: volatilization, biochemical degradation, sorption–desorption, uptake by plants and leaching (Arias-Estévez et al. 2008; Fenoll et al. 2014). The relative importance of these processes varies with molecules properties (LogK_{ow}, K_{oc}, K_d, solubility, pKa,…), soil physico-chemical characteristics (pH, moisture content, cation exchange capacity, soil mineralogy, biological and microbial conditions) and soil organic matter contents (Gai et al. 2014; Cabrera et al. 2014). All these factors separately or in combination with each other affect pesticides behaviour and fate in soil system.

Pakistan is primarily an agricultural country where pesticides use is an integrated component of crop production. The use of pesticide in agriculture is on the rise in Pakistan (Economic Survey of Pakistan 2010–2011). In Pakistan, crop production and yield per acre have increased over the past 40 years (Economic Survey of Pakistan 2010–2011). However, the crop production in Pakistan is not constant, but fluctuates from year to year due to damage caused by insects, pests and diseases. Currently several types of fungicides, insecticides, herbicides, rodenticides and acaricides are being applied in Pakistan for crop protection (Khan et al. 2010). Several previous studies reported pesticide residues in soils and groundwater of Pakistan, however, there is a lack of comprehensive report regarding pesticide residues/persistence in the agroultural soils of Pakistan. The objective of this chapter is to summaries the use of pesticide in agricultural sector of Pakistan and the persistence of pesticides in soil.

2 Pesticide Use and Their Classification

Pesticides constitute a heterogeneous category of chemical substances, either natural or synthetic, specifically designed for the control of pests, weeds or plant diseases. There exist more than 50,000 species of plant pathogens, 9000 species of mites and insects, and 8000 species of weeds, which can damage the crops. Pests may cause annually up to 30 % loss to crop production (Saleem and Ashfaq 2004). According to the Food and Agriculture Organization of the United Nations (UN FAO), the potential human food loss worldwide is about 55 % that include 35 % preharvest and 20 % post-harvest loss. It is reported that approximately 14 % of loss is caused by insect pests, 13 % by plant pathogens, and 13 % by weeds (Pimentel 2009). Without pesticide use, the losses of vegetables, fruits and cereals from pest injury would reach respectively 54 %, 78 %, and 32 % (Cai 2008). Pesticide is so indispensable in agricultural production that approximately 1/3rd of the agricultural products are produced by using pesticides (Liu et al. 2002).

In order to control crop losses by pests, insects and diseases, thousands of different kinds of chemicals are being used worldwide. Some of the pesticide contain several active substances to combat two or more group of parasites, make their classification a real challenging task. According to the status list of active substances available commercially in the European Union (EU), >1100 pesticide substances are currently registered (Húšková et al. 2008). These active substances are classified based on (i) molecular structure of the active molecule, (ii) the formulation and (ii) the biological target. In Pakistan active substances are generally known by their brand name and function in the market and among the farming community.

Based on molecular structure of the active molecule, the pesticides are classified into; organic/botanical and inorganic. Organic pesticides are generally the products of living organisms. Organic pesticides used in Pakistan are nicotine, sabadilla, rotenone, pyrethrum, ryania and neem. Inorganic pesticides include the pesticides that are mined from the earth and ground into a fine powder. Inorganic pesticides used in Pakistan include cryptile, borates and borax. Biorational pesticides refer to synthetic, organic, or inorganic pesticides having low toxicity and little impact on the environment, which are not commonly used in Pakistan.

Taking into account the formulation and the active substances used in the chemical formula, pesticides are classified as (i) organochlorine (commonly used in Pakistan include endosulfan, dichlorodiphenyle trichloroethane (DDT), dieldrin, aldrin, heptachlor, chlordane), (ii) organophosphates (commonly used in Pakistan include malathion, parathion, chlorpyrifos), (iii) phenoxyacetic acid herbicides (2.4-D, MCPA), (iv) carbamate (carbaryl, aldicarb, carbofuran, carbaryl), (v) pyridinium herbicides: (commonly used in Pakistan include picloram, paraquat, diquat), (vi) triazine herbicides: (cyanazine, simazine, trietazine, atrazine are commonly used in Pakistan), and (vii) substitute urea (chlorotoluron, isoproturon). In Pakistan, about 145 active substances have been registered, with pyrethroids having the greatest share (45 %), followed by organophosphates (39 %), organochlorine (9 %) and carbamates (4 %). Organochlorine and organophosphates are formulated and manufactured locally in Pakistan and are used commonly for cotton protection against insects.

Based on their biological target and function, pesticides are generally classified into three families: herbicides, fungicides and insecticides. In Pakistan, currently more than 39 types of herbicides, 30 types of fungicides and 108 types of insecticides are used in Pakistan for crop protection (Khan et al. 2010). Herbicides are reported to inhibit: cell division (pendimethalin, trifluralin), photosynthesis (isoproturon, atrazine), cellulose synthesis (chlorotiamide), amino acid synthesis (glyphosate) and lipid synthesis (cycloxydime) (Dayan and Watson 2011; Dayan et al. 2012). Fungicides fight against the disease of plants caused by fungus. Fungicides are also reported to function in different ways as they can inhibit cell division and respiration of target organism (benomyl) and disturb the metabolism of carbohydrates and biosynthesis of amino acids or proteins (cyprodinil) (Fairbanks et al. 2002; Dane and Dalgiç 2005). Insecticides are employed worldwide against harmful insects to eliminate and prevent them from reproducing. Insecticides can be growth regulators (teflubenzuron), neurotoxins (indoxacarbe) and cell respiration inhibitors (cyhexatin) (James et al. 2008).

3 Pesticide Use History

Use of pesticide by human to protect crops against pest, insects and diseases dated back to 2000 BC. The wave of chemicals introduced by humans commenced with simple elements and plant derivatives (Tierney et al. 2014). Sumerians had been reported to use a sulfur containing pesticide over 4500 years ago. Chinese used sulfur as an antibacterial and fungicide at least 3000 years ago. In the Middle East, arsenic (As) was used for a variety of pests control purposes over 2000 years ago (Bentley and Chasteen 2002). Different metals {(lead (Pb), mercury (Hg) and As)} were commonly used for crop production by the fifteenth century. At some point in antiquity, humans discovered the power of plant-based chemicals for insect and/or pest control. Tobacco extract (nicotine sulfate) was used as an insecticide early in the seventeenth century. Later on rotenone (a derivative of roots of tropical vegetables) was also introduced for crop protection. Until the 1950s, pesticides containing As were dominant, such as: arsenical pesticides were widely used to control ticks in cattle, as well as to preserve the wood timber using a chromium-copper-arsenate (CCA) containing pesticide in many countries e.g., Australia, New Zealand, the USA, China (Niazi et al. 2012).

The mid-twenty century is known as a revolution in pesticide use and development. Use of herbicides was very common in the 1960s. The modern synthetic pesticides were developed around World War II when the insecticidal potential of DDT was discovered in Switzerland. Use of organochlorines, organophosphates and carbamates became common in the late 1970s. DDT and pyrethrin were dominant chemical substances in use in the whole world during 1970–1980. The discovery of DDT and analogues was thought to be miracle and a permanent solution to pest problem.

4 Worldwide Use of Pesticides

Pesticides are used widely and globally in agriculture for crop production, and have become an enduring feature of modern time. It is estimated that almost 3×10^9 kg of pesticides is used annually throughout the world with a price value of nearly $40 billion (Hussain et al. 2009). World pesticide use was more than 33390 billion dollars in 2006 and 2007 (EPA 2007). The contribution of each continent was: Europe ($10568 billion), Asia ($7815 billion), North America ($7507 billion), Latin America ($6170 billion) and Africa ($1330 billion). The quantity of herbicides accounted for the largest part ($16115 billion), followed by fungicides ($8105 billion), insecticides ($8016 billion) and other pesticides ($1154 billion). Of the total quantity of pesticides used worldwide, herbicides shared about 40 % followed by insecticides (18 %) and fungicides (10 %). It is reported that almost 80 % of the total world pesticides produced are consumed in industrialized countries and remaining 20 % in developing countries (EPA 2007). Currently, Europe is known to be the largest consumer of pesticides in the world, followed by Asia. In term of countries, China, United States, France, Brazil and Japan are the largest pesticide producers, consumers or traders in the world. However, the per acre use of pesticide is high in Costa Rica and Colombia (Table 1).

Table 1 World ranking of pesticide use per acre

Sr #	Country	Ranking	Pesticide use per acre
1	Costa Rica	1	51.2 kg
2	Colombia	2	16.7 kg
3	Netherlands	3	9.4 kg
4	Ecuador	4	6 kg
5	Portugal	5	5.3 kg
6	France	6	4.6 kg
7	Greece	7	2.8 kg
8	Uruguay	8	2.7 kg
9	Suriname	9	2.6 kg
10	Honduras	10	2.5 kg
11	Germany	10	2.5 kg
12	Austria	12	2.4 kg
13	Dominican Republic	13	2.1 kg
14	Ireland	14	1.8 kg
15	Slovakia	14	1.8 kg
16	Paraguay	16	1.5 kg
17	Denmark	17	1.4 kg
18	Jordan	17	1.4 kg
19	Czech Republic	19	1.3 kg
20	*Pakistan*	*19*	*1.3 kg*
21	Turkey	19	1.3 kg

Source: Nation Master (Year 2000), derived June 2015

5 Pesticides Use in Agriculture Sector of Pakistan

Pakistan is an agricultural country where an area of about 22.2 million ha is used for crop production (FAO 2006). Agriculture is considered as the mainstay of the Pakistan's economy because it gives jobs to more than 40 % of the population (Economic Survey of Pakistan 2010–2011). Agriculture is the sole key segment and the major source of income for about 66 % of the country's inhabitants. Agriculture sector adds 21 % of the GDP (Economic Survey of Pakistan 2010–2011). In agriculture sector, Pakistan is ranked 3rd, 7th, 9th, 11th, 19th and 20th, respectively for cotton production, farm workers, arable land, gross value added, agricultural machinery and pesticide use in the world (Nation Master 2013). The use of pesticide in agriculture is on the rise in Pakistan (Economic Survey of Pakistan 2010–2011).

The use of different substances for pest control and enhanced crop production in agricultural sector is being practised in Pakistani region since centuries. However, pesticide utilization in Pakistan started in 1954 with an import of 254 metric tons of formulated product. Pesticide consumption in Pakistan increased from 7000 tons per annum by mid-1960s to 906 metric tons in 1980. The use of synthetic pyrethroids started in Pakistan in 1980 when fenvalerate, deltamethrin and permethrin

Table 2 Pesticide imported during 1960–2010

Year	Rs (Millions)	Quantity
1960	20	4979
1970	42	2248
1980	225	7105
1990	1489	13030
2000	3477	21255
2005	8281	41561
2008	6330	27814
2009	5498	16495
2010	8741	27995

Source: Economic Survey of Pakistan

were commercially introduced. More than a dozen brands of pyrethroids were launched during 1980–1985, which made synthetic pyrethroids a major shareholder (70 %) of the total pesticides market in Pakistan. Tariq (2002) reported that during last two decades, use of pesticides increased by about 70 times in Pakistan. According to Economic Survey of Pakistan (2002–2006a, b), the pesticide import increased from 4979 to 27995 tons between 1960 and 2010, and pesticides use increased from 42732 to 46951 tons between 1998 and 2006 in Pakistan (Table 2). One of the key reasons behind enhanced use of pesticides in Pakistan is associated with very soft legislation regarding the registration and import of pesticides at that time, according to which any generic compound registered elsewhere can be imported to country without any field testing. Therefore, a major portion of pesticides applied in Pakistan are imported from Europe, US, China and India (Table 3). Of the total pesticides used in Pakistan, insecticides shared major portion (74 %), followed by herbicides (14 %), fungicides (9 %), acaricides (2 %), and fumigants (1 %) (Fig. 1) (Khooharo et al. 2008). High percentage of pesticides is being applied in the Punjab province (89 %), followed by Sindh (8 %), Khyber Pakhtoonkhaw (2 %) and Balochistan (1 %) (Khan 2000).

In Pakistan, pesticide legislation was not in practice by 1971, and the Federal Government Department of Plant Protection (DPP) was responsible for standardization of pesticides import. The agricultural pesticides ordinance (APO) and agricultural pesticide rules were formulated respectively in 1971 and 1973 under the guidelines of Food and Agriculture Organization (FAO), which governed the formulation, production, import, use, distribution and sale in the country (Mazari 2005). The ordinance also implemented registration scheme for pesticide companies, which was amended later in favour of importers (Ali et al. 2014a, b). Food and agricultural regulation was promulgated in 1965 for controlling the pesticide residues in food samples, and is not amended up-till now. By 1989, the marketing, distribution and sale of pesticides were governed by public sector, which has been transferred to the private sector since 1989. In 1999, Pakistan became the 67th member country of the Convention at United Nations in New York by signing the Rotterdam Convention. Pakistan also endorsed the Stockholm Convention since July 2000.

Table 3 Main products and area of origin of major pesticide companies working in Pakistan

Sr #	Company name	Major products	Origion
1	Syngenta	Polo, DualGold, Poytrin-C	Switzerland
2	FMC (United) Pvt.Ltd	Talstar, Furadon, Commando, Acelan	USA, China
3	Target-Ali Akbar Group	Timer, Capital+, Track, Furon, Pilot	USA, China
4	DJC-Ali Akbar Group	Shark, Shooter, Stater, Fusion, Launcher	China
5	KanzoAg	Referry, Persept, Momentu, Priorty, TopMax	China, India
6	Bayer Crop Sciences	Movento, Oberan, Lasenta, Intracal	Germany
7	Arysta Life Sciences	Padan, Radient, Tracer, Topsun, Susses	USA, China
8	Suncrop Chemicals	Leumax Extra, Trunk	China
9	SunGrow Chemicals	Mauzer, Hiflow, Spartan Super	China
10	Welcone Chemicals Pvt.Ltd	Bruce, Jassper, Jailer	China, India
11	Warble Chemicals Pvt.Ltd	Active, Bruce, Prifle, Hilt, Treasue	China, India
12	Auriga Chemicals Pvt.Ltd	Gangvi, Zarkon, Fokker	China, India
13	Sayban International	Jerk, Grow Up, Pythen	China, India

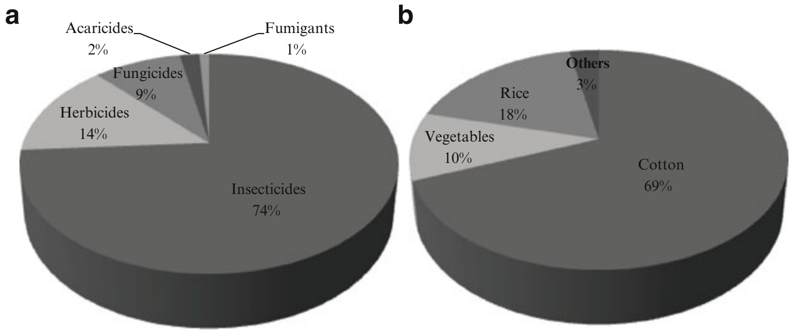

Fig. 1 Percent share of different pesticides (**a**) and their percent use for major crops (**b**) in Pakistan (2007–2012)

6 Major Crops in Pakistan and Pesticides Use

Nature has endowed Pakistan with four seasons (summer, autumn, winter and spring) and versatile land (arid, semi-arid, rainfed and mountains). Therefore, a great variety of crops, vegetables, fruits are cultivated in Pakistan. There are two major cropping seasons in Pakistan i.e., Kharif (hot summer season) and Rabi (cool winter season). Cotton, rice, sugarcane, maize, sorghum and millet are main Kharif crops while wheat, lentil, tobacco, mustard, barley, gram and rapeseed are main Rabi crops in Pakistan. To a great extent, agriculture in Pakistan is supported by major crops such as, wheat, rice, cotton and sugarcane. These major crops are reported to share almost 90 % of the value added in the major crops, which accounts for 31 % of the value added in the agriculture and 5.9 % to GDP (Economic Survey of Pakistan 2008–2009). The minor crops account for 10 % of the value added in overall agriculture. The introduction of Green Revolution technologies (use of hybrid seeds, synthetic fertilizers and pesticides) in Pakistan resulted in significant increase of crop production. For example, wheat production enhanced from 3.3 m tonnes during 1950–1951 to 22.4 m tonnes during 2008–2009. Similarly, rice production rose during the same period, from 0.86 m tonnes to 6.95 m tonnes. The production of cotton reached 11.81 million bales during 2008–2009, which was maximum (14.26 million bales) in 2004–2005. This increase in crop production is mainly attributed to increased use of agrochemical especially pesticides (Tables 4a, 4b, 5, and 6).

Among the major crops, cotton, known as white gold for Pakistan, is the backbone for the economy which contributes 1.4 % of GDP and 7 % of value added in agriculture (Economic Survey of Pakistan 2010–2011). Almost 26 % of all farmers in Pakistan grow cotton, and more than 15 % of the total cultivated area in Pakistan is devoted to this crop (Sabir et al. 2011). In Pakistan, the pesticide use is mostly focused on cotton-growing areas (almost 70–85 % of total pesticides use) (Fig. 1) (Khan et al. 2011), as cotton is the most vulnerable to pest attacks. The spray frequency in Pakistan is 10 sprays per crop season (73 % farmers), which can be upto 16 sprays in one season, especially for Bt cotton (*Bacillus thuringiensis*) (Khan et al. 2011). Most of the pesticides used in Pakistan are insecticides. Whitefly, a vector of cotton leaf curl virus, is considered among the most serious cotton pests. It is reported that during 1993, whitefly caused a loss of about three million bales of cotton, equivalent to almost 25 % of total production. Therefore, a major portion of pesticides used was consumed to control this insect (Khan 1998; Khooharo et al. 2008). However, recently a decreasing trend in cotton cultivation has been observed in Pakistan, particularly in Punjab (Sahiwal, Khanewal, Chichwatni and Vehari), which has resulted in decreased use of pesticide for cotton crop in Pakistan.

In addition to cotton, high quantities of pesticides are also used for other major and minor crops such as wheat, sugarcane, maize, rice and tobacco as well as for vegetables and fruits (Tables 4a, 4b, 5, and 6) (10–20 %) (Eavy et al. 1995). In Khyber Pukhtoonkhwa province of Pakistan, high doses of pesticides are applied on sugarcane, tobacco and maize (Ahad et al. 2000). Spray frequency is sometime more than 10 sprays per crop of tobacco. The proportion of pesticide used for these major crops has increased recently owing to increased cultivation of these and other major and minor crops. For example, during 2010–2011, the production of maize, millet, mustard and tobacco increased by 2.4 %, 18 %, 11 % and 13 %, respectively, in Pakistan. Consequently, the use of pesticides has also increased these days in Pakistan to control insect, pests and diseases of these major and minor crops. Similarly, the fruits (citrus, mangoes, apples, bananas, guavas, grapes) and vegetables (cabbage, okra, carrot, chilies, onion, potato, radish, spinach and tomatoes) are important horticultural crops in Pakistan, and account minor portion of pesticide use (Tables 4a, 4b, 5, and 6). Khan et al (2010) reported that almost 12 % pesticides are being used on vegetables and fruit crops in Pakistan. Indiscriminate and enormous use of pesticides on vegetables has been observed in Pakistan (Khan 2004).

Table 4a Pesticides used against insects, pests and diseases of major crops in Pakistan

Crops	Diseases, insects/pests	Active ingredient	Applied dose	Stage of application
Cotton	Narrow & Broad Leaf	Acetachlore	500–650 ml/acre	With in 24 h of sowing
	Jassid, Thrips, W.Fly	Imadaclopride	8–10 g/kg seed	Seed dressing
	W.Fly, Thrips, Jassid	Imadaclopride	250 ml/acre	3/leaf, 5/leaf, 1.0/plant
	Thrips	Acephate	400–500 g/acre	3/leaf
	Whitefly	Diafenthiuron	200 ml/acre	3/leaf
	Spotted BW, Pink BW, mites	Bifenthrin	250 ml/acre	Apprence of bud
	American BW, Spotted BW, Army BW	Emmamectin Benzoate	200 ml/acre	Apprence of pest
	Armyworm	Leufenoran	100 ml/acre	Apprence of pest
	Spotted BW, Pink BW	Lambada Cyhalothrin	330 ml/acre	Start of squres
	Spotted BW, Pink BW	Profenofos + Lamda Cyhalothrin	500 ml/acre	Start of squres
	Spotted BW, Pink BW	Betacyflothrin + triazohos	500 ml/acre	Apprence of bud
	Spotted BW, Pink BW	Deltamethrin	250–300 ml/acre	Appreance of bud
	W.Fly, Thrips, Jassid, Aphid	Acetameprid	125 ml/acre	5/leaf, 8–10/leaf, 1.0/leaf, 15/leaf
	Spotted BW, Pink BW	Triazophos	1000 ml/acre	Appreance of roset flower
	W.Fly Nymph	Buprofezin	600 g/acre	5/leaf
	Two Spotted, Red Mites	Pyridaben	500 ml/acre	At appreance
	Growth of Plant; escape from virus	Chelated Zinc	500 ml/acre	30–60 days of crop
Wheat	American worm & fruit borer	Leufenoran	100 ml/acre	Friut setting till maturity
	Whitefly, aphid	Acetameprid	125 ml/acre	At appreance
	Smut & Rust, karnal bunt	Thiophenate Methyl	2 g/kg seed	Seed treatment
	Narrow leaf Weeds; Bumbi sitti and jugli jaii	Clodinofop	136 g/acre	40–50 days after sowing
	Dumbi sitte & Broad leaf weeds	Metribuzin	100 g/acre	After 1st irrigation when weeds are at 2–4 leaf stage

(continued)

Table 4a (continued)

Crops	Diseases, insects/pests	Active ingredient	Applied dose	Stage of application
	Narrow Leaf Weeds	Phenoxaprop P-Ethyl	400 ml/acre	40–50 days after sowing
	Narrow leaf weed	Isoproturan	800 g/acre	After first irrigation
	Broad leaf weeds; Including "Matri"	Fluroxypyr Methyl + MCPA	150 + 250 ml/acre	After first irrigation
	Broad Leaf Weeds	Bromoxynil + MCPA	500 ml/acre	After 1st irrigation when weeds are at 2–4 leaf stage
Sugarcane	Whipe smut and Red Rot of Sugarcane	Mencozeb + Cymoxynil	250 g/400 lit water	Soak sugarcane sets in solution for 5–10 min
	Narrow & Broad leaf	Atrazine + Ametryn	1.0–1.5 kg/acre	35–40 days after sowing
	Root, stem, top, Gurdaspur borer	Carbofuron	8–14 Kg/acre	1st at sowing, 2nd at completion of hoeing
	Pyrilla	Lambda Cyhalothrin	330 ml/acre	At appreance
	Black bug	Acetameprid	125 ml/acre	At appreance

BW Bollworm, *W.Fly* White fly

Table 4b Pesticides used against insects, pests and diseases of major crops in Pakistan

Crops	Diseases, insects/pests	Active ingredient	Dose	Stage for application
Rice	Narrow & Broad leaf weeds	Butachlore	800 ml/acre	In soils where water can not stand for 4–5 days
	Narrow & some Broad	Acetachlore	100 ml/acre	In soils where water can not stand for 4–5 days
	Stem borer, leaf roller	Cartap	9 kg/acre	Two application 35 days of crop and 55 days of crop
	Leaf roller	Lambada Cyhalothrin	250 ml/acre	Before attack
	Adult and nymph of White backed Hopper	Acetameprid	125 ml/acre	Application at 45 days crop
	Nymph of White backed Hopper	Buprofezin	300 g/acre	Application at 45 days crop

(continued)

Table 4b (continued)

Crops	Diseases, insects/pests	Active ingredient	Dose	Stage for application
	Grass hopper	Carbryl	1.0 kg/acre	9 days after nursery sowing
	Bakaenee, brown leaf spot	Thiophenate Methyl	2.5 g/kg Seed (seed treatment)	15 days before sowing in dry method
	Bacterial Blight	Copper oxychloride	500–1000 g/acre	500 g for small and 1000 g for large crop
	Rice Blast or “bhabka” and brown leaf spot	Tebuconazol	250 ml/acre	Two application; 5–7 before and after penical apprence
	Rice Blast or “bhabka”	Thiophenate Methyl	500 g/acre	1st at leaves, 2nd 3–4 before penicle, 3rd 6–7 days after penicle emergence
Maize	Narrow leaf weeds	Acetochlor	500 ml/acre	With in 24 h after sowing
	Broad leaf weeds	Atrazine	500 g/acre	After sowing in tar wattar
	Narrow & Broad leaf weeds	Atrazine + Propisochlore	650 ml/acre	After sowing in tar wattar
	Shoot fly, W.Fly	Imadaclοprid	5–7 g/kg Seed	Seed dressing
	Maize Borer, Nematods	Carbofuron	8 kg/acre	1st in whorles at 1–1.5 ft height of crop, 2nd at 2.5–3.0 ft height of crop
Tobacco	Termite	Chlorpyriphos	1500–2000 Ml/acre	With irrigation water
	Bacterial wilt, Black shink angular leaf spot	Chlorthalonil	200 g/acre	Early stage of crop
	Bacterial wilt, Black shink, angular leaf spot	Mancozib + metalyxal	250 g/acre	Mid crop stage
	Bacterial wilt, Black shink, angular leaf spot	Mencozeb + Cymoxynil	250–300 g/acre	Late crop stage
	Army worm, bud worm	Leufenoran	100 ml/acre	Apprence
	Tobacco bud worm, Armyworm	Emmamectin Benzoate	150 ml/acre	Apprence

ml/acre indicates active ingredients in powder or granular form, ml/acre indicates active ingredients in liquid form

Table 5 Pesticides used against insects, pests and diseases of major fruits in Pakistan

Fruits	Diseases, insects/ pests	Active ingredient	Dose	Stage for application
Apple	Aphid, Seen Jozz Scale	Imadacloprid	100 ml/acre	Bud burst
	Codding Moth, American worm	Emmamectin Benzoate	20–25 ml/100 l water	Bud burst to fruit setting
	Spider Mites	Pyridaben	100 ml/100 l water	At symptoms
	Spider Mites	Propargite	100 ml/100 l water	At symptoms
	Powdery mildew	Tebuconazol	50 ml/100 l water	Bud burst to fruit setting
	Powdery mildew	Thiophenate Methyl	200 g/100 l water	Bud burst to fruit setting
	Apple Scap	Mencozeb + Cymoxynil	100 g/100 l water	Bud formation to fruit setting
Banana	Fingure tip rot (rotting of small comb)	Copper oxychloride	1.0 kg/400 lit water	Preventive
	Brown leaf spot (small brown spots, leaves dry and broken)	Copper oxychloride	1.0 kg/200 lit water	Preventive
	Nematodes	Carbofuron	5–10 g/plant	Preventive
	Bunchy top disease	Carbofuron	5–10 g/plant	Before transplanting the young suckers
Citrus	W.Fly, ahid	Imadacloprid	100 ml/100 literer water	Flower stage
	Leaf Minor, Citrus Psylla, lemon butterfly	Bifenthrin	50–60 ml/acre	Flower stage
	Gomosis & die back	Tebuconazol	125 ml/acre	Preventive
	Nematodes	Carbofuron	250 g/plant	August
	Die Back, Anthracnose, Gamosis	Thiophenate Methyl	200 g/100 l water	April
	Sudden death	Thiophenate Methyl	500 g/plant	April
	Fruit Fly	Trichlorofon	100 g/100 l water	May–June
	Citrus canker	Copper oxychloride	500 g/100 l water	July–september

(continued)

Table 5 (continued)

Fruits	Diseases, insects/ pests	Active ingredient	Dose	Stage for application
Mango	Mango Hopper	Imadacloprid	100 ml/100 l water	Preventive before flowing
	Scale	Imadaclopride	100 ml/100 l water	Preventive before flowering
	Fruit Fly	Tricholorofon	100–150 g/100 l water	April at 15 days interval
	Powder mildew/ blosum blight	Tebuconazol	125–150 ml/100 l water	At 30 % flowering
	Antracnose/die back	Copper oxychloride	500 g/100 l of water	Preventive in April
	Sudden death	Thiophenate Methyl	500 g/plant	Canopy of plat with irrigation, preventive

For orchards pesticides are dissolved in big water tanks (100 ml or 100 ml) and sprayed on fruit plants

Table 6 Pesticides used against insects, pests and diseases of some vegetables in Pakistan

Vegetables	Diseases, insects/ pests	Active ingredient	Dose	Stage for application
Onion	Stem rot	Thiophenate Methyl	2.5 g/l of water	Preventive
	Mites	Pyridaben	500 ml/acre	At appreance
	Purple bloch and downy mildew	Chlorthalonil	200 g/acre	Early stage of crop
	Purple bloch and downy mildew	Chlorthalonil	200 g/acre	Early stage of crop
	Purple bloch and downy mildew	Mancozib + metalyxal	250 g/acre	Mid crop stage
	Purple bloch and downy mildew	Mencozeb + Cymoxynil	250–300 g/acre	Late crop stage
	Blast	Tebuconazol	250 ml/acre	Preventive
	American worm	Leufenoran	100 ml/acre	Apprence
Potato	Jassid	Imadacloprid	80 ml/acre	15–30 days after sowing
	Armyworm & american aorm	Leufenoran	100 ml/acre	Apprence
	Americn worm + jassid	Bifenthrin	150 ml/100 lit water	Preventive
	American, Armyworm	Emmamectin Benzoate	150 ml/acre	Preventive
	Purple bloch and downy mildew	Chlorthalonil	200 g/acre	Early stage of crop
	Purple bloch and downy mildew	Mancozib + metalyxal	250 g/acre	Mid crop stage
	Early & Late Blight	Mencozeb + Cymoxynil	250 g/acre	Later stage of crop

(continued)

Table 6 (continued)

Vegetables	Diseases, insects/pests	Active ingredient	Dose	Stage for application
Tomato	Cut worm	chlorpyrifos	1500–2000 ml/acre	Fertigation
	After transplanting within 24 h	Acetochlor	500 ml/acre	Tansplanting
	Cut worm	chlorpyrifos	1500–2000 ml/acre	Fertigation
	After transplanting within 24 h	Acetochlor	500 ml/acre	Tansplanting
	Early blight	Chlorthalonil	200 g/acre	At early stage of crop
	Early and Late blight	Mancozib + Metalyxal	250 g/acre	At early stage of crop
	Fruit budworm	Emmamectin Benzoate	150 ml/acre	Leaves and fruit stage
Chilies	Narrow leaf	Acetochlor	500 ml/acre	24 h after transplantion
	Cut worms	Chlorpyriphos	1500–2000 ml/acre	Fertigation
	Colar rot	Mencozeb + Cymoxynil	250 g/acre	Preventive
	Leaf blight	Copper exychloride	500 g/acre	Preventive
	Bud Mites	Pyridaben	500 ml	At symptoms

7 Pesticide Occurrence in Agricultural Soils of Pakistan

Soil being the vital and most important part of the ecosystem is critically contaminated by persistent organic and inorganic pollutants throughout the world (Pourrut et al. 2013; Foucault et al. 2013; Sultana et al. 2014; Austruy et al. 2014; Shahid et al. 2014a, b). Soil acts as a buffer and filter regarding storage of pollutant (Burauel and Baßmann 2005; Pourrut et al. 2011; Xiong et al. 2014). It has been estimated that less than 1 % of sprayed pesticides reach the target organism while the remaining bulk flows into the soil, water and air environments (Carriger et al. 2006). It is recognized that the soil is also a potential pathway of pesticide transport to contaminate water, air, plants, food and humans. Several previous studies in Pakistan have highlighted the pollution of pesticide residues in soils (Jabbar et al. 1993; Tehseen et al. 1994; Tariq et al. 2007; Anwar 2009; Anwar et al. 2012; Syed et al. 2013; Sultana et al. 2014).

Different groups of pesticides, especially the residues of organochlorine, have been reported in soils and waters in different areas of Pakistan. Organochloride pesticides are organic compounds which contain at least one covalently bonded chlorine atom (Jiang et al. 2009). Organochloride pesticides have been used extensively in Pakistan to control crop pests and against malaria, and are detected in various environmental compartments (Bano and Siddique 1991; Tehseen et al. 1994; Tariq et al. 2007; Eqani et al. 2011; Malik et al. 2010; Syed and Malik 2011). Pakistan does not manufacture organochlorien pesticides (OCPs) and most of the chemicals are generally imported to meet the pesticides demand (Syed and Malik 2011). Organochlorine has been reported to persist in soil for long time and therefore the use of most of the organochlorine pesticides has been banned in Pakistan.

Alamdar et al. (2014) reported surface soil and air pollution of dichlorodiphenyltrichloroethane (DDTs), chlordane, heptachlor, hexachlorocyclohexane (HCH) and hexachlorobenzene in Hyderabad city, Pakistan. Mahmood et al (2014) reported contamination of DDT (320 ng/g) in agricultural soil of Gujranwala, Pakistan. Sultana et al. (2014) showed soil pollution by organochlorine pesticides especially DDT and HCHs at downstream agricultural sites, particularly at Head Panjnad. Dichlorvos soil pollution was reported in Bahawalpur district by Anwar (2009) and later in Lodhran district by Anwar et al. (2012). The Federal Pesticide Laboratories, Karachi continually monitor the pesticides level in food samples and the environment, and reported that upto 0.2–0.59 ppm of DDT was present in the sugarcane and tobacco fields of Khyber Pakhtunkhwa (KPK) and in the orchards of Bhalwal, upto 0.6 ppm in the rice fields around Kala Shah Kaku and upto 6 ppm in cotton growing areas of Multan. Hussain et al (1988) from Nuclear Institute for Agriculture and Biology, Faisalabad reported major portion of the applied DDT in the top 5 cm layer of sandy loam soils, with a very low concentration in deep soil layers. They also reported that the half life dissipation of DDT was 890 days in the laboratory, but 110 days in irrigated and 112 days in rainfed soils under field conditions. Many other researchers also reported that organochlorines (DDT) decompose very slowly and may persist for years, and are retained by soil due to their insolubility in water (Alamdar et al. 2014; Mahmood et al. 2014).

8 Groundwater and Surface Water Pollution by Pesticides in Pakistan

Leaching is a fundamental soil process whereby pesticides and other pollutants move down the soil profile by percolating water. Pesticide leaching is a key factor of groundwater pesticide pollution. The problem has become more prominent in areas where water table is high and the groundwater is the main drinking water resource (Tariq et al. 2004a; Sankararamakrishnan, et al. 2005). In the 1980s, different studies in Pakistan reported traces of pesticides in shallow drinking water wells (Ahad et al. 2001; Tariq et al. 2004a) as well as in the surface waters (Ahad et al. 2006). Parveen and Masud (1988) reported pesticides residues in cattle drinking water in Karachi. Groundwater and surface water in areas of the cotton belt in the south-eastern Punjab and Sindh plains are also reported to be polluted with pesticides (Tariq et al. 2004b). Variable concentrations (0.017–1.06 ng/mL) of DDT were detected in surface water and groundwater of different districts of Punjab, Pakistan (Asi et al. 2008). In Mianchannu, district Khanewal, the concentration of DDT (1.06 ng/mL) was 10 times more than the maximum admissible limits set by the European Community (Asi et al. 2008). Twelve groundwater samples taken from 6 different sites in Multan showed pesticide contamination, with 33 % samples exceeding the maximum threshold levels (Ahad et al. 2001). Jan et al. (2008) reported 0.07–0.40 μg/mL of DDT in and around a former DDT-producing factory in Aman Gharh, Nowshera. Jabbar et al. (1993) analysed shallow groundwater samples in Faisalabad and reported the residues of cyhalothrin (traces to 0.2 μg/L), monocrotophos (40–60 μg/L) and endrine (0. 1–0.2 μg/L).

Groundwater analysis carried out by Tariq et al. (2004b) in four cotton growing districts (Dera Ghazi Khan, Muzafargarh, Bahawalnagar and Rajan Pur) of Punjab province showed that 6 out of 8 pesticides were present in water samples at various levels but they did not exceed the maximum contaminant levels (MCLs) for drinking water set by the United States Environment Protection Agency (USEPA). Similarly, another groundwater study at twelve different sites in Mardan, reported pesticide contamination of all the samples (Ahad et al. 2000). In this study water samples from Madras Kalay (0.64 μg/L), Swabi (0.50 μg/L) and Amber (0.82 μg/L), exceeded the maximum acceptance concentration (MAC) established by the European community. Recently, press news regarding fish killing disaster in the Rawal Lake situated near federal capital (Islamabad) of Pakistan highlighted water contamination by pesticides. It was reported that the resisdues of pyrethroids pesticide residue were almost 4 times higher than Environment – European Commission (EEC) standards for drinking water (Ahad et al. 2006).

In Pakistan, pesticides do not actually present the pollution potential yet they show environmental pollution due to other factors such as shallow water tables, soil characteristics and intensive spraying (Tariq et al. 2006). Moreover, ponding irrigation may also cause pesticide contamination of the groundwater due to faster water flow infiltration (Flury et al. 1994). Other possible reasons of groundwater contamination can be leaching, careless disposal of empty containers and direct runoff (Ahad et al. 2001; Tariq et al. 2006).

9 Fate of Pesticides in Soil

Once pesticides enter the soil environment, they have several fates in soil, including retention or degradation, uptake by animals, plants and leaching to groundwater (Fenoll et al. 2014; Paszko 2014a, b). The processes relating to transformation, retention and transport reflect the fate of pesticides in soil. The fate and charactiristics of pesticides in soils and percolation to deep soil depends on a variety of complex dynamic physical, chemical and biological processes. The relative importance of these processes varies with soil physico-chemical properties (Cabrera et al. 2014).

9.1 Effect of Soil pH on Pesticide Retention in Soil

Soil pH is an important parameter, which affects the fate of pesticide in soil. The half life of pesticides in soil/water is pH dependent (Awasthi et al. 2000; Kumar and Philip 2006). Soil pH affects the adsorption/desorption reactions and chemical forms of pesticides in soils. Soil pH alters the electrical charge of certain pesticides which in turns influences the degree and the type of pesticide adsorption and degradation. The adsorption of pesticides may increase or decrease with pH depending on the pKa of the pesticide (Mamy and Barriuso 2005). Under alkaline soils conditions, endosulfan, particularly the α-isomer, is subjected to significant degradation within a week. Soil pH can influence the pathway of pesticide degradation either by affecting the adsorption of pesticides on soil components or by influencing the microbial activity (Ali et al. 2014a, b; Yenisoy-Karakaş 2006). The effect of soil pH on pesticide adsorption to soil particles is more prominent for less basic pesticides. These basic pesticides become cationic depending on their basicity and soil pH. Generally the pH is alkaline (7.5–10) in most agricultural areas of Pakistan that include arid and semi-arid regions. Under alkaline conditions, the alkaline hydrolysis occurs which breaks down the pesticide. Generally, insecticides (particularly carbamates and organophosphates) are highly susceptible to alkaline hydrolysis. The effects of pH on pesticides degradation vary with the type of pesticides and by the proportion of buffering solutions contained in the pesticide formulation. There is generally very low effect of soil pH on the degradation of pesticides having high proportion of buffering solutions in their formulation.

9.2 Effect of Soil Texture on Pesticide Retention in Soil

Soil texture is an important parameter controlling pesticide retention, leaching or runoff phenomenon. Compared to other soil components, clay is reported to be actively involved in pesticide retention in soil (Rauf et al. 2012). Generally, pesticide retention is the highest in fine grained soils (clay loam or clay soils) compared to coarse grained soils (sand or loam) (Atasoy et al. 2009; Grondona et al. 2014). The high specific surface area of clays makes them capable to bind higher amount of pesticides in soil. Indeed, the soils with high clay contents have large amounts of active surface sites such as Fe- and Mn-oxyhydroxides, clay minerals and humic acids (Owojori et al. 2010), which retain higher amounts of pesticide than coarse textured soils. Richardson and Epstein (1971) reported that endosulfan was primarily adsorbed by soil clay particles when organic matter was removed. Zhou and Zhu (2007) reported that Triton X-100, a non-ionic surfactant, was more efficient in desorbing polycyclic aromatic hydrocarbons (PAHs) pesticides from soils due to low clay content. In Pakistan, soil texture of agricultural areas ranges from sand to sandy loam. Less clay contents in Pakistani soil make it vulnerable to pesticide leaching to groundwater. Several studies in Pakistan have highlighted groundwater contamination by pesticides, which can be due to less adsorption and more leaching of these pesticides in soil.

9.3 *Effect of Soil Organic Matter (SOM) on Pesticide Retention in Soil*

Soil organic matter is one of the most dynamic and largest reservoirs of carbon on Earth (Cerli et al. 2012). Soil organic matter contents play an important role in controlling pesticide mobility and adsorption in soil (Atasoy et al. 2009; Shahid and Hussain 2011). Soil organic matter is one of the most important factors that affect pesticide adsorption, mobility and leaching in soil (Shahid and Hussain 2011). It is well established that the pesticide adsorption/retention in soil is strongly correlated with SOM content (Shahid and Hussain 2011). SOM increases pesticides retention in upper layers of soil by binding pesticides. A soil with higher SOM content is reported to have higher ability for pesticide retention owing to high chemical reactivity of SOM for organic molecules. The sorption/adsorption abilities of SOM vary with their size and chemical composition (Shahid et al. 2012a). The stability, mobility and leaching of pesticide complexes with SOM vary greatly due to variation in size and chemical composition of SOM (Rodríguez-Liébana et al. 2011). This is due to the fact that pesticides binding to SOM may take place by electrostatic interactions (charge transfer, ion exchange or ligand exchange), sorption (hydrogen bonding, hydrophobic bonding and Van der Waal's forces,), covalent bonding or combinations of these reactions (Shahid et al. 2012b). The strength of pesticide binding with SOM depends on the type of bond. Therefore, amount and type of SOM plays a key role in determining pesticide pretension in soil and percolation to deep layers. Recently, several studies reported the application of organic amendments to soil to decrease pesticide mobility in the soil profile (Shahid and Hussain 2011; Rojas et al. 2013). A number of low-cost and locally available organic adsorbents such as straw, peat mix, cow manure and charcoal have been reported by several researchers for pesticide adsorption and removal (Rojas et al. 2013). Agricultural soil in Pakistan has very less amount of organic matter (average <1 % and maximum 1.5 %), which further decreases with soil depth. Therefore, there is low retention of pesticides in Pakistani soils, resulting in maximum leaching to groundwater. SOM is also reported to affect persistence and retention of pesticides by influencing their rate of degradation or half-life in soils. The pesticides are considered persistent when DT-50 is >100 days, slightly persistent when DT-50 is 30–100 days and non-persistent when DT-50 is <30 days.

The pesticides adsorption/desorption in soil and possible leaching to groundwater is calculated using organic sorption coefficient (K_{oc}), which is the ratio of solution-phase and adsorbed-phase pesticides normalized in term of SOM contents. Pesticides are sorbed strongly in soils with high K_{oc} values. Ahmad et al. (2001) reported a positive correlation of aromaticity of SOM and K_{oc} values for several areas of Australia and Pakistan. The survey for soil and groundwater pollution by pesticides was carried out by Tariq et al. (2004b) to determine the degradation and buffering potentials of different soil series of Pakistan on the basis of pesticide half lives and observed Koc. Ahmad et al. (2001a) used solid-state Cross-Polarization Magic Angle Spinning Carbon-13 Nuclear Magnetic Resonance (CPMAS ^{13}C

NMR) to evaluate the relationships between the nature of organic matter and Koc of different pesticides by determining the structural composition of SOM in twenty seven soils of Australia and Pakistan. They reported highly significant positive correlations of Koc values and SOM aromaticity, and revealed that the aromatic component of SOM is a good indicator of a soil's potential to bind pesticides. Later on, Ahmad et al. (2001b) determined the sorption affinities of phosalone and carbaryl pesticides on forty eight different soils from the United Kingdom, Pakistan and Australia, which confirmed their initial findings (Ahmad et al. 2001a). Similarly, Tariq et al. (2004b, 2006) reported that persistence and hydrophobicity are the key properties of pesticides which control their accumulation in different soil series of Pakistan.

10 Toxic Effects of Pesticides in Soil

From environmental and health perspectives, high use of pesticides in contemporary agriculture has enhanced the impact of these chemicals on environment (Baxter and Cummings 2008; Kouser and Qasim 2011). Despite a number of benefits, pesticides may have toxic side effects, causing potential environmental and health risks. Therefore, the use of agro-chemicals, especially pesticides has become controversial owing to their environmental concerns (Henry et al. 2012; Popp et al. 2013). Soil contamination with pesticides draws great attention because of their potential threat to food safety and detrimental effects on the ecosystem. Application of pesticides in agriculture has significantly decreased the biodiversity of stream invertebrates in Australia and Europe, which resulted in a loss of 42 % species pools (Beketov et al. 2013). Pesticides pollution in agricultural soils may lead to the functional disorder of soil that interferes with soil properties and nutrient behaviour (Niemi et al. 2009; Karpouzas et al. 2014; Rodríguez-Liébana et al. 2014). Pesticides may disturb the soil ecosystem by harming soil microorganisms. Several previous studies have reported the harmful effects of pesticides on soil microbial diversity and activities (Littlefield-Wyer et al. 2008; Karpouzas et al. 2014). It is reported that pesticides can adversely influence the proliferation and associated biotransformation of beneficial soil microorganisms in the soil. Pesticides can inactivate phosphorus-solubilizing and nitrogen-fixing microorganisms in soils, and consequently affect the vital processes of biological nitrogen fixation and phosphorous solubilzation in soil.

Pesticides also affect the microbial assisted mineralization of organic matter and nutrient dynamics and bioavailability in soil (Mahía et al. 2007; Hussain et al. 2009). Soil pesticides pollution may cause functional disturbance of soil resulting in reduced soil and crop productivity (Tariq et al. 2007; Hussain et al. 2009; Tarcau et al. 2013).

Soil contains enzymes within microbial cells, immobilized extracellular enzymes and free enzymes (Mayanglambam et al. 2005; Hussain et al. 2009). Pesticides can disturb enzymatic activity of soil which is considered as useful integrative indicators of soil health (Niemi et al. 2009; Hussain et al. 2009). Soil enzymes play an important role in nutrient mineralization (urease, amidase, sulfates, phosphatase) and the breakdown of organic matter (hydrolase, glucosidase). Pesticides influences soil biochemical processes driven by microbial and enzymatic reactions (Kinney et al. 2005; Mahía et al. 2007). Negative impact of pesticides on soil enzymes such as dehydrogenase, oxidoreductases and hydrolases activities has been extensively documented previously (Menon et al. 2005).

Generally, pesticides do not affect soil enzymes activities when applied at normal/recommended doses. On the contrary, considerable effects on soil enzymatic activity have been reported when pesticides are sprayed for long periods or at higher than recommended doses. For example, Voets et al (1974) reported significant reduction in the activity of β- invertase, glucosidase, urease and phosphatase in soils after long-term atrazine applications. Pozo et al. (2011) showed a temporary reduction in phosphatase and dehydrogenase activity under chlorpyrifos application. Other similar reports include a reduction in the activity of phosphatase after long-term glyphosate applications (Sannino and Gianfreda 2001), a decrease in arylsulfatase and dehydrogenase activity following long-term atrazine applications (Megharaj 2002), and a significant reduction in the activities of urease and dehydrogenase following 15 years application of 2,4-D (isoctyl ester formulation) (Rai 1992). Some current reports have indicated the increase in development of resistance in insects and pests against pesticides. Azeem et al (2002) stated that the condition of the environment and agricultural sustainability in cotton growing areas of Punjab are going steeply downhill. Despite tremendous increase in pesticide use, cotton crops cannot be properly protected from pest's damage.

11 Risks Associated with Pesticides Use

Concerns regarding environmental and human health of pesticides have increased over the last three decades (Lekei et al. 2014). Pesticide poisoning can cause severe health hazards to agricultural workers who are at elevated risk of being poisoned (Lekei et al. 2014). Prolonged exposure to multiple pesticides may cause cytotoxic changes and negatively affect the regular functioning of organs like kidney and liver (Azmi et al. 2006; Khan et al. 2008). Pesticide poisoning results in allergic reactions and peripheral neuropathies (Corsini et al. 2013). Pesticide-induced chronic toxicity may vary from skin irritation to dysfunctioning of essential organs resulting in death, and found to be the major cause of cancer in farming community (Horrigan et al. 2002). Besides, pesticides poisoning can adversely influence the endocrine systems of humans, which may result in hormonal dysfunctioning (Ejaz et al. 2004).

The presence of pesticides in food items and their accumulation in tissues has direct toxic effects on humans and other non-target organisms. The organochlorine pesticides present in human and cow's milk are transferred to the infants. Due to their lipophilic nature, organochlorine insecticides accumulate in fat tissues of animals and are released in situations of fasting or pregnancy. Numerous previous studies in Pakistan have showed pesticide residues in fat samples and blood serum in residents of cotton-growing areas in the Punjab, Sindh and Balochistan provinces (Naqvi and Jahan 1996; Parveen et al. 2004). Hayat et al. (2010) reported pesticide in blood samples of cotton cultivating farmers. Unsafe use of pesticides is damaging the health of the farmers and the community in Pakistan. According to the UN's 1998 report, over 500,000 Pakistanis suffered annually from poisoning due to agro-chemicals, out of which 10,000 died (DAWN 2004). According to some reports, annually 10,000 farmers and field worker get poisoned by pesticides in Pakistan while unintentional acute pesticide poisoning cases are observed due to occupational exposure (Hashmi and Khan 2011; Tahir and Anwar 2012). This presents an alarming situation and serves food for thought for all those who are interested in ameliorating the plight of farming community. The situation is very much similar in other developing Asian countries. Jayaratnum et al. (1987) carried out a detailed survey of acute poisoning among farming community in four Asian countries. They reported 69 % pesticide poisoning (out of total poisoning cases) in Sri Lanka, 54 % in Malaysia, 27 % in Thailand and 23 % in Indonesia.

12 Management of Pesticide Use and Integrated Pest Management in Pakistan

Integrated Pest Management (IPM) is economical, effective and environmentally sensitive approach that combines different management practices and strategies to cultivate healthy crops with minimum use of pesticides. FAO endorses IPM as the best approach for crop protection and consider it as a mainstay of environmentally sustainable crop production. During early 70s through Agricultural Pesticide Ordinance (APO 1971), the Government of Pakistan tried to regulate production and consumption of pesticides. The legislation regarding specifications of pesticide exists in the Agricultural Pesticide Rules 1973. Regulations have also been developed for safe use of pesticides (Rasheed 2007). Recognizing and realizing health and environmental hazards attached to pesticide use, reliance on IPM has been stressed in the National Agricultural Policies. A Farmer Field School led Integrated Pest Management model popularly known as "Vehari Model", was implemented in Pakistan during 1996, which clearly showed that IPM technique can be practiced at the farm scale level. It was concluded that pesticide led control of pests and insects has actually further enhanced the pest problems, by disturbing the agroecosystem and killing the environment friendly and non-targeted organisms such as predators, parasitoids and birds. The results of this model led to the establishment of National lPM Programme of Pakistan in December 2000. This programme helps to create awareness among the farming community of the worth of biodiversity. Under this programme, Farmers Field School (FFS) activities and Training of Facilitators (TOF) were organised during 2001 in Punjab, Sindh and Balochistan provinces, in order to enhance capacity building of the farmers, through participatory learning processes. The monetary reliability of IPM has already been well established in Pakistan by the research trials in the cotton growing area of the Punjab during 1995–1996, which showed that pesticide use can be decreased upto 50 % without any major decrease in crop yield. After the successful completion of National IPM Project, currently, the National IPM Programme of Pakistan has implemented two projects i.e. “Management of cotton leaf curl virus (CLCV) disease through IPM technique by adopting Farmers Field School (FFS)” supported by International Center for Agricultural Research in the Dry Area (ICARDA) and “Integrated Crop Management Practices to enhance value chain outcome for Mango industry in Pakistan and Australia” supported by Australia Pakistan Agriculture Sector (ASLP). Despite wide acceptance and institutionalization of IPM through National IPM Programme, concerted approaches are still necessary by the government to educate the farming community on a large scale. Moreover, future research on the risk assessment, cost-benefit and feasibility of various active ingredients and other alternatives is essential to develop an effective pesticide use strategy.

13 Conclusion

In Pakistan food demand has increased due to rapid increase in population. This population flux enforced the farmers to increase the crop yield by using the agrochemicals especially the pesticides. Use of pesticides in Pakistan started in 1954, which increased rapidly with time especially during 1980–2000 owing to very soft legislation regarding pesticide registration and import. Pesticide usage is not properly regulated due to lack of awareness, ineffective legislation and technical know-how among the farming community in Pakistan. Currently, about 145 active substances have been registered in Pakistan. Insecticides are main pesticides utilized in Pakistan especially in Punjab province. Cotton shares about 80 % of pesticide use in Pakistan, therefore maximum soil and water contamination is observed in cotton zone. Pesticide residues especially organochlorines have been reported in groundwater, surface water, wells and soils of Pakistan particularly in cotton growing areas of Sindh and Punjab. The soil of Pakistan generally contains less clay, low organic matter contents with alkaline pH. Therefore, pesticides do not persist for long time in soil of Pakistan. Pesticide leaching to groundwater is common in Pakistan. Pesticides poisoning has been observed in farming community, which is causing sever health issues in Pakistan. Despite several environmental issues related to pesticide use, still the use of chemical pesticides is the only possible and feasiable way of crop protection in Pakistan and there is no shift away from it. The government of Pakistan has launched National lPM Programme in December 2000 to educate the farming community regarding minimize use of Pesticides. Still there is a dire need of rigorous approaches at national level to educate the farming community regarding pesticide use and poisoning.

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