Chapter 8
Pesticide Residue and Food Safety: Retrospection and Prospects

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8.1 Introduction

Chemical pesticides have been one of the key means and will be the major one in the future as well to protect crops from pests. Various pesticides were used as insecticides, fungicides, herbicides, rodenticides, molluscicides, nematicides, etc. Furthermore, pesticides are classified as biopesticides, biochemical pesticides, chemical pesticides, organic and inorganic pesticides based on their targets, action mechanism, chemical properties, etc. (Leong et al. 2020). Pesticides use in agricultural production systems have been increasingly practiced these days to minimize crop losses whose ultimate goal is to feed the growing population worldwide. Food production needs to feed 9.73 billion people until 2050 for which it is expected to increase agricultural product demand by 50% (FAO 2017). Therefore, realizing the need to grow more in the future, along with improvement in various inputs of agriculture, an increase in the use of pesticides in the future seems inevitable. Since the formulation of the DDT by Paul Muller (Anonymous 1965), the continuous use of chemical pesticides in the agriculture and the health sector has impacted in both positive and negative ways. Positive impact is reduced crop loss due to pests which increase food in terms of quality and quantity (Damalas 2009). The use of different pesticides in vector control has also reduced the transmission of vector-borne diseases to humans (WHO 2019). For example, 42% reduction in mortality due to malaria was observed in 2000 due to the control of vectors (https://croplife.org/wp-content/uploads/pdf_files/Vector-Control-fact-sheet.pdf) by an integrated approach including pesticide use (WHO 2017). Not only in agricultural pest and vector control, but an increase in pesticides has also contributed to overall economic development (Hedlund et al. 2020). Though pesticide has an immense positive

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contribution to humankind it has a negative impact as well (Damalas 2009). Since pesticides are toxic, their effect on human and livestock health is always at risk if guidelines for pesticide handling are not properly maintained. There is another problem associated with the frequent use of the pesticide where resistance to create pests switching to alternate pesticides. Resurgence and outbreaks of pests are the major problems, while vulnerable natural enemies die due to the toxic effect of chemical pesticides. Residue problem from the use of DDT was realized as early and was discouraged to use in forage crops (Decker 1946). Pesticide contamination could pollute the air, water, and soil (Tudi et al. 2021) as well as it has some negative effects on the whole ecosystem (Sharma et al. 2019; Pisa et al. 2021) where the accumulation of persistent pesticides as residue could occur. Bio-magnification and bioaccumulation of persistent pesticides is another problem that increases the risk to the organism. There are large differences in implementing and executing international rules and regulations related to pesticide management due to the lack of proper knowledge, funding, infrastructure as well as skilled manpower in developing or low-income countries than developed countries. Therefore, this chapter aims to look at the pesticide residue problem in retrospection and prospects for mitigation giving emphasis to developing countries.

8.2 Pesticide Consumption

Total pesticide (active ingredients, a.i.) use in the world has increased from 1.7 million tons in 1990 to 2.7 million tons in 2020 (FAOSTAT 2022) (Fig. 8.1a). Total pesticide consumption in Nepal has also increased from 60 to 681.5 tons. Though the total pesticide used for agriculture in 2020 was only 681.5 tons (Fig. 8.1b), the increase in pesticide use in Nepal when compared to 1990 was very high (91.2%) among the countries.

FAOSTAT (2022) showed that the USA used the maximum amount (407779.5 tons) of pesticides in 2020 followed by China (273375.5 tons), Brazil (231621.2 tons), Argentina (132255.1 tons), and France (81463.79 tons) (Fig. 8.2a). The top

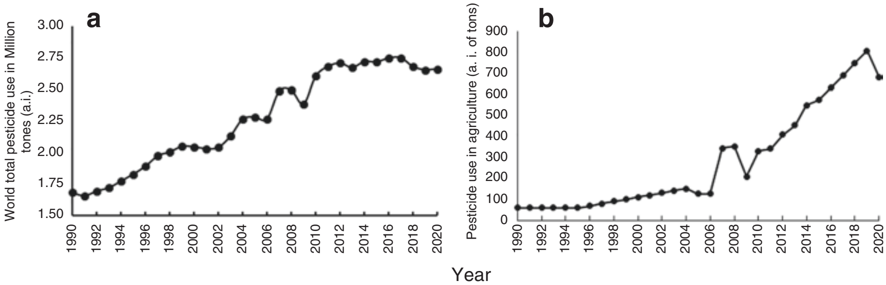


Fig. 8.1 Rise in total pesticide use in Agriculture (**a**) World, (**b**) Nepal from 1990 to 2020 (FAOSTAT 2022)

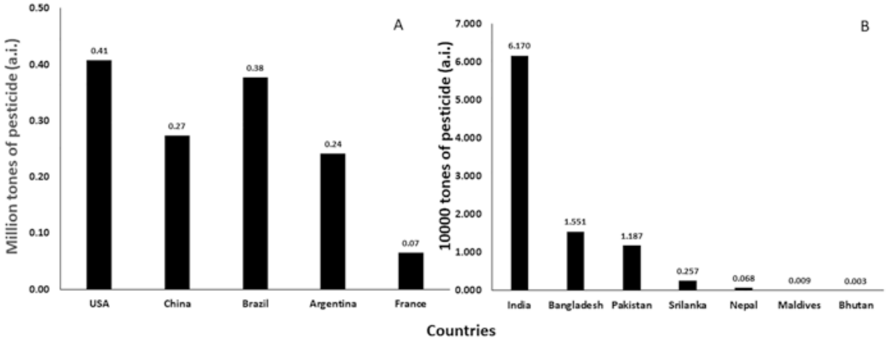


Fig. 8.2 (**a**) Top 5 countries that uses maximum amount of total pesticide in agriculture during 2020. (**b**) Total pesticide use in agriculture by South Asian (SAARC) countries during 2020

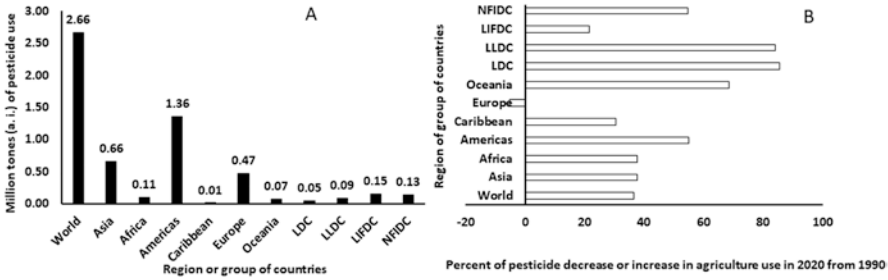


Fig. 8.3 (**a**) Total pesticide used in agriculture by different region or countries during 2020. (**b**) Percent increase or decrease of pesticides use in agriculture by region or group of countries during 2020 compared to 1990. LDC Least Developed Countries, LLDC Land Locked Developing Countries, LIFDC Low Income Food Deficit Countries, NFIDC Net Food Importing Developing Countries

total pesticide user in South Asia is India (61701.9 tons) followed by Bangladesh (15506.47) in 2020 (Fig. 8.2b).

Pesticide consumption for agricultural use has been in increasing trend in many countries. The concern is that most of the pesticide (89%) was only used in vegetables (PRMS 2015) 1.45 to 1.6 kg a.i./ha (Sharma 1994; Thapa 1997, PRMS 2015). Similarly, the pesticide used in agriculture increased rapidly as compared to the world total with the regions and group of developing countries. When compared to the world total Americas (1.36 million tons) used most pesticides in agriculture followed by Asia and Europe while group of developing countries have less pesticide use in agriculture (Fig. 8.3a). Though the group least developed and developing countries have far less use of pesticide in agriculture, the problem of pesticide residue there persist because of improper handling of pesticides and lack of regular advance monitoring and residue analysis systems (GC and Palikhe 2021). When total pesticide used in agriculture during 2020 is compared with use in 1990, all the regions across the world have increased use of pesticide while use of pesticide amount has been shown decreased by 5.2% for European countries. Least Developed Countries (LDC), Land Locked Developing Countries (LLDC), Low Income Food Deficit Countries (LIFDC), Net Food Importing Developing Countries (NFIDC) have increased pesticide use in agriculture; LLDC and LDC being countries with high increase of pesticide use (Fig. 8.3b). These statistics clearly showed that the countries with low income and food deficit group need assistance in many aspects of pesticide use and monitoring.

Though pesticide use was very less in low-income countries, there is a clear gap in knowing the pesticide efficacy and its ill effects on human health and the environment in various stages of the pesticide cycle like policy formation and implementation, pesticide application, implementation of IPM, etc. (van den Berg et al. 2020). Awareness regarding various aspects of pesticide use like proper pesticide handling, proper doses, and frequency, safety measure while application, proper disposal, selection of proper pesticides for targeted pests especially in low-income countries are very limited and the problem is very prominent (Maharjan et al. 2004; Giri et al. 2004, 2014; Aryal et al. 2020; Staudacher et al. 2020; Negatu et al. 2021). The lack of adequate adoption of IPM also causes pesticide-related problems. Low adoption of the IPM may be due to low funding, insufficient knowledge and inputs, policies, user preferences, and lack of practical technologies, especially in low-income and developing countries (Tiwari et al. 2020; Day et al. 2022). Problem of pesticide residue arises when there is improper use and management of pesticides while contaminated shipment from abroad also causes health risks to the consumers. During 2018, countries that used maximum amount of pesticides per unit of cropland were Mauritius (28 kg/ha), Ecuador (26 kg/ha), Trinidad and Tobago (25 kg/ha), Costa Rica (22 kg/ha), Bahamas (21 kg/ha), Barbados (21 kg/ha), Saint Lucia (20 kg/ha), China (13 kg/ha), Israel (13 kg/ha), and Seychelles (12 kg/ha) whereas in 2020 top 10 countries are different than in 2018 which were Saint Lucia (20 kg/ha), Maldives (17 kg/ha), Oman (16 kg/ha), Israel (15 kg/ha), Ecuador (14 kg/ha), Seychelles (12 kg/ha), Japan (12 kg/ha), Belize (11 kg/ha), the Netherlands (11 kg/ha) and the Republic of Korea (10 kg/ha) (Table 8.1).

8.3 Problems and Effects of Pesticide Residues

After the formulation of dichlorodiphenyltrichloroethane (DDT) by Paul Muller in 1939, its use was widespread in vector and agriculture pest control (Anonymous 1965). But residue of DDT was detected as early as 1946 and was discouraged to use in forage crops (Decker 1946). Since then, effects and problem arose by pesticide residue has been experimentally proved or reviewed by various researchers around the globe.

Table 8.1 Top ten countries for pesticide use per unit of cropland during 2018 and 2020

SN	Countries	2018[a] (kg/ha)	2020 (kg/ha)[b]
1	Mauritius	28	–
2	Ecuador	26	14 (5)
3	Trinidad and Tobago	25	–
4	Costa Rica	22	–
5	Bahamas	21	–
6	Barbados	21	–
7	Saint Lucia	20	20 (1)
8	China	13	–
9	Israel	13	15 (4)
10	Seychelles	12	12 (5)
11	Maldives	–	17 (2)
12	Oman	–	16 (3)
13	Japan	–	12 (7)
14	Belize	–	11 (8)
15	The Netherlands	–	11 (9)
16	The Republic of Korea	–	10 (10)

Source: FAO (2018, 2020)
[a]Data in third column are for top 10 countries in ranked order as listed in column 2
[b]Data in fourth column are representing the top 10 countries without ranked order. Ranking is given in parenthesis

8.3.1 Effect on Non-target Animals

Out of the total pesticide use, 80% of the pesticide directly affects non-target animals (Sajjad Ali et al. 2021) which can also contaminate ecosystems of soil and water (Aktar et al. 2009; Giri et al. 2016). Active ingredient of the pesticide can also affect non-target animals in agro-ecosystems like vertebrate and invertebrate predators and parasitoids. Contact toxicity of some pesticide residue has already been tested as early in 1963 where most of the tested pesticides cause high to medium toxicity on hymenopterous parasites (Bartlett 1963). Barros et al. (2018) showed that the residue of chlorantraniliprole, chlorfenapyr, spinosad, lambda-cyhalothrinn, methidthion, pymetrozine and thiamethoxam caused mortality to parasitoids in cotton ecosystem. Similarly, Pesticide residue increases in plant and animal through the phenomenon called bioaccumulation and bio-magnification (Bro-Rasmussen 1996; Carvalho 2017; Chormare and Kumar 2022). Honey bee decline is also responsible due to the use of organophosphate, pyrethroid, systemic neonicotinoids, imidacloprid and thiamethoxam in agriculture (Ali et al. 2021).

8.3.2 Bioaccumulation and Bio-magnification

Pesticide uptake from contaminated food and water inside the body of an organism is referred to as bioaccumulation whereas the increased accumulation of the pesticide residue in organisms as increased in trophic level is the ecological magnification (Gupta and Gupta 2020). Chemical pesticides applied to agricultural crops may be deposited in soil, washed by runoff, and could contaminate rivers and ponds. This process of contamination of water bodies was presented by Kale et al. (1999) who found that Metabolized DDE bio-accumulated in the aquatic food chain and ultimately was transferred to humans. Most vulnerable to be affected by these two phenomena are the members present at higher trophic levels i.e. humans where bioaccumulation could occur when uptake of marine and agricultural diet, while contaminant enters through respiration has less likely to get accumulated (Czub and Mclachlan 2004). Rossi et al. (2020) tested the pesticide in fish inhabiting rice fields before and after the application of the pesticide where he found that all the specimens of *M. nigripinnis* had tested pesticide accumulated inside it after 21 days of applications in considerable amount. Fish reared in rice fields have increased levels of lambda-cyhalothrin and tebuconazole accumulated in muscles (Clasen et al. 2018) which have inflicted significant adverse effects on fish itself as well as possess a risk to humans who consume pesticide bioaccumulated fish. Similarly, tigerfish (*Hydrocynus vittatus*) from the Luvuvhu river had a high level of accumulation of organochlorine pesticides which even exceed the maximum residue level set by the European Union (Gerber et al. 2016) which even poses a high risk of cancer to the populations who consume contaminated fish around the area. Bonansea et al. (2016) exposed fish *Jenynsia multidentata* to cypermethrin and chlorpyrifos individually and in combination where they found that cypermethrin and chlorpyrifos accumulation is measured higher in the liver followed by the intestine, gills, and muscles in the mixture than exposed with single pesticide. Panseri et al. (2019) studied the persistent organic pesticide accumulation in Tuna, Sea bream, and Dentex fishes where they found high OC accumulation occurred in tuna fish. Organochlorine residue accumulation of some fish species from East Kolkata also reveals contamination of DDT, endosulfan, and dicofol in three fish species. Moreover, Pérez-Parada et al. (2018) reviewed and discussed the pesticide bioaccumulation on freshwater fish which ultimately concerns human food safety. Biomagnification in the aquatic ecosystem was assessed by Tongo et al. (2022) at Ikpoba River of Nigeria where they showed transfer of the pesticide in trophic levels where Food Chain Bio-magnification value for certain organochlorines, glyphosate, carbofuran, and diazinon were high.

Bio-magnification in the terrestrial food chain is much higher than that of aquatic food chain (Gobas et al. 2013). Terrestrial ecosystem contamination was basically from the aquatic sources of pesticides which could be due to biologically mediated pathways like terrestrial food webs or abiotic pathways from runoff, flooding, and groundwater contamination (Schulz and Bundschuh 2020). Terrestrial organisms around the pesticide factory were also not pardoned due to the pesticide residue problem. Though the highest level of residues of organochlorine was found in soil around the factory, the concentrations of residues in insects, chickens, and birds were moderate and are within the acceptable safe limits (Tang et al. 2016). Wild life terrestrial populations have higher levels of POPs pesticides, and are at a higher level of trophic levels (De Solla 2016). Trophic magnification factors in the terrestrial food web were between 1.2 and 15 for POPs pesticide which indicated that it has a greater capacity to get magnified (Fremlin et al. 2020). Transfer process and bio-magnification of pesticides in the terrestrial ecosystems from soil to vegetation and animal was well described by Connell (2018). Not only the pesticide cause problems in the application area but can also inflict a problem in the neighboring area or even neighboring countries. Yadav et al. (2015) reviewed that the POPs in the air, water, and soil can possibly affect neighboring countries.

8.3.3 Pesticide Residue in Agriculture Products and Food

Residues on fruits and vegetables coming to the Nordic countries from South East Asian countries have been studied where pesticides were detected in 111 samples out of 721. 14% of the sample contained residue more than MRL of EU standard some of which could cause an acute health risk for consumers (Skretteberg et al. 2015). EU-coordinated control program has collected 88,141 food samples and analyzed the residue level across the EU member states on 2020 which showed 94.9% of samples fell below MRL where 5.1% exceeded the level and 3.6% were non-compliant (EFSA et al. 2022). The samples which were non-complaint were increased by 1.3% than 2019 where non-compliant samples were about 2.3% (EFSA et al. 2022). Non-compliant subjected to legal sanctions or enforcement action.

Research in Bangladesh showed that 50% of green bean sample was contaminated with insecticide above EU MRL which poses threats to adult and children's health where an estimated daily intake of 2.79×10^{-4} to 2.96×10^{-4} in an adult with a hazard quotient of 0.56–0.59 and 9.79×10^{-4} to 1.77×10^{-3} with hazard quotient of 1.96–3.55 in children were reported. Children are more vulnerable to pesticide residue exposure (Parven et al. 2021). Carbendazim and chlorpyrifos residues were detected in eggplant, chilli and tomato samples in the Nepalese vegetable market (Bhandari et al. 2019) where pesticide residues in 4% of the eggplant, 44% of the tomato, and 19% of the chilli samples exceeded the EU MRLs. Further they also performed a risk analysis of human health where the highest acute hazard quotient (aHQ) was for triazophos (tomato) in adolescents (aHQ = 657) and adults (aHQ = 677), showing the highest risks of dietary exposure. There are some studies on pesticide residue by Nepal Agricultural Research Council and other organizations in Nepal which were comprehensively reviewed by Aryal et al. (2020) and Giri et al. (2016). When analyzing the consumption data, the group of least developed and developing countries have shown far less use of pesticide in agriculture, the problem of pesticide residue still persists because of improper handling of pesticides and lack of regular advanced monitoring and residue analysis systems.

Neonicotinoid residue has been extensively studied these days due to its toxicological effects in mammals and honey bees. One of the studies in US showed that, of the collected samples, all the vegetable samples except nectarine and tomato, and 90% of honey samples were detected positive for at least one neonicotinoid residues (Chen et al. 2014). A review paper from Pakistan reflects that 50% of samples were contaminated either with organophosphate or pyrethroids or organochlorine pesticides where 50% of the samples were having residues above maximum residue limits (Syed et al. 2014). Another review paper revealed that milk and milk samples collected from different parts of Pakistan contaminated with organophosphates and organochlorine pesticides (Akhtar and Ahad 2017). Pesticide residue in animal feed may cause problems in dairy animals which ultimately results in the loss of meat production (Choudhary et al. 2018). Not only pesticide residue related to own products but imported produce also need to be monitored and scrutinized to protect the health of the consumers.

8.3.4 Pesticide Residue Problem in Trade

There are many instances that the agricultural produce acceptance has been denied by importing countries because of non-compliance with food safety and health standards set by importing countries (Goyal et al. 2017). Most of vegetable shipment into the United States was refused because of pesticide residue problems (Buzby et al. 2008; Bovay 2016). China's refusal of food imports due to violations in complying with standards or excessive set values for some additives and chemicals including pesticides accounted for 27% of the total refusal from 2013 to 2019 (Gale 2021). Being more interdependency is prevailing among countries, the demand is for integration and harmony on rules and regulations on international trade (Whitehead 2019) but there is still asynchrony in the agricultural food trade due to asynchronous MRLs set by different countries which ultimately create trade problems worldwide (Yeung et al. 2017). Further, the differences in MRLs standards were described by Racke (2007) who compared the standard of MRL set by Codex, EU, Japan, and the US for some pesticides. There is a great threat in the trade of agricultural food products due to a lack of harmonization in pesticide regulation including different MRLs of different countries (Yeung et al. 2017). There are some differences in national or regional MRLs than that of Codex (Table 8.2). Some countries specified MRL for individual pesticides for a particular commodity or group of commodities.

Revision and changes in regulation (MRL setting) making them stringent could cause an exporting country hard to comply in time, and could be a great setback for them. Such example has been reviewed by Yeung et al. (2017) for revision of MRL for banana which causes difficulties for the Philippines to export them. Ghana cocoa exporters need seeking alternate market after stringent MRL value was set by Japan. Canada exporter could not meet the standard after EU asked to reduce MRL of

Table 8.2 Example of the MRLs comparison set by a different group of countries or specific countries for some commonly used pesticides for tomato (mg/kg or ppm)

	Pesticides	Codex	EU	US	S. Korea	India	Nepal
1	Chlorpyrifos	NA	0.01	NA	NA	NA	NA
2	Abamectin	0.05	0.09	0.07	0.05	NA	0.05
3	Spiromesifen	0.7	1	0.45	1	0.7	NA
4	Imidacloprid	0.5	0.3	NA	1	1	0.5
5	Malathion	0.5	0.02	8	NA	NA	0.5
6	Chlorantraniliprole	NA	0.6	NA	1	0.6	NA
7	Spinosad	0.3	0.7	0.4	1	NA	0.3
8	Cypermethrin	0.2	0.5	0.2	0.15	NA	0.2
9	Metalaxyl	0.5	0.3	1	0.5	NA	0.5
10	Tebuconazole	0.7	0.9	1.3	1	2	0.7

Sources:
https://www.fao.org/fao-who-codexalimentarius/codex-texts/dbs/pestres/pesticides/en/
https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/mrls/?event=download.MRL
https://www.fas.usda.gov/maximum-residue-limits-mrl-database
https://www.foodsafetykorea.go.kr/foodcode/02_01_02.jsp?s_option=EN&s_type=12
https://www.fssai.gov.in/upload/uploadfiles/files/Compendium_Contaminants_Regulations_20_08_2020.pdf
http://www.dftqc.gov.np/noticedetail/80/2021/45518958
NA Not Available

chlorothalonil from 2 to 0.01 ppm. A total of 33,911 samples were analyzed for pesticide residues that were imported into the UK from 2000 to 2020 where 50.2% samples contained of detectable residue with 3.3% of samples having residue beyond MRLs (Mert et al. 2022). Food that exceeds MRLs is due to the amendments in food monitoring programs of the UK with strict provisions. Likewise, Stringent MRLs of European countries hinder the exports of fruits and vegetables by the US by 13.8% whereas worldwide bilateral trade is reduced by 8.8% due to stringent MRLs policy (Hejazi et al. 2022). Even developed countries like the US have found difficulties meeting the stringent standard set by importing countries, developing and underdeveloped countries are far less able to meet those standards. Ferro et al. (2015) clearly presented that exporters from low-income countries are having difficulties in exporting goods and are restricted to export due to stricter standards set by importing countries. Wilson and Otsuki (2004) showed that an increase of 1% in stringent regulation and tighter restrictions on chlorpyrifos resulted in a decrease in banana imports by 1.63%. They also simulate the gravity model to establish a difference in trade flow when regulatory standards are changed which directly affect the developing countries that export banana to OECD countries. They further analyze the loss of US$ 5.5 billion of exports occurs per year due to stringent standards set by the EU in contrast to a world standard i.e. Codex standards.

8.3.5 Human Health Risks Associated with Pesticide Exposure

Pesticide residues in food and their impact on human health were reviewed as early during the sixties when Durham (1963) explained its neurotoxicity and carcinogenic effects. POPS are known to have many adverse effects on human health such as diabetes, thyroid problems, endocrine disruption, behavioral problem, and even cancer (Islam et al. 2018). Pesticide residues can pose a concern to human health which may have short as well as long-term effects. Short-term effects may be headache, nausea, stomach pain, blurred vision, dizziness, vomiting, sweating, skin itching, etc. (Maharjan et al. 2004; Gerage et al. 2017) whereas long-term exposures could cause carcinogenic effects, Neurological effects, Endocrine disruptions, effect on reproduction and fertility (Debnath and Khan 2017; Ali et al. 2021) as well as the cause of mutagenic abnormalities are also associated with pesticides (Giri et al. 2002). Pesticide is responsible for causing cancer and was reviewed by Weichenthal et al. (2010) who revealed that lung, pancreas, colon, rectum, leukemia, multiple myeloma, bladder, prostate, brain, melanoma, lymphoma cancer was associated with at least one kind of different group of pesticides.

Acetylcholinesterase (AChE) enzyme activity was assessed using the modified Ellman method by Serrano-Medina et al. (2019) where they found anxiety was associated with 23.9% of farmers who have inhibited enzymatic activity whereas 23.5% showed effects of both depression and anxiety. Chronic exposure to organophosphate pesticides associated with neurological disorder includes anxiety, reduced motor conduction velocity, reduced serum AChE, reduced verbal memory, reduced motor speed, and motor coordination, and delayed polyneuropathy (Kori et al. 2018; Silver and Meeker 2020). Similarly, Kori et al. (2018) also pointed out the disorder associated with organochlorine, pyrethroids, and carbamates are neurochemical and behavioral disorders. Prenatal and early childhood exposure to organophosphate pesticide among children results in cognitive deficits in prenatal stage, behavioral deficits in toddlers and motor deficits in the children at age 7 (Muñoz-Quezada et al. 2013). Silver and Meeker (2020) also concluded that prenatal exposure of organophophates impact neurodevelopment, organochlorine may cause obesity, POPs may be associated with premature birth and it badly affects fetal growth, congenital abnormalities and childhood cancer (leukemia and brain tumors).

To overcome the problem associated with pesticide residue, there are several rules and regulations set worldwide and by individual countries, international convention on pesticide management, various activities proposed by countries to reduce the use of highly hazardous chemical pesticides. Those mitigation processes are discussed.

8.4 Techniques in Pesticide Residue Analysis

According to chemical properties and for level of detection different methods are employed for residue extraction and end analysis. Sample pre-treatment and extraction method may also vary depending upon which pesticide being analyzed. Various extraction methods are used since the residue analysis technique has been in practice. Liquid-liquid and solid-liquid extraction was common for residue extraction earlier (Narenderan et al. 2020) but now QuEChERS methods (Anastassiades et al. 2003) are used in most of the extraction which were further enhanced with various modifications. This QuEChERS method utilizes minimum quantity of solvent and reagents than earlier method of residue extraction. Likewise, chromatography was also got evolved from TLC to much sophisticated equipment's like GLC, GC coupled with detectors, GC/MS, GC/MS/MS, HPLC, LC/MS, LC/MS/MS, TQ UHPLC-MS/MS, UHPLC-IMS-QTOF MS and Surface enhanced Raman spectroscopy (Martins et al. 2017; Sarath Chandran et al. 2019; Narenderan et al. 2020; Lacalle-Bergeron et al. 2020; Soltani Nazarloo et al. 2021; Wahab et al. 2022). Further, reflective spectroscopy (VIS/NIR) can be used to detect pesticide without destruction of sample (Yu et al. 2020; Narenderan et al. 2020).

A rapid bioassay of pesticide residues (RBPR) has been introduced by TARI and has been adopted by many countries for quick detection of certain group of pesticide which involve acetylecholinesterase (Kao et al. 2010; Aryal et al. 2020). Recent year ELISA technique which employ antibodies or enzymes for different 18 pesticides have been developed which can detect pesticide residue ranging from 0.01 to 2.24 ppb (Chang et al. 2018). Some improvement and modification to enzyme-linked immunosorbent assay (ELISA) to enhance the sensitivity of pesticide detection were also performed these days (Li et al. 2019; Ji et al. 2020). Chemiluminescence immunoassay is another technique for pesticide residue analysis which can be used in conjunction with many detection systems (Al Yahyai and Al-Lawati 2021). TiO2-CPE nanocomposites electrode provide very good sensitivity for the cypermethrin and sensitivity can be increased with the increase of anatase TiO2 concentration which can detect down to the level of ~0.1 ppm (Nurdin et al. 2019). Modified TiO2-CPE can also effectively detect fipronil pesticide (Maulidiyah et al. 2019).

8.5 Mitigation of Problems Associated with Pesticide Residue Analysis

8.5.1 *Rules and Regulations on Pesticide Residues Mitigation*

8.5.1.1 Global and FAO

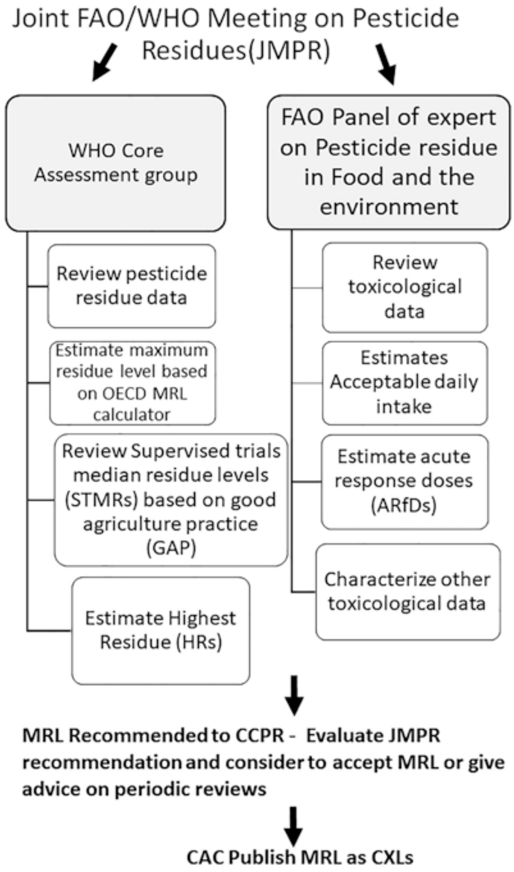
Pesticide residue in ecosystem is one of the pressing issues which need to be dealt with proper manner. International code of conduct was first approved by FAO in 1985 whereas the fourth version of the same was approved in 2013 and published during 2014. The code has 12 articles and one annexure which comprised guideline of pesticide management, labeling, packaging, storage and disposal and other aspects which directly help in reducing pesticide residues (FAO/WHO 2014; FAO/WHO 2022). This code is especially for those countries who could not establish their own standards or the standards available are inadequate. Stockholm convention which entered into action on 2004 is a global treaty whose objective is to protect human and environmental health from exposure to Persistent Organic Pollutants (POPs). It prohibits or aims in the elimination of production, use, import and export of POPs with some exceptions. Similarly, Rotterdam convention was adopted in 1998 and entered into action from 2004. Its major role is to create obligation to implement Prior Informed Consent (PIC) which facilitates exchange of information about hazardous chemicals among the parties in order to protect human health and environment. Montreal Protocol which regulates and phase down 100 man-made ozone depleting substances (ODS).

Food and Agriculture Organization (FAO) of United Nations therefore has formulated guideline for pesticide management via various forums. Those were Joint Meeting on Pesticide Management (JMPM), the Joint Meeting on Pesticide Specifications (JMPS) and the Joint Meeting on Pesticide Residues (JMPR), where JMPM advices FAO and WHO on the International Code of Conduct on Pesticide Management and the development of its technical guidelines, JMPS recommends to FAO and WHO on the adoption, extension, modification or withdrawal of pesticide specifications and to develop guidance and procedures in establishing pesticide specifications, and JMPR provides scientific advice to Codex Alimentarius, who sets maximum residue limits (MRLs) for pesticides in food and feed. Before a Codex establish MRL, JMPR, FAO/WHO experts review toxicological data and data from supervised trials in accordance with good agricultural practice. JMPR also conducts dietary risk assessment and then only report to the Codex Committee on Pesticide Residues (CCPR) who is authorized for establishing Codex Maximum Residue Limits (MRLs) for pesticide residues in food items or in groups of food or feed which are part of international trade, which ultimately report to Codex Alimentarius Committee (CAC) for adoption as Codex Maximum Residue Levels (CXLs) (Fig. 8.4). Codex has established over 5200 MRLs covering 300 pesticides (Wieck and Grant 2021).

8.5.1.2 EU and US

European Union has formulated the regulation on 23rd February 2005 on maximum residue level of pesticides in or on food and feed of plant and animal origin (EU 2005) which has amended time to time as necessary. Similarly European Food Safety Authority (EFSA) has promulgated different technical guidelines to determine pesticide MRLs and has also set MRLs of different pesticides compounds on different commodities (https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/mrls/?event=download.MRL). These MRLs have to be set in accordance with the guidelines set by the Environment Directorate, Joint Meeting of the Chemicals Committee and The Working Party on Chemical, Pesticides and Biotechnology based on Organization for Economic Cooperation and Development (OECD) MRL Calculator user guide (OECD 2011). OECD maximum residue limit calculator is harmonized among member organization for Economic Cooperation and Development. EU has regular monitoring program to assess the pesticide

Fig. 8.4 Schematic representation of step-wise process of MRL setting by Codex Alimentarius Commission (CAC)



residue which is published yearly in the annual report by EFSA. Pesticide residue database for Europe can be assessed through https://ec.europa.eu/food/plant/pesticides/eu-pesticides-database/mrls/?event=download.MRL.

In United States, Environment Protection Agency is regulatory agency which formulated the Code of Federal Regulations (40 CFR), Title 40 which is entitled as "Protection of Environment." Before allowing the pesticide to use, EPA sets tolerance or maximum residue limits of pesticides. Office of Chemical Safety and Pollution Prevention of EPA advises to assess and regulate pesticides and toxic substances under various Federal acts (CFR 2021). MRLs of US could be access through https://www.fas.usda.gov/maximum-residue-limits-mrl-database.

8.5.1.3 South Asia

South Asian countries has a common forum called The South Asian Association for Regional Co-operation (SAARC) which includes Afghanistan, Bangladesh, Bhutan, India, Maldives, Nepal, Pakistan, and Sri Lanka. These SAARC countries have their national act or regulations to address pesticide management. All the SAARC countries are member of Codex Alimentarius Commission (CAC) and have delegated representative as National Codex Contact Point (NCCP) (WHO 2014).

Bangladesh has promulgated pesticide ordinance 1971, pesticide amendment ordinance 2007 & 2009, the pesticides rules 1985 and its amendment on 2010. Pesticide ordinance regulate pesticide registration, import, manufacture, repacking, sale, distribution formulation, and use of pesticide (http://bdlaws.minlaw.gov.bd/act-details-364.html). The ordinance provisioned the pesticide technical advisory committee which give advice to the government on technical matters. The Department of Agricultural Extension, Government of the People's Republic of Bangladesh provides the lists of registered and banned pesticides (The Bangladesh Gazette 1985).

Bhutan established The Pesticides Act of Bhutan, 2000 which is used to manage import, sale and use of pesticides. It also enforces rules and procedures related to pesticide management (RGB 2000) which ensure proper pesticide management. Bhutan Agriculture and Food Regulatory Authority (BAFRA) under Ministry of Agriculture and Forests has a goal to protect health and lives of plants, animals, humans and environment. It also envisions to safeguard biosecurity and ensure safe food for all. BAFRA is also responsible as National Codex Contact Point (NCCP) to establish minimum safety standard for food which is facilitated by Codex (Bhutan) Secretariat (https://www.bafra.gov.bt/index.php/codex-bhutan-2/).

Pesticides are regulated in India through the Insecticides Act, 1968 and Insecticides Rules, 1971 which has its third amendment, 2020 (GoI 2020). Further pesticide management bill, 2020 approved by the Union Cabinet seek to regulate the manufacture, import, sale, storage, distribution, use and disposal of pesticides in order to ensure use of safe pesticide and minimize risk to human, animal and environment, which will replace the pesticide act (Kumar and Reddy 2021). The pesticides' regulations in India are governed by two different bodies: The Central Insecticides Board and Registration Committee (CIBRC) and the Food Safety and Standards Authority of India (FSSAI). Food contaminants, toxins and residue level can be assessed for India through https://www.fssai.gov.in/upload/uploadfiles/files/Compendium_Contaminants_Regulations_20_08_2020.pdf (FSSAI 2020).

Similarly, Maldives manage pesticide use and regulate through Pesticide Inspection Manual, 2021 and Guideline for Pesticide Disposal which were published in 2021. Representative from Maldives Food and Drug Authority, Ministry of Health was regarded as Codex contact points.

Government of Nepal has assigned Department of Food Technology and Quality Center (DFTQC) to regulate and monitoring of the food and feed for quality assurance. DFTQC has a legal body that enforces food and feeds acts, regulations, directives, and other related issues. DFTQC, under the Ministry of Agriculture Development, has also been established as a Codex contact point (CCP) since 1974 (WHO 2014). NCCP of Nepal as a separate organizational structure was established in 2004 with DFTQC as the Secretariat office (WHO 2014). Pesticide residue is one of the components that DFTQC has a right to determine the MRLs of food and feed in the country. Plant quarantine and Pesticide Management Center (PQPMC) enforces the Pesticide management act 2019, new acts which replaced the existing Pesticide Act, 1991. PQPMC also issue license to register pesticide, declare list of banned pesticides and create awareness on the safe use of pesticide storage and disposal. Nepal Agriculture Research Council conducts research on pesticide residue (Giri et al. 2016). Maximum Residue Level (MRL) establishment needs a lot of researches on pesticide residue experiments with the application of good agriculture practice (GAP) (EFSA 2015; OECD 2016) and results of this pesticide residue are used to estimate MRLs (OECD 2016) with lots of procedure followed by experts (FAO 2016). The process for establishing of the commodities can take up to 24 months after the application is registered for approval to concern authorities (European Commission 2021). Therefore, a country like Nepal, can adapt the MRL level of Codex Alimentarius Commision (CAC), FSSAI, EU, etc. until it to be able to involve in rigorous research to the establishment of its own MRLs level. However, efforts have been made by various researchers and organizations to find out the residue of pesticides in agriculture commodities which gives a generalized overview of pesticide residue status in Nepal (Aryal et al. 2020). With thorough review and discussion with an expert, DFTQC, Nepal has established MRLs for different vegetables, and fruits in Nepal (DFTQC 2022) which helps facilitate the trade.

Agriculture pesticide rules, 1973 of Pakistan deals with the Registration of pesticide formulation of pesticide, Packing, Repacking, Refilling, Labelling, storage and use, and overall pesticide management issues in the country. Codex contact point for Pakistan is the Ministry of National Health Services Regulation and Coordination (MoNHSR&C), Islamabad, Pakistan. Pakistan National Food Security Policy has also addressed the issue of pesticide management and pesticide residues problems in the food supply chain of fruits and vegetables that exceed above maximum residual limits (GoP 1973).

Democratic Socialist Republic of Sri Lanka has promulgated the Control of Pesticide Act and Pesticide Technical and Advisory Committee Rules in 1980 which directs to constitute a pesticide registrar who has licensing authority for pesticides. This act also envisaged a committee which advise Registrar on pesticide registration, formulation, import, sale, storage, and use of pesticide and other related matter of pesticide management. Ministry of Health (MoH) is designated Codex Contact Point (CCP) for Sri Lanka. The NCCP in Sri Lanka was established in 2005. Maximum residue limits for pesticide in food was standardized by Sri Lanka Standard Institutions (SLSI 2021).

8.5.1.4 Other Asian Countries

In Indonesia, the NCC is led by the National Standardization Agency of Indonesia (NSAI); NSAI is the Codex Contact Point (CCP) for Indonesia. The Director of Food Safety at the Food and Drug Administration (FDA) is on the role of the new Codex Contact Point (CCP) for Myanmar and the Food Division of FDA is providing administrative services to the CCP.

The National Bureau of Agriculture Commodity and Food Standard is in charge of the Codex Contact Point (CCP) of Thailand. Controlling the quality and safety of raw materials used for food production, transportation, preparation, and selling to consumers as well as imported raw materials and food products are the responsibility of the Thai FDA under the Food Act of 1979.

Ministry of Food and Drug Safety, Food Standards Division, Korea Food and Drug Administration established MRLs for specific crops or crop groups and processed food in Korea (http://www.foodsafetykorea.go.kr/foodcode/index.jsp). The pesticide residue database for South Korea can be assessed through https://www.foodsafetykorea.go.kr/foodcode/02_01_02.jsp or https://faolex.fao.org/docs/pdf/kor190507.pdf.

8.5.2 Policy-Related Reform on Residue Mitigation

Access to advanced pesticide application and residue measurement equipment is limited in less developed countries. Consequently, the risks of pesticide exposure are likely to be higher. All the member countries should abide by the rules and guidelines set by FAO/WHO such as the "International code of conduct on pesticide management" (FAO/WHO 2014), "guidelines on retail distribution of pesticides with particular reference to storage and handling at the point of supply to users in developing countries" (FAO 1988), and other related guidelines related to pesticide management. But Low and mid-level-income countries' capabilities are required to be increased with the technical and financial support for them to be able to adapt to the pesticide management guidelines and also need technical guidance in setting MRL. Since setting MRL by country needs rigorous research and laboratory analysis with high precision having good laboratory practices, low-income and developing countries can adapt to Codex and the Codex MRL should be harmonized among all countries which have even stringent MRL levels. Yeung et al. (2017) have categorized the countries from group A to D depending upon the use of Codex MRLs and give some suggestions on how to harmonize MRL among trading partners. This could facilitate both trading as well as the risk associated with consumers. The PAN (Pesticide Action Network), FAO/WHO/CAC, WTO, OECD etc. can take initiative in global harmonizing MRL, GAP, residue analysis, application equipment, and procedures.

8.5.3 Good Agricultural Practices (GAP)

Good Agricultural Practices (GAP) arises from the need of producing healthy products without harming the environment. Adoption of GAPs may be applied to production and postharvest systems. They are applied through sustainable agricultural methods. GAP aims for the combined application of IPM (Integrated Pest

Management) and ICM (Integrated Crop Management). The application of Hazard Analysis in Critical Control Points (HACCP) is emphasized in GAP (ITESDES 2018).

The public standards for GAP are to be harmonized in production as well as post-harvest practices among the countries to ensure safe and quality food intake in general.

8.5.4 Reduction in the Use of Pesticides in Crop Production

The adoption of pest preventive cultural practices is an important strategy to avoid or minimize the pest's impact on the crop and reduce pesticide use. Cultural control practices are the regular farm operations that are used to destroy the pest or prevent the plant from damage. Several methods of crop cultivation have been practiced such as field sanitation, crop rotation, soil solarization, alteration of time of planting and harvesting, use of resistant varieties, intercropping, mixed cropping, mulching, deep tillage, etc. (Karaye et al. 2017). This method is most effective when the targeted pest is monophagous or oligophagous and does not disperse rapidly in the environment. This is the most important component of IPM (Integrated Pest Management), which emphasize an environmentally friendly method of pest control, pest prevention, and control prioritizing on alternative pest control methods and keeping the use of chemical pesticide as the last option. Jepson et al. (2020) has develop a system to categorized pesticide based on their hazards and grouped 243 pesticides of lower risk that could require only single layer PPE which have been in use in IPM program in US since 2016. Safer pesticide use could have less impact on human and environment. IPM programs can lead to reductions in the frequency and dose of pesticide use (Shahraki et al. 2011). Barrera (2020) emphasize changes in IPM strategies where we have to approach for holistic pest management considering socio economic aspects of farmers and interaction of pest problem with other elements of socio-environmental system. Problem of pesticide residue in Low-income and middle income countries arise because of their improper use which can be reduced by implementing IPM which ultimately can lower the risks of pesticide contamination to environment and exposure to farmers and consumers (Dahal et al. 2020). The FAO has launched three regional IPM programs comprising Asia, Near East and West Africa with several national projects, which provide technical assistance in capacity building and policy reform and facilitate collaboration among the nations (FAO 2022).

Suppression of pest population by using different manual devices is the new but widely used to keep pest population below damage level. It includes various practices, such as hand picking, trapping and use of suction devices, clipping, pruning, screening or setting barriers, manipulation of temperature and relative humidity, etc. (Oseto 2000). The use of traps may involve the use of pheromones that disturbs the natural mating cycles of the pest. These are the some lethal or some non-lethal pest control options without the application of chemicals in the crop.

The use of biological control agents could be the best option for protected cultivation (Van Lenteren and Woets 1988). Traditionally, the most important biological control agents are predators, parasitoids, and pathogens (Hawkins et al. 1997). Biological control involves three major techniques viz. introduction, conservation, and augmentation (Eilenberg et al. 2001). If there is a lack of natural predator populations like lady beetles, mantids, spiders, etc. can be released in the field in inundative or augmentative ways. Additionally, parasitic wasps (parasitoids) and other pathogens (virus, bacteria, fungus, nematode, protozoa) can be applied as pest control agents. For instance, the use of NPV to control European corn borer, the use of lady beetle to control aphids, and *Trichoderma* to control a broad range of plant pathogenic fungi. Bio-pesticides are more favorable and pest specific than conventional pesticides.

The restriction on the number of pesticide applications over time and space is recommended to minimize the risk of chemical pesticides. Application of pesticides based on the economic threshold level of the pest, alteration of pesticides with a different mode of action, pre-harvest interval (PHI), and use of pesticides with appropriate equipment at the most vulnerable stage of the pest life cycle are the important combination of pest management methods. The selection of minimally hazardous pesticides and avoiding HHPs, pesticide use by only licensed users, are other effective ways to manage pests by lessening the chance of pesticide resistance and pest resurgence.

8.5.5 Public Awareness Programs

In most cases, the rejection of consignment from the importing country is due to a higher level of pesticide residue than the determined MRL of that country. It occurs due to unknowingly using high doses of pesticides just before harvest or after harvest leaving more quantity of residues in the produce. In this situation, it is necessary to have appropriate knowledge of MRL and GAP on the producer's and trader's levels. The training and workshops on a regular basis need to be organized by the corresponding bodies so that the respective stakeholders can update their knowledge about the latest national and international regulations that are accepted for every farming method in the world. To increase the adoption of IPM or ICM strategies, it is necessary to focus on the educational and motivational programs for farmers by the implementing agencies (Rahman 2012). It is important to be aware of the effects of using harmful pesticides and the importance of alternative pest control methods (van Eeden and Korsten 2013).

8.5.6 Residual Detoxification by Transformation

Among pesticides, organophosphorus insecticides (OPIs) are the most common broad-spectrum insecticide that is globally used in agriculture (Ragnarsdottir 2000). They account for about 34% of worldwide insecticide use (Ning et al. 2021).

Carbamates are also important in agriculture due to their broad spectrum activity but are degraded relatively easily and generally have a low degree of toxicity to humans (Wolfe et al. 1978). In nature, various biotic and abiotic transformations of chemicals can detoxify the harmful chemicals. The natural lactonase enzymes like Phosphotriesterase- like Lactonases (PLLs) could be used as biocatalysts for OPIs degradation and remove toxic residues from the environment in a safer manner. Besides this, bleach treatment, alkaline hydrolysis, oxidation, and reduction are important activity that could be employed for detoxification and metabolites formation of OPIs (Paidi et al. 2021). Simple techniques like washing, blanching and peeling in household condition and thermal treatments in small scale industries are effective for reducing pesticide residues. Further use of novel technologies like cold plasma, pulsed electric field, irradiation, hydrostatic pressure and ultrasonication have been in use to lower pesticide residues (Mir et al. 2022).

8.5.7 Reduction in the Pesticide Exposure

There are many instances in certain stages of pesticide life cycle, i.e. from formulation of rules, manufactures to use and disposal of pesticide waste, exposure is inevitable if safety measure are compromised (Van den Berg et al. 2020). Similarly, major route of pesticide exposure to humans in the world is also through the consumption of food products (Claeys et al. 2008; Drouillet-Pinard et al. 2011). Various household and industrial strategies could be used to reduce pesticide exposure like washing, peeling, blanching, and thermal treatment. Nowadays, some novel technologies have been used to reduce pesticide residue in agricultural goods depending on the type of pesticide residues like cold plasma technology, pulsed electric field, and irradiation methods. In cold plasma technology, plasma (apparently neutral ionized gas consisting of ions, free electrons, atoms, and molecules) are in thermal non-equilibrium and degrade many pesticide residues in various commodities (Sarangapani et al. 2017; Misra 2015). In pulsed electric field method, a short burst of electricity is used to degrade pesticide molecules (Mosqueda-Melgar et al. 2008). The gamma radiation at various doses can also degrade pesticide residues (Dessouki et al. 1999).

It is important to protect the user from direct exposure to pesticides during application. Using proper equipment and wearing appropriate clothing provides a layer of protection during the handling, mixing, application, and storage of pesticides (Yarpuz-Bozdogan 2018). The type of equipment and the clothing depends on the type of pesticides being used. The user should follow all the directions and instructions indicated on the labels. The personal protective equipment (PPE) should be clean, and in good condition. The PPE includes gloves, chemical goggles, apron, waterproof boots, mask, hat, and ear plugs. The equipment should be thoroughly cleaned with soap and water after every use before storage to keep ready for next use. The empty containers should be disposed of according to the instructions provided in the pesticide packing. The safe storage of pesticides requires attention to the location and features of storage. The pesticide storage should be located at a safe location without any kind of leakage and made with fire-resistant materials. Entry to the storage should be limited to authorized persons only. Herbicides, insecticides, and fungicides should be stored at a separate location in the storage area to avoid cross-contamination and misuse.

8.5.8 Product Inspection and Traceability

The practice of inspecting materials delivered in the market has been used in many countries for a long time to ensure the quality and safety of goods. Government regulations requiring product inspection or traceability (with the database of production) exist in many countries. The objective of inspection or traceability is to avoid the double cost of effect from unsafe food and the associated cost of buying. The provision of pesticide residue testing at border points or at the market can curb the excessive use of pesticides. There are many events of the consignment being rejected due to the presence of pesticides above MRLs.

8.6 Conclusion

There is challenge to feed the growing population as safe food which is the fundamental food right of the humans. To increase the food production, use of different inputs including pesticides seems inevitable which was evident from the increase in global pesticide use. The rate of increase of global pesticide use seems to be higher in low income and food deficit countries than developed nations. So there is a great challenge to increase food production for growing population while maintaining the toxin level below MRLs. Considering the risk associated with improper use of pesticides like resurgence of pest, outbreak of secondary pests, pesticide residues, environmental contamination and risk to human health, it is high time to opt many of the mitigation options to reduce pesticide related hazards. Country specific rules and regulations for pesticide management should be strictly enforced. Crops should be grown with good agricultural practice following integrated pest management strategies which certainly resolve the issue of exceeding MRLs to some extent. Food and agriculture trading around globe should not be hindered because of pesticide residue related problems. Exporting goods are restricted to export due to stricter standard set by importing countries where developing countries suffer. Pesticide regulation including different MRLs of different countries needs to be harmonized for smooth trade. Further technical and financial support is required for the low income and developing countries to be able to meet the international standard. All the international forums like FAO, WHO, OECD, PAN, WTO, and international conventions could play a vital role to facilitate activities related to pesticide management, particularly for low-income and developing countries.

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