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Full Length Research Article

Statistical Analysis of Pesticide Consumption in India and Review of Pesticide Residue Determination

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Abstract

To increase crop yield along with the maintenance of adequate water levels and fertilizers, crops must be protected from feral animals, insects, fungi, or herbs. For this, the use of pesticides is very common. However, its selection, proportion, and usage interval are important. The extensive use of pesticides results in serious health problems for consumers as well as creates long-lasting adverse effects on the environment as well. There is an utmost need for the detection of pesticide residue on eatables. One has to ensure that the detected level of pesticides does not exceed the maximum residue levels (MRLs) fixed up by the government. The residues of pesticides are found either in primary or/and in derived agricultural products. Pesticides are classified according to application, function, chemical composition, toxicity (adverse short-term/long-term effects), and mode of entry. Mainly pesticides can be grouped as insecticides, herbicides, fungicides, bio-pesticides, and rodenticides. Various techniques are developed to detect pesticide residues on eatables. Here an overview of different pesticides commonly used in agriculture is presented. The state-wise consumption of pesticides in India for the last six years is reviewed. The paper also reports the comparative study of the various methods used to detect the pesticide residing on eatables.

Key words: Insecticides, Maximum residue levels of pesticides, Pesticides, Pesticide consumption, Pesticide detection

Agriculture is the major source of living for almost 58 percent of India's population. The Indian agricultural industry is witnessing continuous growth in the world food trade. India is the world's sixth-largest market for food and grocery, with a retailing contribution of 70 percent of the sales. According to (IBEF 2020) almost 32 percent of the country's whole food market is captured by the Indian food processing industry. In India, the food industry has secured fifth rank for production, consumption, and export. One of the major reasons for this increase is an increase in the population. This demands more food as food is a vital component of all living being. This has created the need for more focus on the agriculture field and more concentration on increasing crop yield. To achieve this, farmers are adopting various remedies like controlling the water level of soil, pH of the soil, use of fertilizers, and so on. Many times, large farming is supported by advanced technologies such as automated irrigation systems, smart agriculture systems, controlled greenhouse farming, etc. In short, crop productivity has been increased by farming in a controlled environment. Along with this crop must be protected from feral animals, insects, fungi or plants, etc. This is achieved by using pesticides at various growth stages of crops and at the stage of food storage. For good health, the food must be fresh and pesticide free. Excessive use of pesticides is not advisable and is harmful if they remain on eatables. According to [1] pesticides are toxic and can cause a number of health issues. There may be short-term adverse health effects like stringing eyes, rashes, blisters, blindness, nausea, dizziness, and diarrhea. It may cause some chronic adverse effects like cancers, birth defects, reproductive harm, neurological and developmental toxicity, immune toxicity, and disruption of the endocrine framework. Thus, pesticide residues on food can put living being at risk. Even long-term antagonistic effects on the environment are also reported [1]. India is the largest contributor to agricultural production in the world, so it is necessary that final eatable products must be hygienic and free of residues. To produce residue-free agricultural products one must aware of the use of pesticides, and follow the guidelines carefully during their use.

Different kinds of pesticides are available in the market which is considered a vital component of modern farming. In high-input intensive agricultural production systems, pesticides are used in a considerable amount. Pesticide residues are present in all agroecosystems but the real risk to human health is pesticide residues in primary and derived agricultural products. Research shows that on agricultural products like

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fruits and vegetables, sixteen types of pesticides are present which are toxic to human health [2]. Important pesticides are imidacloprid, deltamethrin, malathion, and cypermethrin. Various methods are developed to detect the residues of pesticides. The traditional pesticide detection system uses various types of sensors to sense the pesticide level. Some of them are time-consuming, much tedious, and unaffordable to individual people. Here the review of the pesticides used during the growth and during storage of fruits and vegetables is presented. The comparative study of pesticide residue-detecting methods is also presented.

MATERIALS AND METHODS

A) *Agriculture in India*

India has wide and diversified nature for agricultural products. It is the second largest producer of vegetables and fruits in the world after China [3]. It topped the production of vegetables like okra and is in second position in the production of potato, tomato, onion, cabbage, cauliflower, and brinjal in the world. Table 1 shows the study of comparison of area, production, and productivity of vegetables and fruits in India during the last 5 years.

Table 1 Comparison of area, production, productivity of fruits and vegetables in India for 2016-17 and 2020-21

Year	Area		Production		Productivity		References
	Fruits	Vegetables	Fruits	Vegetables	Fruits	Vegetables	
2016-17	6.37	10.23	92.98	178.17	16.6	17.4	[4]
2017-18	6.50	10.26	97.36	184.39	14.96	17.97	[5]
2018-19	6.59	10.07	97.96	183.17	14.85	18.18	[3]
2019-20	6.77	10.31	102.08	188.28	15.07	18.26	[6]
2020-21	6.91	10.96	103.03	197.23	14.90	17.99	[6]

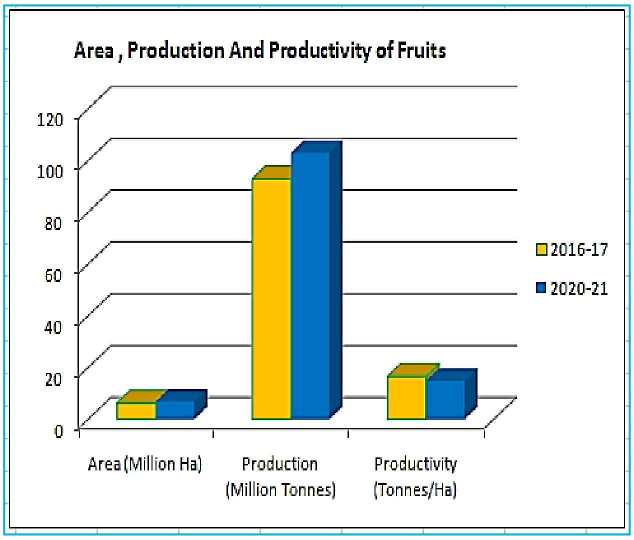

Fig 1 Growth in area, production and productivity of fruits

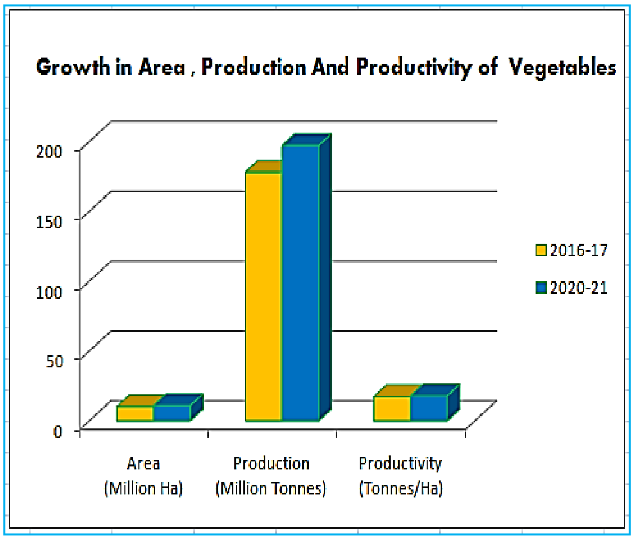

Fig 1 Growth in area, production and productivity of vegetable

The (Fig 1-2) show the growth rate of area, production and productivity of vegetables and fruits in India from 2016-17 to 2020-21.

During 2016-2017 the area covered by fruit crops is 6.37 million hectares with a production of 92.98 million tons [4] upgraded during 2020-2021 as the area under fruit crops is 6.91 million hectares with the production of 103.03 million tonnes [6]. Over the period from 2016-17 to 2020-21, the area and production of fruits has increased by 8.4% and 10.8% respectively.

During 2016-2017 vegetable crops occupied an area of 10.23 million hectares with a total production of 178.17 million tonnes [4] upgraded during 2020 - 21 as the area under vegetable crops 10.96 tonnes per hectare with a total production of 197.23 million tonnes [6]. Thus, during the period 2016-17 to 2020-21, the area and production of vegetables increased by 7.1% and 10.70%. Respectively.

B) *Pesticide consumption in India*

Industrialization of agricultural sector has totally damaged the natural ecosystem in order to increase the crop productivity. Pesticides play an important role for crop protection and sustaining production by managing the pests and diseases during the cultivation and post-harvest practices of food commodities. As today's agricultural practices need wide production, large amount of chemicals are used causing degradation of natural environment [2]. Tremendous use of pesticides and agrochemicals in agriculture is causing adverse health and environment effects. Under Ministry of Health and Family Welfare the Food Safety and Standard Authority of India (FSSAI) has fixed the Maximum Residue Levels (MRLs) considering the dietary exposure and risk assessment compliance of pesticide.

The consumption of pesticides in various states of India during year 2016-17 to 2021-22 is presented in (Fig 3). It is based on the data from ministry of agriculture and farmers welfare [7-8]. State wise pesticide consumption is almost same for all six years except for Maharashtra. Consumption is highest in Maharashtra followed by Uttar Pradesh, Punjab, Telangana, Haryana as agricultural land is more in these states.

The pesticides are mixture of chemical substances intended for preventing, destroying or controlling any pest or unwanted species of plants and animals. They are classified according to their usage (where they used to kill specific bug organism), working, chemical composition, toxicity(adverse short term / long term effects), mode of entry, etc. [2].

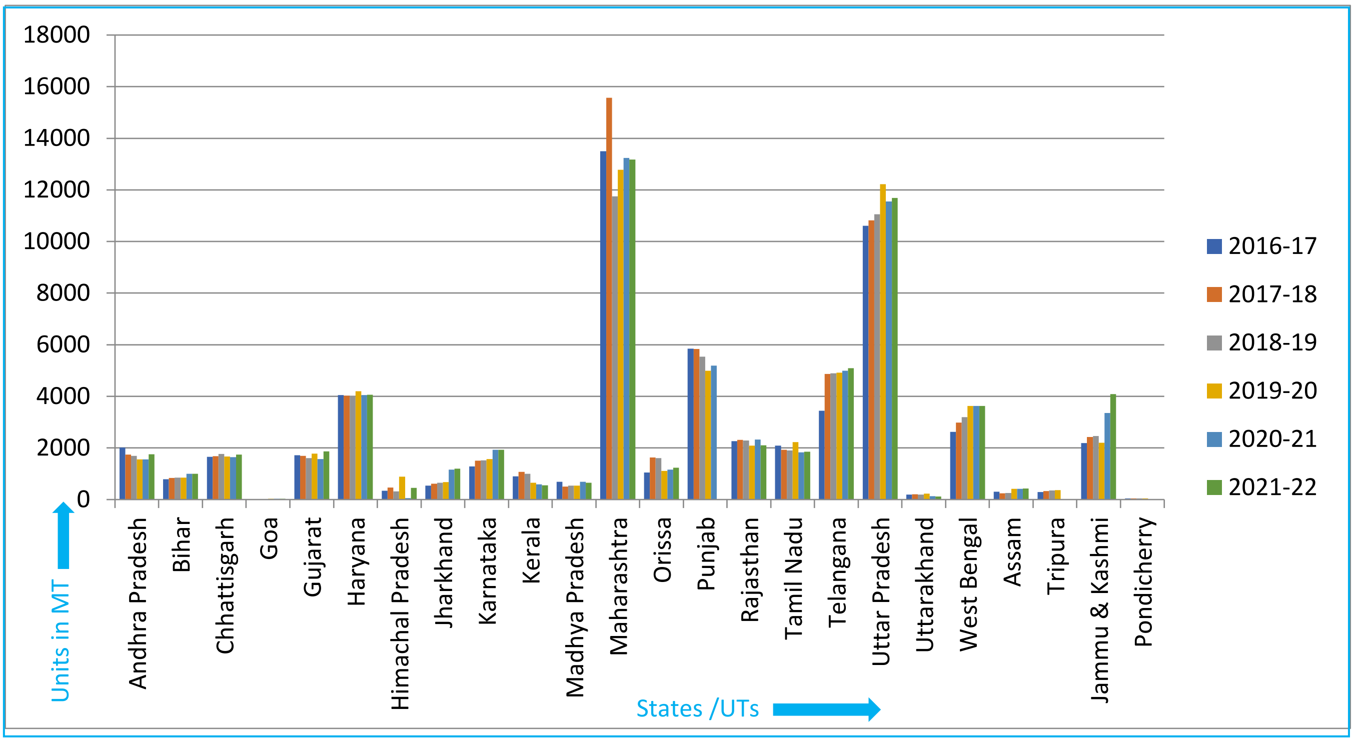

Fig 3 State wise consumption of chemical pesticides (technical grades) in India

According to application and functioning, there are total 30 different types of pesticides [9]. They can be grouped as insecticides, herbicides, fungicides, bio-pesticides, rodenticides. WHO had classified pesticides according to their toxicity as extremely hazardous (Parathion, Dieldrin, Phorate), highly hazardous (Aldrin, Dichlorvos), moderately hazardous (DDT, Chlordane) and slightly hazardous (Malathion). Classification based on mode of entry is dependent on how pesticides affect the target. Here they are classified as systemic pesticides (2,4–D, glyphosate), contact pesticides (Paraquat, diquat), fumigants (Phosphine) and repellents (Methiocarb). According to mode of action, pesticides are classified as physical poison (Activated clay), protoplasmic poison (Arsenicals), respiratory poison (hydrogen cyanide), nerve poison(malathion). Classification based on chemical composition is organochlorides, organophosphates, carbamates, pyrethroids, triazines etc.

The most regularly used pesticides are insecticides like chlorpyrifos, Dichlorodiphenyltrichloroethane (DDT), malathion etc., herbicides like 2,4-D, fungicide like thiabendazole, larvicides like Methoprene [10]. (Fig 4) shows the pesticide wise consumption in India [11]. Amongst them insecticides contribute the highest share in total pesticide consumption. According to [12], bio-pesticide is a type of pesticide derived from natural materials like animals, plants, bacteria and minerals [12]. There is total 299 registered active ingredient bio-pesticides and 1401 registrations of active bio-pesticide products. They are less toxic than conventional pesticides. However, its consumption is very less (only 9%) as compared to chemical pesticides.

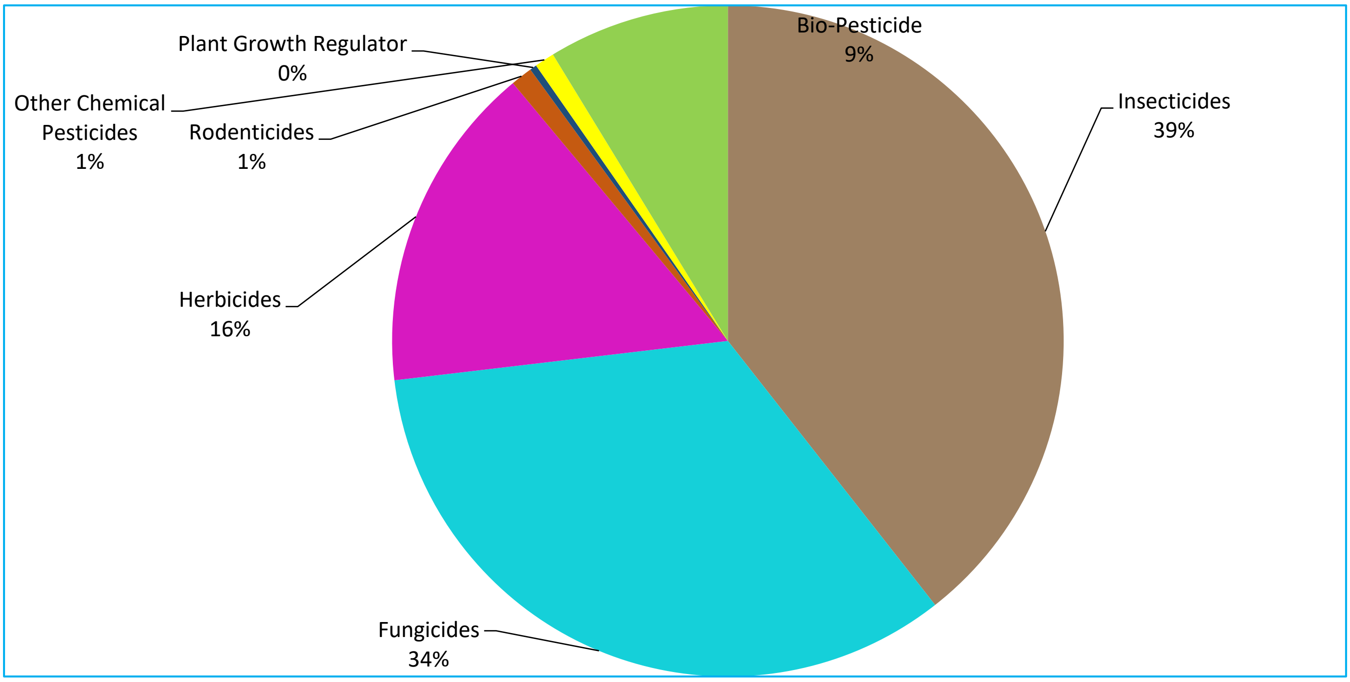

Fig 4 Pesticide wise consumption in India

Consumption of remarkably used insecticides during year 2019-2020 in Mega Tones (Tech. Grade) is tabularized in (Table 2). The data is collected from ministry of agriculture and farmers welfare [11]. The table presents consumption data for five major groups namely, insecticides, fungicides, herbicides, rodenticides and bio-pesticides. Highest utilization is of sulphur (3878 M.T.) from fungicides group. In insecticides, chlorpyriphos had been utilized in large amount (1431 M.T.) followed by Cypermethrin (675 M.T.), Fenvalerate (667 M.T.) and so on. It is seen that overall consumption of insecticides is high. Rodenticides show least consumption of pesticide.

Table 2 List of majorly used pesticides during year 2019-20 in M. T. Tech. Grade

Group I Insecticides		Group II Fungicides		Group III Herbicides		Group IV Rodenticides		Group V Bio-pesticides	
Ingredient active	M.T.	Ingredient active	M.T.	Ingredient active	M.T.	Ingredient active	M.T.	Ingredient active	M.T.
Chlorpyriphos	1431	Sulphur	3878	2,4-D Amine Salt	1067	Zinc Phosphide	123	*Tricoderma viride*	583
Cypermethrin	675	Mancozeb	2181	Pretilachlor	621	Aluminium Phosphide	92	*Pseodomonas flurescens*	401
Fenvalerate	667	Carbendazim	687	Glyphosate	571			NPV (H)	352
Malathion	647	Propineb	197	Butachlor	354			*Tricoderma Spp*.	215
Phorate	641	Thiophanate – Methyl	178	Atrazine	346			Neem based insecticides	185
Quinalphos	565	Hexaconazole	154	Isoproturon	292			*Beauveria bassiana*	181
Monocrotophos	551	Zineb	135	Pendimethalin	199			Anilphos	138
Diclorvos	537	Propiconazole	131	Chlodinafop Propargyl	147			Azadirachin	135
Fipronil	444	Captan	124	Anilphos	138				
Profenophos	425	Ziram	118	Paraquat dichloride	113				
Acephate	406								
Imidachloprid	372								
Dimethoate	368								
Cartap Hydrochloride	358								
Thiamethoxam	235								
Carbofuran	207								
Carbaryl	181								
Lamda-cyhalothrin	163								

C) *Recent developments in pesticide residue determination*

As discussed in previous sections, there is utmost need of detection of pesticide residue on eatables. One has to ensure that detected level of pesticides does not exceed the maximum residue levels (MRLs) fixed up by government. This section discusses the various methods used to detect pesticide levels on eatables. The outcome of the method is dependent on the reliability of methods, analytical and technical skills of the operator, reliability and accuracy of the equipment. The method must be designed considering safety and prevail the contamination of the samples. The analysis must be in accordance with the standard operating procedures, receiving and storing of samples. Validation of methods must be followed by confirmatory tools with Maximum Residue Limits (MRLs).

Chemical techniques

In chemical analysis methods [12], the chances of getting in contact with toxic solvents and reagents are high. So, there must be awareness about pesticide toxicity and high care is necessary while working in a laboratory. Moreover, contamination may lead to false or negative results. Contamination may arise from organic solvents, glassware, water, reagents, etc. For analysis, pesticide reference standards also need to store in a suitable form [12].

Chromatography techniques

Traditional laboratory methods use chromatography techniques. Three types of chromatography techniques are gas chromatography, liquid chromatography, and mass spectrometry [13]. Chromatographic methods use selective detectors. Mass spectrometry gives better results because of higher sensitivity, selectivity, reliability and efficiency. Nonetheless, all chromatography methods are time-consuming and laborious and need expensive equipment and highly-skilled technicians. Ramadan *et al*. [14] carried out liquid chromatography-mass spectroscopy (UHPLC – MS/MS), and gas chromatography–mass spectroscopy (GC – MS/MS) for the detection of pesticide residue on vegetables. They claimed that methomyl, imidacloprid, metalaxyl, and cyproconazole were the most often used pesticides. Schusterova *et al*. [15] introduced the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) extraction method followed by ultra–high–performance liquid chromatography used for the detection of pesticide residues and their metabolites in grapes and wines. The method is useful for the detection of fungicides (e.g., boscalid) and insecticides (e.g., methoxyfenozide).

Flow injection analysis

Other commonly used techniques for pesticide detection include flow injection analysis, use of enzyme linked immune sensors and electro-analytical techniques [16]. These are time-consuming methods as a lot of time is required to prepare the samples and to produce the test results.

Biosensors

The newly developed biochemical techniques detect specific chemicals like bioassay for pesticide detection. Different types of biosensors are also developed. The electrochemical cholinesterase-based biosensors are used to detect pesticides like Chlorpyrifos, Dimethoate, Carbaryl, and Methylparaoxon are detected using the Amperometry method [17]. Dimethyldithiocarbamate can be detected using Fluorescence of CdSe/ZnS quantum dots (QDs), capped with 3-mercaptopropionic acid technique [18]. The pesticides 2,4-D, atrazine and methyl parathion pesticides are detected using field ready FPIA device. Sodium polyacrylate (SPA) is used in this biochemical FPIA [19]. A telemetry method with the generation of immune biosensors for remote monitoring of pesticide residues was developed by [20-21]. Researchers developed the cell phone application to detect the pesticide residues. They had used SERS chip and the system was interfaced with a cell phone. Guo *et al*. [22] carried out pesticide residue detection by using amperometric acetylcholinesterase (AChE) biosensor. The detection system could measure the residue in 15 min with good precision and high stability as compared with traditional analytical methods.

Constrained energy minimization (CEM)

Ma *et al*. [23] developed a detection system with an increased pesticide detection rate using a band weighting process and band selection (BS) process and used four algorithms as spectral information divergence (SID) to decide the threshold, orthogonal subspace projection (OSP) to estimate the water and skin of fruit, constrained energy minimization (CEM) to examine the pesticide residue, and support vector machine (SVM) to find an optimum hyperplane. They had identified pesticide residues on a different fruit. According to the CEM method had the highest detection rate of pesticides and could replace the other traditional methods. Chen *et al*. [24] used Automatic Target Generation Process (ATGP) followed by Constrained Energy Minimization (CEM) with hyperspectral imaging processing techniques. The results put forward by them prove that this method is more effective than traditional image processing methods. Nagabooshanam *et al*. [25] fabricated the Electrochemical micro analytical Device by performing electrochemical techniques like Cyclic Voltammetry (CV), Electrochemical Impedance Spectroscopy (EIS), and Differential Pulse Voltammetry (DPV) used for the detection of chlorpyrifos in vegetables. Mukherjee *et al*. [26] developed a bio-sensing device using organophosphate hydrolase to detect pesticide residue in fruits and vegetables. On-spot residues were detected within a range from 100 ng mL^{-1} to 0.1 ng mL^{-1}.

Wireless sensor network (WSN) based techniques

Leccese *et al*. [27] developed the electronic nose to monitor pesticides in the air. A cluster of many gas sensors were connected together by Wireless sensor network (WSN) technology. The automated electronics system developed doesn't need qualified skilled person/chemical analysts for detection. Jin *et al*. [28] evolved mobile based highly sensible absorption meter by using photo-detection sensors to determine organ phosphorus compounds for food safety tracking. The whole system was based on the new emerging technology Internet of Things (IoT).

Paper based sensor

Kim *et al*. [29] developed a paper-based sensor for the detection of an organophosphate pesticide. The sensor was fabricated using a layer of three sheets of patterned plates and by the reaction between acetylcholinesterase and indoxyl acetate restrained by pesticide molecules existing in a sample solution.

Hyperspectral imaging

Jia *et al*. [30] used hyperspectral imaging technology for the pesticide residue detection of chlorpyrifos and carbendazim on apple surface. The infected region was determined by using the Hough circle transformation and feature band selection by successive projection algorithm. Zhan-qi *et al*. [31] discussed hyper-spectral technology and machine learning-based di-methoate pesticide residue detection on spinach leaves. ENVI (the Environment for Visualizing Images) tool was used for detecting the infected region and analysed the spectral data by principle component analysis (PCA). This study found out the results that the PCA can effectively discriminate spinach samples with different concentrations at the visual level. Ye *et al*. [32] introduced rapid hyper spectral imaging for rapid pesticide residue detection with machine learning. The method is very costly.

Most widely suggested detection methods for pesticides are compiled in (Table 3).

Table 3 Different Pesticides and their existing detection methods

Pesticide detected	Class of pesticides	Detection method	Limit of detection	References
Cypermethrin	Insecticide-Pyrethroid		0.0013-0.0030 $mg.kg^{-1}$	[13]
Deltamethrin		GC-MS	0.0019-0.0028 $mg.kg^{-1}$	
Fenpropathrin			0.0700-0.1869 $mg.kg^{-1}$	
Malathion	Insecticide	Amperometric Detection	2-6 nM	[33]
Methyl parathion	Insecticide-organophosphate	SPA enhanced FPIA based detection	3 ppb	[19]
Paraoxon, Dichlorvos, Malathion, Triazophos	Organophosphorus pesticides	Biosensors based CdTe Quantum Dots	1.62×10^{-15} M, 75.3×10^{-15} M, 0.23×10^{-9} M, 10.6×10^{-12} M	[34]
Chlorpyrifos	Insecticide-Organophosphate	Amperometry	100 µg/L	[22]
Atrazine 2,4-D	Herbicide	SPA enhanced FPIA based detection	0.5 ppb 0.1 ppb	[19]
Profenophos	Insecticide-organophosphate	GC-MS	0.0018-0.0021 $mg.kg^{-1}$	[13]
Methyl parathion	Insecticide	Portable SERS	0.011 µg cm^{-2}	[35]
Oxamyl	Insecticide-carbamate	LC-MS/MS	0.0020-0.0031 $mg.kg^{-1}$	[13]
Diemehoate	Organophosphate Insecticide	Portable SERS	5×10^{-7} M	[36]
Imidacloprid	Insecticide-neonicotinide	LC-MS/MS	0.0009-0.0014 $mg.kg^{-1}$	[13]
Acetamiprid			0.0021-0.0031 $mg.kg^{-1}$	
Chloropyrifos	Insecticide-Organophosphate	Colorimetric Paper Sensor	8.60 ppm	[29]
Metalaxyl	Fungicide	LC-MS/MS	0.0007-0.0021 $mg.kg^{-1}$	[13]
Organophosphate	Organophosphate pesticides	OPH	100 ng mL^{-1} to 0.1 ng mL^{-1}	[26]

RESULTS AND DISCUSSION

It has been found that from all pesticides, use of insecticides is more. Survey showed that about 39% pesticides are from group insecticides and insecticides mainly attack on nervous system of pests. Obviously, pesticides resided on eatables are much harmful for living being. Review showed that insecticides like chloropyrifos, cypermethrin, diemethoate, malathion, dichlorvos, methyl parathion, imidacloprid, profenophos mainly used for protection of crops and their residue remain there on eatables.

CONCLUSION

Cultivated area and crop production has shown increasing trends for last five decades. At the same time consumption of pesticides is also increasing. It has been found that from all pesticides, use of insecticides is more. Survey showed that about 39% pesticides are from group insecticides and insecticides mainly attack on nervous system of pests. Obviously, pesticides resided on eatables are much harmful for living being. Review showed that insecticides like Chloropyrifos, Cypermethrin, Diemethoate, Malathion, Dichlorvos, Methyl parathion, Imidacloprid, Profenophosate mainly used for protection of crops. Its residue remains there on eatables. So, bio-pesticides should be encouraged. At the same time consumers must be aware of residues of pesticides on eatables. Many techniques are developed to detect the same. Each technique has their own advantages and limitations. There is utmost need of handy, portable, smart and economic pesticide residue detection system so that consumer can ensure that they are eating healthy and pesticide free food.

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