

A Systematic Review on Environmental Impact Pesticide Residues in Fruit and Vegetables and their Detection Methods

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Abstract

Background: Pesticides are used mainly to protect agricultural crops from various insects since the old times. Four basic needs for human beings are namely food, water, cloth and shelter. For the survival of living things, food is mandatory and it plays a primary role. Based on global reports, the world population is increasing geometrically, therefore, the demand for food, also increasing.

Objectives: To fulfil this basic need, farmers produce food by applying various pesticides that can increase the production of food. Due to the unscientific way of pesticides use, the grains, fruits and vegetables accumulate the pesticides as. Pesticides contaminate foods which is hazardous for the consumer because the long-term consumption of these contaminated foods may cause serious health problems such as cancer, diabetes, hypertension etc.

Methods: Previous studies showed that more than 50% of analysed crops samples were contaminated by different pesticides namely organophosphate, pyrethroids and organochlorine. Several methods were used to isolate the pesticides based on the detection methods from the fruits and vegetables.

Results: Several studies showed that the pesticide residues in fresh fruits and vegetables namely tomatoes, apples, watermelons, mangos, grapes, and plums exceeded the FAO/WHO permissible limits. Several methods have been discovered and modified for the detection of pesticide residues in various foods, fruits, vegetables and water samples. Therefore, this present review aims to update the status of pesticide residues in various food items and their detection methods that are used currently for the detection of food contamination.

Conclusion: The present review is to explain different aspects of food contaminating pesticides and it will help the scientist with the current scenario of pesticide residues.

Keywords: Pesticides, Fruits and Vegetables, Contamination, Pesticides Isolation, Detection Methods

1. Background

The world population is currently reached 7.9 billion according to the United Nations report [1]. Every year the population increases by approximately 81 million. Therefore, it is very difficult to provide food for a large population. Even though the density of population in some of the countries is very high. They have a shortage of food for surviving in some places. However, the farmers use pesticides excessively to kill the harmful insecticides for the production of more food [1].

Most of the pesticides are organic chemical compounds that applied often to kill pests and insects. Pesticides are chemical or

biological agents such as virus, bacteria, fungi, or disinfectant that prevents, incapacitates, kills, pests [2]. The use of pesticides in the agriculture sector is very common and the meaning of pesticides is to protect the plant product from the animal and insects. Those pesticides are commonly applied to destroy or control harmful agricultural pests that can destroy crops and livestock as well as reduce the production of crops. The applied pesticides are considered insecticides that kill insects, herbicides, rodents, and fungicides [1]. Based on the chemical structure and physical properties, pesticides are broadly classified as organochlorines, organophosphates, thiocarbamic derivatives, carboxylic acid derivatives, urea derivatives, phenolic derivatives,

fluorine and copper-containing compounds, and natural and synthetic pyrethroids [2]. Most leading countries are producing those pesticides related approximately 68% agrochemicals and fertilizers for the agricultural sectors. The majority of surveys that are conducted by several institutes globally, it showed that 50-70% of vegetables and fruits are seriously contaminated by harmful pesticide residues when the farmer applied pesticides excessively in an unscientific manner [3].

Vegetables and fruits are the staple food and they are an essential part of our daily. Oman is not an agricultural country, fruits and vegetables are produced on a small scale. The country is not self-sufficient in food, therefore, most of the vegetables and fruits are imported from China, India, Pakistan, Bangladesh, Iran, Egypt etc. Vegetables are an important category of foodstuffs that mainly provide carbohydrates, protein, vitamins, minerals, and fibres. Those mentioned ingredients are mandatory for the maintenance of our healthy life. Different vitamins from vegetables and fruits that can help our vision improvement [4]. Both vegetables and fruits are not only provided us nutrition but also fulfil the antioxidants that antioxidant can be extracted from various parts of plants as well as fruit peels and seeds. The mechanism or properties of antioxidants is to protect or prevent human chronic diseases like cardiac disorders, diabetes mellitus, inflammatory, neuro diseases and cancer [5].

The use of pesticides is related to health and environmental issues [6-12]. Some pesticides used in the agricultural are unrestricted [2]. Therefore, the pesticides could be absorbed through the skin, ingestion, or inhalation. However, mostly the health effects of pesticide exposure depend on the type of pesticide, duration, the path of exposure and individual health conditions [13-15]. In the human or animal body, most pesticides may be metabolized, excreted, stored, or bioaccumulated [1,2,13]. As result, several negative health effects have occurred with the bioaccumulated and metabolized chemical pesticides including dermatological, gastrointestinal, neurological, carcinogenic, respiratory, reproductive, and endocrine effects [10,14-29]. In addition, high occupational, accidental, intentional exposure to pesticides results in death [1,30].

Pesticides residues are commonly found in all kinds of foods, vegetables and beverages namely cooked foods, water, soft drinks, processed juices, various refreshments, as well as animal feeds [31-38]. Moreover, it should be noted that the pesticides residues cannot be removed from the samples completely by washing and peeling [39]. Most of cases, the concentrations of harmful pesticides do not exceed the permissible limit [35,38,40,41]. In the breast milk samples, pesticides residues were detected, and it is a prenatal exposure and health effects in children [13,42-44]. In Oman, most of the fruits and vegetables are imported from other countries. Therefore, we have to monitor the pesticide residue level of all imported foods and vegetables items before consumption to avoid pesticides exposure. The aim of this review is to update

the status of pesticide residues in various food items and their detection methods that are used currently for the detection of food contamination.

1.1. Types of Pesticides

Several types of pesticides are used in the agriculture sector to kill our crops from harmful insects. The classification depends on the chemical structures and their physical properties. Organochlorines, organophosphates, thiocarbamic derivatives, carboxylic acid derivatives, urea derivatives, phenolic derivatives, fluorine and copper-containing compounds, natural and synthetic pyrethroids are the major class of pesticides [2,31].

1.2. Organochlorines Pesticides

Organochlorine pesticides are the most commonly used pesticides in the agriculture sector. They are namely dichlorodiphenyltrichloroethane (DDT), dieldrin, endosulfan, heptachlor, dicofol, methoxychlor etc. Globally, including in Oman, the farmers used frequently the said pesticides to protect fruits, and vegetables from insects. However, the farmers are use these pesticides uncontrolled way therefore many health effects are created due to exposure of pesticides [2,45,46]. Due to the health effect, DDT is ban items most of the countries, but still it is used in some countries due to its easy application. The general side effects of organochlorine pesticides are endocrine problems, embryonic development, and haematological and hepatic problems [10,47-49].

1.3. Organophosphorus Pesticides

Organophosphates are also commonly used pesticides in the agriculture sector. The most important pesticides in this class are malathion, parathion, and dimethoate [49,50]. Some pesticides are known for disrupting potential endocrine disrupting properties [10,51-54]. They could be promoted as an ecological alternative to organochlorines [52]. The most commonly used pesticide is known as glyphosate. It has directly linked with inhibiting cholinesterase enzymes that can decrease the secretion of insulin, interrupt the normal metabolism function such as proteins, carbohydrates and fats [52,55]. In addition, the genotoxic effects and mitochondrial effects can cause oxidative stress and nervous and endocrine disruption systems [54,55]. Previously, several population-based studies were conducted and they showed that exposure to organophosphorus pesticides can cause serious health problems such as cardiovascular diseases, reproduction system, nervous system (CNS), and lymphoma [56-58].

Recently, some studies showed that the correlation between glyphosate and genetically modified crops could directly affect health deterioration in the USA. Correlation analyses showed the possible link between glyphosate use with different health problems and chronic diseases namely high blood pressure, diabetes, several types of strokes, autism, chronic kidney failure, Parkinson and Alzheimer's diseases, and various types of cancer [47]. Additionally, glyphosate can cause gluten intolerance,

deficiency of essential amino acids, trace metals, reproductive, therefore, the risk of lymphoma increases [50].

1.4. Carbamate Pesticides

The third commonly used group of pesticides in the agriculture sector is the carbamate pesticides, namely aldicarb, carbofuran, and ziram. They have also a negative impact by disrupting the endocrine system, destroy the reproductive system, metabolic and mitochondrial functions [10,47,55,58]. However, several *in vitro* studies showed that carbamate pesticides can cause cancer and genotoxic effects, ovarian cancer, immune cells effect, and killer cells [33,42,43]. Research also showed that the carbaryl as well as carbamate pesticides, it can link with the hydrocarbon receptor and enhance dioxin toxicity [44-47,59].

1.5. Human Health Risk Assessment

The health risk and contaminated food with pesticides are related to each other. However, the assessment of pesticides in the foods is mandatory for the protection of our human health. Most of the foods available in the global markets are contaminated by harmful toxic chemicals such as pesticides residues, polycyclic aromatic hydrocarbons, toxic phenolic derivatives etc [28-30]. Due to the consumption of contaminated foods, toxic chemicals are deposited in the human body. Long-term consumption of these contaminated foods in our daily diet, results in several diseases such as high blood pressure, diabetes, strokes, autism, chronic kidney failure, Parkinson's and Alzheimer's diseases, and various types of cancer [34-43,60]. The FAO and WHO are recommended the permissible limit of pesticide residues in fruits and vegetables [15-18]. Monitoring of pesticide residues in our daily dietary foods is necessary to ensure the limit of pesticides and to compare with the limit provided by the WHO and FAO [22-34]. If the values of fruits and vegetables are within the permissible limit then it is, considered safe food. However, if the values exceed the permissible, it will create health problems like high blood pressure, diabetes, brain strokes, autism, chronic kidney disorders, Parkinson's and Alzheimer's diseases, and various types of ovarian cancer [34-43,60]. Therefore, in the current review, we compare the data that are available in the literature on pesticide residues in fruits and vegetables. The previous studies also showed that it is possible to assess human health risk by hazard risk index [48]. This review also aims to define the complete structure of pesticide residues in various fruits and vegetables that are collected from all over the world and the experimental data was used to assess the human exposure to the contaminated fruits and vegetables.

1.6. Extraction of Pesticides Residues

Several methods have been developed for the extraction of pesticide residues from vegetables and fruits. After extraction, the vegetable and fruit extracts contain various interfering chemicals such as proteins, fats, wax etc., they can inhibit the extraction of pesticides. Those interfering chemicals create a problem for the analysis of pesticide residues by analytical methods. Therefore, a clean-up process is badly needed for the extraction of pesticides. The most commonly used methods are the dispersion solid-phase

method, the solid-phase extraction method, the liquid-liquid extraction method and the QuEChERS method [43,49-52]. The QuEChERS stands for 'Quick, Easy, Cheap, Effective, Rugged and Safe' method involves three vital steps: extraction by using an organic solvent, salts for partition and cleanup by dispersion solid-phase method. Since the development of the extraction procedure of pesticides, people have been used extensively the QuEChERS method. QuEChERS is a more scientific and sensitive method than other methods currently used for pesticide residues extraction from vegetables, fruits and many other plant matrices [15-34]. However, scientists are searching for more effective, sensitive and reliable methods for extraction and quantification of various classes of pesticide residues in vegetables and fruits. More recently, the QuEChERS extraction method has been considerably modified by the scientist to raise its effectiveness and sensitivity, particularly the cleanup methods. The modified method has been used simultaneously for the extraction of various classes of pesticide residues.

1.7. Detection of Pesticide Residues

Several chromatographic and spectroscopic methods are currently used for the separation and quantification of pesticide residues in the fruit and vegetable samples. They are namely gas chromatography-mass spectrometry (GC-MS) and liquid chromatography-mass spectrometry (LC-MS). Advanced sensitive mass spectrometry (MS/MS) coupled with GC and LC is currently used for the separation and quantification of pesticides to improve their detection performance. Nowadays, GC-MS/MS, LC-MS/MS, and MS/MS techniques are most commonly applied for pesticides detection are periodically reviewed [33-36].

Casado et al, developed a method for the analysis of pesticides in water samples by using a multi-residue analysis method [26]. Their method was applied to determine more than 250 pesticide residues in surface water samples. This method was also able to detect more than 215 pesticides with detection limits of quantification (LOQs) less than 5 ng/L.

Lara-Ortega et al., reported that dielectric barrier discharge ionization (DBDI) as an LC-MS ionization interface is a good and sensitive method for the determination of pesticide residues [27]. The advantage of this method is electrospray ionization (ESI). In addition, DBDI can detect organochlorine pesticide residues by using GC-MS, it also showed the performance of electrospray ionization (ESI).

Zhang et al., reported the development of a solid-phase microextraction method for the extraction of pesticide residues and it was detected by using gas chromatography mass spectrometry (SPME-GC-MS) [32]. Currently, this method is used to determine polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), and pesticide residues in seaweeds and water samples.

2. Results and Discussion

Since the ancient times, both organic inorganic compounds and their salts substances were currently applied as pesticides to protect our food against pests and insects [47]. Various chemical pesticides are produced by agrochemical companies to enhance food production. The newly produced chemical substances with pesticide properties have been applied to the crops by the traditional agricultural methods. However, the current practices for agriculture sectors are based on the extensive use of pesticides that have been associated with negative impacts on human health, wildlife, and the natural environment [9,11,45-47].

Agriculture can control some important factors namely the growth of population, food safety, health hazards from pesticides, the resistance of pesticide, break the chain of the natural environment as well as climate change [14-20]. Recently, various updated concepts of food production have been constructed. One concept, the agriculture climate-smart, pursues several solutions regarding the climate change [61,62]. Secondly, an ongoing argument has occurred between the genetically modified engineered based pesticide-resistant plants, it will help us their safety food as well as the impact on pesticide use [28,50-54].

Besides, exposure to the mixture of pesticides and their real-life with possible protective or synergistic effects are determined by using in depth research. The mixture of toxic ingredients might cause anonymous adverse health effects in the human body. Therefore, it is mandatory to determine the safe levels of pesticides in foods exposure might miscalculate the health effects in the human body.

Different grains, vegetables, and fruits contains different classes of pesticide residues. The majority of pesticides is considered as a metabolic product that can remain excess in grains, vegetables and fruits when the farmer applies it to their crops. Several biochemical residues, especially chlorinated pesticides, might be accumulated in high levels in the human body [10]. The excess chemicals can be transferred through the food chain that can be quantified in various food products such as meat, poultry, fish, vegetable oils, nuts, fruits and vegetables [11,54,56-58]. Due to the insects and pests that can cause a loss in the quality and amount crops and their furnish products. Since the ancient times, several pesticides have been used to protect our crops before and after harvest. In addition, during the cultivation as well as the storage of crops farmers regularly use pesticides the residue of which can be found in the crops and the prepared foods items [12]. Sometimes farmers apply degradable pesticides such as organophosphates, carbamate, and insect growth regulators to the cereal grains during the storage period and before shipment to prevent loss caused by insects. [13]. The most applied pesticides in the agriculture sector are namely sulphur, endosulfan, methyl parathion, isoproturon, chlorpyrifos, malathion, carbendazim, butachlor, quinalphos, copper oxychloride, and dichlorvos for the protection of vegetables, fruits and food grains. Therefore, the vegetables, fruits and food grains accumulate pesticide residues in the highest levels that is legally tolerated by the food or feed when

the pesticides are applied appropriately. Most of the international bodies namely European Union, WHO, FAO, and North American Free Trade Agreement regulate the pesticide content by setting the highest residue limits. However, these limits remain are not constant in different countries.

In south Asian countries such as India, Pakistan and Bangladesh agriculture sector is the most pesticide-consuming sector. Globally, about 14% of agricultural land is used for agricultural activities. It is also reported that 37-79% of the crops are lost due to the effect of harmful weeds that can be managed by applying of herbicides. Recently, the application of organochlorine pesticides (OCPs) is applied in the agriculture sector has potentially decrease in the developed and developing countries. Even though, some countries they are still using organochlorine pesticides (OCPs) in the agriculture sectors in illegal way.

3. Conclusion

Pesticides from food such as vegetables and fruits that can accumulate in the human body. Due to the consumption of food containing pesticides may cause a variety of human health effects such as damage CNS (central and nervous systems), ANS (autonomous nervous systems), cancer, hypertension, immune system disorder, diabetics, and reproductive system disorders. To minimize the negative impact on human health due to pesticide residues some precautions must be taken such as proper use of pesticides, washing properly, processing of the food products properly, and promoting organic farming, applying of natural pesticides as well as strictly following pesticide-related laws.

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