

## Review Article

# Residue of Pesticides in Fruits, Vegetables, and Their Management in Ethiopia

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In Ethiopia, using pesticides to manage pests in the growing of fruits and vegetables is a standard practice. Various classes of pesticides have been approved to combat pests, but the majority of those in use now are outdated broad-spectrum insecticides with significant residual effects on crops of freshly eaten fruits and vegetables. This review reveals that Ethiopia's assessment of the residual pesticide level in fruits and vegetables has been lacking. According to the reviewed literature, crops that are often treated with pesticides in many countries have significant residual pesticide levels. However, Ethiopia has not adequately reported on this issue. Furthermore, due to a lack of knowledge regarding the impact of pesticide residues on human health, Ethiopians frequently use pesticides improperly to control pests in fruits and vegetables. The majority of consumers eat their fruits and vegetables unprocessed, without washing or cooking them first. To reduce the risk of pesticide residues in fruits and vegetables for consumer safety and to battle the health effects of toxic chemicals in humans, monitoring pesticide residues and raising awareness about the adverse effects of pesticides on humans are urgently needed. Before they may be registered and sold, pesticide residues in fruits and vegetables as well as in the environment must also undergo proper testing and evaluation. New pesticide generations that have fewer side effects on fruits and vegetables must also be developed. By washing, peeling, canning, or boiling fruits and vegetables before consumption, the detrimental effects of pesticide residues on human health can be minimized.

## 1. Introduction

Fruits and vegetables are essential elements of our daily diet and play a significant role in human nutrition and health and are important sources of carbs, vitamins, trace minerals, and antioxidants, including fruits and vegetables [1]. Vegetable and fruit consumption and demand have increased as a result of greater public knowledge of their health advantages. Increased consumption of fruits and vegetables has been recommended to prevent conditions such as vitamin deficiencies and to lower the occurrence of serious illnesses such as cancer and cardiovascular disorders [2]. Based on the National Bank of Ethiopia, fresh fruits and vegetables earned \$56 million in export sales, or approximately 2% of all agricultural exports from Ethiopia in 2016-17 [3].

One of the main production challenges that Ethiopian fruit and vegetable growers encounter is pests, and in the Ethiopian agricultural system, weeds, illnesses, and insects all play significant roles in lowering crop yields and causing food poverty [4]. Pesticides are used in the majority of agricultural production sectors to reduce pests, increase output, and enhance product quality. Pesticides are used during cropping in conjunction with other pest control approaches to eradicate insects and stop illnesses to minimize loss and maintain the quality of fruits and vegetables during harvest [5]. To avoid, eliminate, or deter pests that could harm crops, pesticides are used in the production of fruits and vegetables, and because pesticides function quickly and require less work than other pest management techniques, their use has expanded [6]. To avoid crop

damage from insects, mites, rodents, and other pests or to limit the growth of weeds and fungi, pesticides are routinely used in a number of various ways during the production of food. It is currently a necessary component of modern life and is employed to safeguard agricultural land, grain bins, and flower gardens and to eliminate pests that spread infectious diseases that are deadly, and nearly \$38 billion is thought to be spent annually on insecticides worldwide [7]. However, fruits and vegetables commonly have pesticide residues after harvest because pesticides are frequently used throughout production [8]. Numerous elements of the water, air, and soil ecosystem have been contaminated by the continual application of persistent and nonbiodegradable pesticides [9]. Additionally, pesticides have bioaccumulated at the upper tropic level of the food chain, and more recently, exposure to pesticides has been linked to a number of acute and chronic human disorders [10].

Although Ethiopia has previously used few chemical pesticides, recent changes in increased agricultural production and the floriculture business have led to increased pesticide consumption [11]. Food quality has significantly declined because of extensive pesticide use in agricultural fields, and small-scale vegetable growers in Ethiopia disregard recommendations and use pesticides carelessly [12]. The environment, farmer and consumer health, and agricultural sustainability are all affected by these pesticide use practices, and a major global public health concern is the presence of pesticide residues in horticulture products at unsafe levels [13]. Since the majority of them are consumed raw, fruits and vegetables are likely to have higher levels of pesticide residue than other food groups of plant origin [14].

Pesticide residual effects have been a major source of worry; however, replacing high-toxic chemicals with new pesticide formulations that have less of an impact on humans and taking into account nonchemical pest control strategies such as biological, resistance cultivar, and cultural control, as well as technological innovation for producing low-risk pesticides and developing effective application approaches and improving organic farming systems, can lessen the impact of pesticide residue [15]. In addition, depending on the type of pesticide and the time of treatment, pasteurization, blanching, boiling, heating, steaming, canning, and scrambling have all been reported to be beneficial in the degradation of different pesticides [16]. To increase agricultural output, many pesticides, including herbicides, insecticides, fungicides, pyrethroids, organochlorines, and organophosphorus, are commonly used in Ethiopia to grow fruits and vegetables [17]. The amount and use of pesticides in agriculture have significantly increased over the last several years, and it is projected that this development trend will remain in the near future [18]. Despite the benefits of pesticides, their negative effects on human health and environmental quality have been extensively studied worldwide and are a major source of concern on a local, national, regional, and international scale [19]. Ethiopia has limited knowledge regarding the quantity of pesticide residues present in fruits and vegetables and how such residues affect human health [20]. Thus, the objective of this review is to better inform the public on the impacts of pesticide residues

and available strategies for reducing them in fruits and vegetables.

## 2. Pesticide Use in Fruits and Vegetables

When a product or mixture of compounds is used to kill, deter, or control pests such as rodents, weeds, mites, or insects, it is referred to as a pesticide, and pesticides are usually categorized as insecticides, herbicides, fungicides, acaricides, rodenticides, and other substances used to control specific target pests [21]. In agriculture, pesticides are frequently employed mostly to increase crop yields and generate a large amount of food to feed the world's expanding population; additionally, they are utilized to control insect-borne diseases and safeguard crops from pests [22]. Pesticide residues in food products accumulate excessively, and the increased usage of pesticides contaminates the environment, both of which have long been of concern [23]. The main benefits of employing pesticides include increasing crop yields or productivity by protecting crops from weeds, diseases, and pests, as well as preventing crop products from going bad while being kept and extending the shelf life of fruits and vegetables to maintain marketability.

Different types of pesticides are used on different crops in different nations to avoid pests, insects, and weeds, and more crops that have been treated with pesticides are being imported into other countries as global trade expands [24]. Public health issues arise from the spread of pesticide residues across international borders because of interactions. Pesticides come in a wide range, 500 insecticides with diverse applications are now in use, and the most hazardous insecticides to the environment are those that include organochlorines [25]. The recent addition of a number of diverse chemical groups to pesticides has increased agricultural production in Ethiopia by providing crop growers with a variety of options for improved insect management. The increase in investment in agricultural fields is to blame for the worrisome increase in the sensible use of pesticides, and pesticides are, therefore, imported without being registered or put through an efficacy test [26]. In the central rift valley of Ethiopia, vegetable growers utilized 24 pesticides, of which 2/3 were not approved for use on vegetables [11]. Additionally, as a result of the recent rapid expansion, particularly of large-scale floriculture firms, the nation now utilizes more pesticides and handles them poorly. Many pesticides, such as carbamate, pyrethroid, organochlorine, and organophosphorus insecticides, fungicides, and herbicides, are frequently used in the production of fruits and vegetables to increase agricultural productivity [27]. *Ridomil*, *Selecron*, *Mancozeb*, *Ethiotate*, *Cruzate*, *Profit*, *Karate*, and *Malathion*, among other pesticides, are routinely used 5–8 times per season on agricultural fields that grow irrigated crops [28]. Organophosphates, in particular *acephate*, *diazinon*, *dichlorvos*, *monocrotophos*, *dimethoate*, *profenofos*, and *cadusafos*, have been outlawed since 1990 as one of the classes of pesticides most dangerous to vertebrates. However, Ethiopia continues to utilize the bulk of organophosphate insecticides to manage pests on fruits and vegetables [29].

Pesticide residues, which are sometimes present in food products after harvesting, are beyond the consumer's control and are harmful to human health, and pesticide residues are a significant barrier to the worldwide trade of food products [30]. Some international markets do not accept horticulture exports from some poor countries due to residual pesticide levels, and the location of pesticides in food varies depending on the type and amount of food material, the type and amount of the pesticide molecule, and environmental conditions [31].

What happens to pesticides after being applied to fruits and vegetables?

As a result of transportation, partitioning, transformation, or degradation, an agent's fate refers to the pattern of distribution of that agent, its derivatives, or its metabolites in an organism, system, compartment, or (sub) population of concern [32]. After being applied to crops, pesticides may interact with the surfaces of the plants, are exposed to environmental variables such as wind and sunlight, and may be washed off during rain [33]. The pesticide may be absorbed by the plant surface (waxy cuticle and root surfaces) and go systemically into the plant or it may remain on the plant's surface (contact), and the pesticide can degrade chemically and microbiologically while it is still on the surface of the crop through wash-off, volatilization, photolysis (Figure 1), and other processes [34]. Only 1% of pesticides sprayed on the ground actually kill the intended insect; the other 99% end up polluting the environment (bodies of water, soil, air, and nontarget creatures) through drift, volatilization, leaching, and runoff [35]. The three main mechanisms reported by scholars that determine the fates of pesticides on the target site are adsorption, transfer, and degradation [36].

**2.1. Adsorption.** A pesticide is chemically bonded or adsorbed to a soil particle through the process of adsorption, and for instance, fragments of a positively charged pesticide molecule might electrically bond with negatively charged clay minerals or organic material [37]. The characteristics of the soil and pesticide affect the adsorption, and the interaction between the chemical characteristics of the pesticide, its concentration in the soil water, the pH of the soil, and the makeup of the soil determines the strength of the bonding (percent sand, silt, loam, clay, and organic matter). The herbicide is unlikely to leach or discharge if it is bonded to the soil, and some insecticides that are extremely soluble adhere firmly to the soil [38]. The soil holds the pesticide more tightly and makes it immobile the more clay and organic matter there are in the soil, and pesticide molecules that have been heavily adsorbed do not leak or move until the soil particles to which they have adhered do so (via erosion) [39]. A pesticide's molecules are more likely to undergo microbial breakdown the longer they are retained, which lowers the risk of leaching and runoff.

**2.2. Transfer.** The term "transfer" describes the procedures that take the pesticide from the application site away, such as crop removal, volatilization, runoff, leaching, and

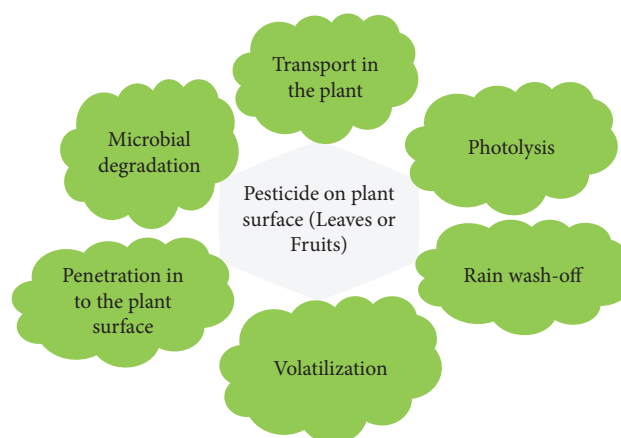


FIGURE 1: Fate of pesticides in plant surface chemicals.

absorption, and transferring the insecticide is sometimes necessary for pest control [40]. For instance, certain pre-emergence herbicides require irrigation or rainfall to penetrate the soil and reach the roots of weed seeds that germinate.

**2.2.1. Volatilization.** When a liquid or solid transforms into a gas and spreads away from the original application location, this process is known as volatilization, and the insecticide typically begins to volatilize immediately after being applied in the field [41]. The procedure is reliant on the pesticide's vapor pressure, and low vapor pressure pesticides stay on the surface for a longer period of time than those with high vapor pressure, which tend to volatilize quickly into the air [42]. The rate of volatilization is also influenced by external variables, including temperature and wind speed, and the rate of pesticide evaporation increases with increasing speed and temperature [43].

**2.2.2. Absorption.** The uptake of pesticide compounds into plant tissues is referred to as absorption, and this action eliminates the herbicide from the environment and stops it from contaminating the water supply [44]. Once a pesticide is ingested, the majority of it degrades, and when a plant decomposes, pesticide residues may be broken down or may still be there and be released back into the environment [44]. Some pesticides persist in the soil long enough for plants planted in a field to be exposed to them years later.

**2.2.3. Movement in Runoff Water.** Pesticides that are either dissolved in or suspended in runoff waters travel across the soil surface from the application location when they are either soluble or insoluble [45]. Pesticides that are dissolved or suspended in runoff water can swiftly contaminate surface waters, including lakes, streams, and rivers, and the ease with which a pesticide dissolves in water depends on its water solubility [46]. A pesticide that is very soluble has a higher chance of being removed from any surface where it has been used, and the maximum amount of a pesticide that will

dissolve in 1 liter (1.06 quarts) of water is how solubility is typically expressed [47].

**2.2.4. Leaching to Groundwater.** Pesticides migrate downward in the soil through pores and fissures, which is known as leaching, and as water descends, soil typically filters it to remove impurities such as pesticides [48]. Pesticide migration can be influenced by the characteristics of the soil, the pesticides, location, and weather (leaching), and pesticides that leak through soil may contaminate ground water [49]. Pesticide application (rate of application and application method), soil qualities (organic matter, soil texture, and soil acidity), pesticide properties (solubility, adsorption, and persistence), and weather conditions are the elements that affect leaching [50]. If the pesticide is water soluble, the soil is sandy, a rain event happens soon after spraying, the pesticide is not strongly adsorbed to the soil, or all four, leaching may be exacerbated [40].

**2.3. Degradation.** Degradation is the process by which a pesticide is broken down after use, and microbes, chemical processes, and light or photodegradation breakdown pesticides [51]. Depending on the surrounding environment and the chemical properties of the pesticide, this process can take hours, days, weeks, or even years [52].

**2.3.1. Microbial Degradation.** Microbial metabolism has the potential to breakdown certain pesticides and microorganisms, such as fungi, bacteria, and other soil microbes, which is known as microbial degradation, breaking down pesticides [39]. Microbial degradation is influenced by soil organic matter, texture, and site conditions such as moisture, temperature, aeration, and pH, and most microbial activity typically occurs in soils that are warm, moist, well aerated, and pH neutral [53]. When the following conditions are met: soil pH is favorable, soil moisture and oxygen are sufficient, and soil fertility is high, microbial decomposition tends to rise, and in places with large levels of organic matter, particularly in the surface soil layers, the microbial breakdown happens more quickly [54]. The rate often drops as one goes deeper into the soil, where microbial activity is less favored by factors including moisture, temperature, and aeration [55]. Pesticides can be broken down into carbon dioxide and water by microorganisms by using them as nutrients, or they can be converted into metabolites [39]. Pesticides cannot always be assimilated by bacteria due to variations between their molecules and those found in naturally occurring organic compounds and pesticides, although they may be changed at reactive sites, and depending on the original substance, the metabolites produced might be more or less harmful [56].

**2.3.2. Chemical Degradation.** Hydrolysis and chemical reduction or oxidation reactions are a few examples of chemical degradation processes, and when a pesticide interacts with water, oxygen, or other compounds in the soil, chemical breakdown takes place [57]. Microbial activity

often declines as soil pH goes from severely acidic to excessively alkaline, and these circumstances might, however, encourage quick chemical deterioration [58]. Pesticides are broken down chemically in the soil through chemical reactions, and soil temperatures, pH levels, and pesticide binding to the soil influence the rate and kind of chemical reactions that take place [59].

**2.3.3. Hydrolysis.** By breaking down large molecules into smaller ones through a process known as hydrolysis, water also breaks down pesticides, and pesticides can hydrolyze on the soil's surface, in the root zone, or wherever there is access to water [60]. At or close to the soil surface, warm water may have high hydrolysis activity, and the rate of hydrolysis decreases as the water temperature drops below the root zone and hydrolysis significantly slows down in deep groundwater [61].

**2.3.4. Photodegradation.** Photolysis, also known as photodecomposition, is the process by which compounds are broken down by light, and plants, soil, water, and any other surface that receives sunshine all experience photolysis [62]. When molecules take in solar energy, photolysis takes place, which leads to the breakdown of pesticides, and the indirect reaction can also result from other compounds that are broken down by sunlight and their byproducts reacting with insecticides [63]. To some extent, photodegradation can affect all insecticides, and the rate of photodegradation is influenced by the amount of sunlight, the amount of time exposed, and the characteristics of the pesticide. Pesticides that are integrated into the soil are less likely to photodegrade than those that are applied on foliage or the soil's surface, and pesticides may deteriorate more quickly in greenhouses wrapped in plastic than in glass since the latter blocks most of the UV light that causes pesticide degradation [64].

### 3. Residue Levels of Pesticides

Based on the appropriate daily intake (ADI) and acute reference dosage, it has been shown that consuming plant food products with pesticide residue levels over the MRLs can result in acute illness and chronic disorders (ARfD) [65]. It has become known that appropriate daily intake for short-term exposure or ARfD is used to compare safety limits, and if the estimated dietary intake of a pesticide residue does not exceed the ADI or the ARfD, the consumer is not regarded as being at risk. To prevent the negative effects of hazardous chemicals on human health, monitoring and setting maximum residue levels for pesticide residues in food products is an efficient control method [66]. The highest amounts of residues anticipated to be present in food when a pesticide is used in accordance with approved agricultural practices are known as maximum residue levels [67]. The use pattern established from effectiveness studies that results in the lowest effective rate for the specific 12 pest-crop combinations is known to be a good agricultural practice (GAP) and is characterized as such [68]. The application rate and the

preharvest interval, often known as the time between the most recent application and harvest, are part of the use pattern (*PHI*), and a variety of climates, growth techniques, crops, and cultivars that the pesticide has been sprayed to utilizing *GAP* are covered by the residue data used to calculate the *MRL* [69]. To establish the *MRLs*, a minimum quantity of field trials must be conducted, and when a pesticide is used in crucial *GAP*, the supervised trials should accurately represent the range of residues that are expected to be present in typical agricultural practices [70]. Critical *GAP* describes the situations in which the pesticide formulation's maximum application rate and minimal *PHI* are employed and each country and region will inevitably have its own *GAP*, but the *GLOBALGAP* organization has launched an endeavor to create one standard for *GAP* with a variety of product applications that may be applied to all global agriculture [71]. More than 100 countries around the world already have organizations in operation, and *MRLs* are set using modeling and statistical techniques, expert judgment, or both [72]. There are currently no procedures that are universally applicable for estimating *MRLs* for pesticides, and expert opinion is necessary for calculating *MRL*, particularly during the data selection stage. It is important to realize that *MRLs* are not absolute safety thresholds; food residues might have levels beyond *MRL* and still be safe to eat, and risk assessment organizations, such as the *EFSA* in the *EU* or *JMPR* for *CODEX Alimentarius*, evaluate the data from supervised trials [73]. Safety limits are evaluated in relation to acute reference doses (*ARfD*) for short-term exposure or recommended daily intakes (*ADI*) for long-term exposure, and the lowest limit of the analytical determination is established as the *MRL* in the absence of the *MRL* [74]. The *EU* standard is 0.01 mg/kg, and *MRLs* are established according to legal requirements in most countries [75].

#### 4. Monitoring of Pesticide Residues

Pesticide monitoring systems are designed to ensure that fruit and vegetable residues do not exceed the maximum residue levels (*MRLs*) permitted by the nation's government. They make sure that pesticides are not misused in a way that leaves unintended residues in food and that *GAP* is upheld [76]. Some initiatives are carried out as a result of expectations placed on them by international trade, primarily in developing nations. The outcomes of these monitoring programs are also utilized by regulatory organizations for upcoming *MRL* innovations and public health risk assessment exercises [77]. Since pesticide residues in food have drawn much attention as a crucial component of food safety, national and international legislation has tightened *MRL* observance, and reliable analytical techniques are needed to monitor residue levels in food [78]. However, pesticides are typically found in very small amounts in both the environment and food, and they are numerous and have various physicochemical characteristics. Researching and quantifying their residues is an ongoing task that calls for the use of extremely sensitive and trustworthy multiresidue analysis techniques, and there are various methods of analysis, which

one is used depending on the type of pesticides being investigated and the matrices being targeted [79]. Analyzing pesticide residues is a crucial step in establishing the safety of applying particular pesticides, and there are several analytical techniques intended to identify various pesticide residues [14]. New extraction techniques, such as solid-phase microextraction and supercritical fluid extraction, have been developed in recent years [80]. The most popular approach for determining pesticide residue in vegetables and fruits includes *HPLC* and *GC* (Tables 1 and 2), and they are straightforward application technologies [14]. The primary benefits of these technologies include streamlining laboratory sample preparation tasks and lowering solvent and glassware usage, low cost, and generation of small amounts of waste, unlike other conventional techniques [92].

QuEChERS' benefits include using less material and solvent, taking less time to prepare the sample, and having a highly effective extraction process [93]. More than 200 different compound types can be detected simultaneously, and the recovery rate is better than 80%. Correction is carried out using an internal standard method, which has high precision and accuracy. It is also easy to use and has a short detection time, and 30–40 preweighed samples can be processed in one hour. The QuEChERS approach, however, has a poor purifying capacity, which might cause contamination issues and impair measurement accuracy [94]. It has always been challenging to prepare samples for the investigation of trace chemicals in problematic matrices [95].

#### 5. Determination of Pesticides

After the extraction procedure is finished, the isolated chemicals are separated, recognized, and tested in the analysis process, and gas chromatography (*GC*) and liquid chromatography are typically utilized for the identification and quantification of pesticides, depending on the type of pesticides being examined [96]. Gas chromatography, *GC*-mass spectrometry, *GC*-ion trap mass spectrometry, and *GC*-tandem mass spectrometry are typically used to determine pesticides [97]. Other conventional quantification techniques exist in addition to *GC*-*MS*, such as high-performance liquid chromatography (*HPLC*), *HPLC*-mass spectrometry, low-pressure gas chromatography-mass spectrometry, and liquid chromatography-tandem mass spectrometry [98].

#### 6. Pesticide Residues in Fruits and Vegetables

Fruits and vegetables are significant components of Ethiopian horticulture, where pesticides are heavily utilized [99]. While the histories of pest control, increased pesticide use, and pesticide problems in these two regions are similar, they differ in terms of their organizational structures, farm sizes, on-farm technical and human capacities, the state's commitment and involvement, the degree of international embeddedness of the product chain, and the actions (strategies) taken to influence pesticide use [100]. Diseases and insect pests are some of the main issues facing Ethiopian growers of fruits and vegetables, and these are extremely

TABLE 1: HPLC monitoring and determination of pesticides in fruits and vegetables.

Class	Detection	Column	Limit of detection (mg/kg)	Specific samples analyzed	References
Dithiocarbamates	DAD/APCI MS	CN: 250 mm × 4.6 mm × 5 µm; C18–250 mm × 4.6 mm × 5 µm water-MeOH (80 : 20); isocratic	0.01–0.1		
4 multi-class	DAD	C18: 250 mm × 4.6 mm × 5 µm fitted with guard column 4 mm × 3 mm CAN & water: gradient	0.5–1	Grapes: 93 µg/L	[81]
Carbamates phenylureas	ESI-MS	C18: 150 mm × 4.6 mm × 5 µm; MeOH & water: gradient	0.001–0.01		
Neonicotinoids	ESI-MS	125–4: 100 mm × 5 µm; water & 0.01% acetic acid in MeOH: gradient	0.010–0.025		
Guanidines	ESI-MS ESI-MS-MS	C18: 150 mm × 2.1 mm × 5 µm; 0.3% HCOOH in water and 0.3% HCOOH in ACN: gradient	0.0004–0.008		
Azadirachtoids	ESI-MS-MS	C18: 250 mm × 4.6 mm × 5 µm; ACN; 0.1% HCOOH and 0.01% sodium acetate: gradient	0.002–0.007		
9 multi-class	ESI-MS-MS	C18: 150 mm × 2.1 mm × 3.5 µm; 0.1% HCOOH in water and 0.1% HCOOH in ACN: gradient	—		[82, 83]
6 multi-class	ESI-MS-MS	75 mm × 2.0 mm × 4 µm; 10 mM aqueous ammonium formate, pH 3.9 & ACN: gradient			
8 multi-class	ESI-MS-MS; TQ	C18: 100 mm × 2.1 mm × 5 µm; 0.01% HCOOH in MeOH & 0.01% HCOOH in water: gradient			
7 multi-class	ESI-MS-MS	C18: 100 mm × 3 mm × 4 µm; ammonium acetate-acetic acid 20 mM in water and ammonium acetate acetic acid 20 mM in MeOH-water (95 : 5): gradient C18:	0.002–0.013	Orange: 0.0007–0.02 mg/kg	
3 multi-class	ESI-MS-MS	125 mm × 2.1 mm × 5 µm; 2.5 mM ammonium acetate in water & 0.01% HCOOH in MeOH: gradient			
12 multi-class	ESI-MS-MS	150 mm × 2.0 mm/0.1% HCOOH, 0.1% HCOOH in CAN & ACN: gradient C18:	0.0007		[84]
Triazoles	ESI-MS-MS	50 mm × 2.1 mm × 5 µm; 0.01% HCOOH in ACN-water (35 : 65): isocratic			
Carbamates	ESI-MS-MS	C18: 10 mm × 2.1 mm × 5 µm; 0.01% HCOOH in water; 0.01% HCOOH in MeOH: gradient			
8 multi-class	ESI-TOF-MS	C8: 150 mm × 4.6 mm × 5 µm; gradient	0.0005–8	Berries: 0.005–0.01 mg/kg	
Carbamates	ESI-MS	C8: 150 mm × 4.6 mm × 5 µm; MeOH-water (70 : 30): Isocratic			
Carbamates	FD	C18: 150 mm × 63 mm × 3 µm; ACN-water (45 : 55): gradient			
Ureas	FD	C18: Guard column: 20 mm × 3.9 mm × 4 µm; MeOH, water & ACN: gradient	0.000055–0.00015		
Carbamates	FD	C18: 30 × 4 mm × 5 µm/0.01 M ammonium, acetate-ACN (70 : 30) and 0.01 M ammonium acetate-CN (45 : 55): gradient			
Phenols, azoles	FD	C18: 75 mm × 4.6 mm × 3 µm; MeOH & water: gradient C18: 75 mm × 4.6 mm × 3.5 µm;	0.01–0.02	Cucumbers: 0.05 mg/kg	
Neonicotinoids	MS	water, MeOH & 10% acetic acid: gradient			
7 multi-class	MS-MS	C18: 150 mm × 4.6 mm × 5 µm; MeOH, water with 10 mM ammonium formate: gradient			
Carbamates, organophosphorus	MS-MS	150 mm × 2.1 mm × 5 µm; water-MeOH & ACN with 1.0 mM ammonium acetate: gradient	0.00001–0.00097		[85]
Carbamates	MS-MS; TQ	C18: 50 mm × 2.1 mm × 3.5 µm; ACN-MeOH 5 mM aqueous ammonium-acetate (43 : 43 : 14): gradient	0.0004–0.003		
Benzoylphenylureas	MS-MS	C18: 150 mm × 2.1 mm × 5 µm; 10 mM aqueous ammonium acetate & MeOH: gradient			
23 multi-class	MS-MS	C18: 150 mm × 2.0 mm × 5 µm with a C18 Meta guard cartridge 30 mm × 2.0 mm		Banana: 0.01–0.23 mg/kg	
11 multi-class	MS-MS	MeOH-buffer (2 mM ammonium formate, pH 2.8): gradient			
5 multi-class	TOF-MS	C8: 150 mm × 4.6 mm × 5 µm; 0.1% HCOOH in water & ACN: gradient C8: 150 mm × 4.6 mm × 5 µm; 0.1% HCOOH in water & ACN: gradient	0.000000–0.00009		

TABLE 1: Continued.

Class	Detection	Column	Limit of detection (mg/kg)	Specific samples analyzed	References
Azole, dicarboximide	TOF-MS	C8: 150 mm × 4.6 mm × 5 μm; 0.1% HCOOH in water & ACN; gradient	0.00025–0.0008		
Ureas	TOF-MS	C18: 50 mm × 2.1 mm × 5 μm; water & MeOH; gradient			
Organophosphates	TQ-MS-MS	C18: 150 mm × 4.6 mm × 5 μm; MeOH in water; gradient	0.010–0.025		
5 multi-class	TQ-MS; QIT-MS	C18: 100 mm × 2.1 mm × 1.7 μm; 0.005 M ammonium acetate in water & MeOH; gradient			
18 multi-class	ULPC-MS-MS	C18: 100 mm × 2.1 mm × 1.7 μm; MeOH & 0.01% HCOOH in water; gradient C18: 100 mm × 2.1 mm × 1.7 μm; 0.01% HCOOH in water & MeOH; gradient C18: 100 mm × 2.1 mm × 1.7 μm; 0.01% HCOOH in MeOH & 0.01%	0.5–20	Apples: 4.6 μg/L	
34 multi-class	UPLC-MS-MS	HCOOH in water & MeOH; gradient NH <sub>3</sub> ; 250 mm × 4.6 mm × 5 μm connected to NH <sub>2</sub> guard column 20 cm × 4.6 mm × 5 μm; MeOH-water (70:30); isocratic C18:			
20 multi-class	UPLC-MS-MS	25 cm × 4.6 mm × 5 μm; ACN, water and ammonia solution: isocratic	0.0007–0.0003		[86, 87]
15 multi-class	UPLC-MS-MS; ESI	C18: 125 mm × 3 mm × 5 μm; guard column 4 mm × 4 mm; ACN:0.01% aqueous; ammonium hydroxide, pH 8.4 (35:65); isocratic	<0.01		
Tetrazines	UV	C18: 15 cm × 4 mm × 5 μm; MeOH-phosphate buffer (60:40) and MeOH-ammonium hydroxide (90:10); isocratic	0.05	Coffee bean: 0.016–1.115 (mg/kg)	
Benzimidazoles	UV	—	0.21–0.51		
3 multi-class	UV-vis	—	0.036–0.071		
3 multi-class	UV-vis	—	—		

TABLE 2: GC determination of pesticides in fruits and vegetables.

Class	Detection	Column/Chromatography	Limit of detection (mg/kg)	Specific samples analyzed	References
Strobilurines	ECD	100% PDMS 25 m × 0.32 mm × 0.25 μm	3		
Organochlorine, pyrethroid	ECD; MS; EI	5% phenyl methyl polysiloxane 30 m × 0.25 mm × 0.25 μm; 30 m × 0.25 mm × 0.25 μm; Splitlessmode	0.003–0.015		
3 multi-class	ECD; MS; EI	5% phenyl methyl polysiloxane 30 m × 0.25 mm × 0.25 μm; 30 m × 0.25 mm × 0.25 μm; Splitlessmode	0.0003–0.015	Tomatoes: 0.001–0.070 μg/L	[88, 89]
10 multi-class	ECD; MS	5% phenyl 95% dimethylpolysiloxane 30 m × 0.25 mm × 0.25 μm; 35 m × 0.25 mm × 0.25 μm; Splitlessmode	—		
Azole	ECD	30 m × 0.53 mm × 1.25 μm	0.05		
Organochlorine	ECD; MS	Methylpolysiloxane 30 m × 0.25 mm × 0.25 μm; 5% phenyl polysiloxane 30 m × 0.25 mm × 0.25 μm	0.001		
6 multi-class	ECD; MS	Methylpolysiloxane 30 m × 0.25 mm × 0.25 μm; Diphenyl dimethylpolysiloxane 30 m × 0.25 mm × 0.25 μm	0.001	Green pepper: 0.004–0.063 mg/kg	[88]
Organophosphorus, pyrethroids	ECD;MS;EI	25 m × 0.25 mm; 50 m × 0.25 mm × 0.33 μm	–0.004–0.057		
Organochlorines	ECD	30 m × 0.32 mm × 0.25 μm; 25 m × 0.22 mm × 0.25 μm	—		
Pyrethroids	ECD	—	0.1–0.2		
Organochlorines	ECD, FPD	30 m × 0.25 mm × 0.25 μm	—		
5 multi-class	ECD;MS	5% phenyl methylpolysiloxane 30 m × 0.25 mm × 0.25 μm	–0.000008		
Organophosphorus	FID	100% dimethylpolysiloxane 30 m × 0.25 mm × 0.1 μm	0.00004		
Organophosphorus	FPD	30 m × 0.32 mm × 0.25 μm	0.00021–0.00056		
Organophosphorus	FPD	30 m × 0.32 mm × 0.25 μm	0.00098–0.00220		
Organophosphates	FPD	30 m × 0.53 mm × 1 μm	0.01	Cucumbers: 0.05 mg/kg	
8 multi-class	GC-TOF-MS; GC × GC-TOF-MS	30 m × 0.25 mm × 0.25 μm; 1 m × 0.1 mm × 0.1 μm	—		
7 multi-class	MS	30 m × 0.25 mm × 0.25 μm; Split/splitlessmode	–0.00001–0.0083		
14 multi-class	MS; MS-MS; Alternatively CI/EI	30 m × 0.25 mm × 0.25 μm; Split/splitlessmode	—		
3 multi-class	MS; EI	5% phenyl 95% PDMS 30 m × 0.25 mm × 0.25 μm; Split/splitless mode	0.01–0.02		
13 multi-class	MS	30 m × 0.25 mm × 0.25 μm			
17 multi-class	MS;EI	5% phenyl polysiloxane 30 m × 0.25 mm × 0.25 μm; Split/splitlessmode	0.0001–0.0047	Onion: 0.001–0.094 μg/L	
4 multi-class	MS	5% phenyl polysiloxane 30 m × 0.25 mm × 0.25 μm	0.0001–0.0016		
Organophosphorus, organochlorines	MS; EI	30 m × 0.32 mm	—		
Pyrethroids	MS;EI	30 m × 0.25 mm × 0.25 μm	0.0009–0.0138		
18 multi-class	MS	30 m × 0.25 mm × 0.25 μm; Splitless mode	–0.003–0.025		
Pyrethroids	MS	30 m × 0.25 mm × 0.25 μm			
5 multi-class	MS	30 m × 0.25 mm × 0.25 μm			
Organophosphorus	MS	5% phenyl methylpolysiloxane 30 m × 0.25 mm × 0.25 μm	–0.0052–0.0127	Spinach: 0.005–0.01 mg/kg	[81]
Organophosphorus	MS; EI	30 m × 0.25 mm × 0.25 μm	0.001–0.024		
Chlorobenzenes, organochlorines	—	—	—		



TABLE 2: Continued.

Class	Detection	Column/Chromatography	Limit of detection (mg/kg)	Specific samples analyzed	References
Unclassified	MS	30 m × 0.25 mm × 0.25 μm	—		
8 multi-class	MS-MS	30 m × 0.25 mm × 0.25 μm			
Organophosphorus, unclassified	NPD	30 m × 0.25 mm × 0.25 μm	−0.0019–0.0073		
Organophosphorus, unclassified	NPD	30 m × 0.25 mm × 0.25 μm	0.019–0.082		
Organophosphorus	NPD	30 m × 0.32 mm × 0.25 μm	0.00007–0.006	Okra: 0.005–0.01 mg/kg	[90]
Organophosphorus	NPD; MS;EI	Dimethylpolysiloxane 30 m × 0.25 mm × 0.25 μm; 5% phenyl polysiloxane 30 m × 0.25 mm × 0.25 μm	0.0001–0.00006		
8 multi-class	MS; EI	60 m × 0.25 mm × 0.25 μm	0.001–0.003		
26 multi-class	MS; EI	5% diphenyl 95% dimethylsiloxane 15 m × 0.15 mm × 0.15 μm; PTVmode	0.0001–0.0065		
3 multi-class	MS	5% diphenyl 95% dimethylpolysiloxane 30 m × 0.25 mm; Split/splitless mode	0.005–0.025		
Organophosphorus	MS	30 m × 0.20 mm × 0.25 μm; Splitlessmode	0.002–0.090	Potatoes: 0.003–0.082 μg/g	[91]
Organophosphorus	MS; EI	30 m × 0.25 mm × 0.25 μm; Large volume injection (LVI)	—		
Organophosphorus	TSD	30 m × 0.25 mm × 0.25 μm	—		

susceptible to a variety of illnesses and insect pests, necessitating careful pest management [101]. Fruit and vegetables are frequently sprayed with pesticides during growth by most farmers and commercial producers because pesticides reduce the toxins produced by food-infecting organisms, boost productivity, and require less labor [102]. Because pesticides are known to have potentially hazardous effects on humans, the presence of pesticide residues worries customers, and when data presented for fruits, vegetables, and processed crop-based foods were evaluated independently, higher rates of pesticide residues in conventional crops were found [102]. Pesticide residues were more frequently found in conventional fruits than in vegetables and crop-based compound foods, although contamination rates among the various organic crop types were quite similar [103]. Detectable residues were found more frequently in conventional fruits (75%) than in vegetables (32%), which may indicate that crop protection inputs were used at higher levels in fruit crops [104]. However, the use of more persistent chemicals, different sprayer technologies, and/or the timing of pesticide applications closer to harvest could also explain this difference [105]. There were up to nine residues found in grapes and tea, up to five to nine residues in citrus fruits such as oranges, mandarins, lemons, peaches, and pears, and up to three residues in pomegranates, plums, cucumbers, tomatoes, and strawberries [106]. Many commodities included multiple residues per product, and imazalil, thiabendazole, chlorpyrifos, maneb group, procymidone, methidathion, lambda-cyhalothrin, carbendazim, iprodione, orthophenylphenol, vinclozolin, endosulfan, pyrimethanil, fenhexamid, prochloraz, cyprodinil, and boscalid were the pesticide residues [107]. Thiabendazole and imazalil residues are frequently found because these pesticides are frequently applied to citrus fruits and bananas after harvest to protect the crop during the transport process, which can take several weeks [108]. Apples have been rated as the most contaminated crop for five years in a row, followed by strawberries, nectarines, peaches, celery, grapes,

cherries, spinach, tomatoes, sweet bell peppers, cherry tomatoes, and cucumbers on the Environmental Working Group's (EWG) 2014 list of the 12 most pesticide-contaminated vegetables and fruits [109]. Pesticides are routinely applied indoors and outdoors in Ethiopia to boost productivity and protect various food items from pests both before and after harvest. Smallholder farmers frequently use pesticides improperly, which can result in acute poisoning and health problems such as headaches, vomiting, skin irritation, and eye irritation, as well as high residual pesticide levels in food and drinking water [110]. Additionally, the Ethiopian Federal Ministry of Health uses indoor residual pesticides such as DDT and dieldrin to shield people from diseases spread by mosquitoes [111]. These operations might possibly contaminate various food products made in Ethiopia, which could, therefore, have an impact on public health and extensive and incorrect pesticide application in the field, resulting in pesticide residues (MRLs) on commercialized maize, teff, red pepper, and coffee that are too high according to the Codex Alimentarius. The remaining one-third of the samples had residue levels over the maximum residue limits, whereas two-thirds of the samples had residue levels below the respective maximum residue limits [111]. Pesticide residues have been found in frequently consumed fruits and vegetables in Kuwait, and in 21% of the samples, pesticide residues over the maximum residue limits (MRLs) were found, while in 79% of the samples, no pesticide residues were found or the amount of residue found was below the MRL [112]. Four samples were contaminated with more than four pesticide residues, and 40% of samples containing two to four pesticides included multiple residues. Sixteen of the pesticides under investigation were found, with the MRLs being surpassed for imidacloprid, deltamethrin, cypermethrin, malathion, acetamiprid, monocrotophos, chlorpyrifos-methyl, and diazinon [113].

In Ghana, fruits and vegetables have been shown to contain pyrethroid, organochlorine, and organophosphate pesticides, and the analysis results revealed that 39.2% of the

samples of fruits and vegetables had no detectable amounts of the pesticides under observation, 51.0% had trace levels of pesticide residues below the maximum residue limit (*MRL*), and 9.8% had levels over the *MRL* [114]. A total of 317 samples of fruits and vegetables from Poland's central and eastern regions were examined in 2014 for pesticide residues, and in 89 (28.1%) of the tested samples, pesticide residues were found in 65 (38.2%) fruit samples and 24 (16.3%) vegetable samples [115]. In 2 samples (0.6%), *MRLs* were surpassed, and 100% of the gooseberry samples and 71.4% of the apple samples had pesticide residues.

In 518 samples from 20 different types of vegetables used in this investigation, a total of 32 pesticide residues were found, and the *MRLs* were exceeded by 7.7% of the observed pesticide residues [116]. For leafy, melon and fruit, and root vegetables, the percentages of residues that exceeded the *MRLs* were 11.2%, 5.1%, and 1.6%, respectively, and the percentage of samples that exceeded the *MRLs* for various vegetables did not vary by season [117]. A total of 84.3% (27/32) of pesticides were found in quantities that were higher than *MRLs*, and in addition, 11 (40.7%) of the 27 pesticides that exceeded *MRLs* were prohibited from use in agriculture [118]. The three pesticides that were most commonly found were dimethoate (8.1%), dichlorvos (8.7%), and malathion (9.4%) [119].

## 7. Management of Pesticide Residues in Fruits and Vegetables

Different pesticides are employed in many nations for a variety of crops to control pests, insects, and weeds, and foods that have been pesticide-treated are being imported into more nations because of increased global trade [120]. These international trades contribute to the spread of pesticide residues around the globe, posing a risk to public health. By taking preventive measures, such as using pesticides responsibly, washing and properly processing food products, utilizing organic farming practices, using natural pesticides and biopesticides, and strictly enforcing and amending pesticide-related laws, the impact of pesticide residues can be reduced [121]. Depending on the type of pesticide and the time of the treatment, several thermal processing techniques, such as pasteurization, blanching, boiling, heating, steaming, canning, and scrambling, have been proven to be beneficial in the degradation of various pesticides, and other studies have shown that it is crucial to wash, peel, cook or boil, fry, ferment, or grind food products to reduce pesticide residues [122].

**7.1. Organic Farming.** Eating organic foods rather than conventional foods was advised to reduce pesticide residue and is excellent for human health as one of the strategies used to reduce the influence of pesticide residue in food [123]. In conventional meta-analyses, nonorganic crops were four times more likely than organic crops to contain detectable pesticide residues [124]. There is evidence to suggest that eating organic food may lessen exposure to pesticide residues in food, and in general, across areas and

production seasons, organic crops have fewer pesticide residues than their nonorganic counterparts [22]. Pesticide residues were significantly more common in conventionally cultivated fruit ( $75 \pm 5\%$ ), or roughly seven times more frequently than in organic fruit [125]. In conventional vegetables and crop-based processed foods, the frequency of pesticide residues was three to four times higher than that in organic foods [126].

**7.2. Washing Food Products.** Removing pesticide residues from fruits and vegetables requires washing with water or detergent, and the washing solution, the pesticide's chemical characteristics, the surface area, the type of food, the amount of time the pesticide is in contact with the food, and the pesticide's formulation and application method all affect how effective washing treatments are at removing pesticides [127]. The pesticide typically becomes embedded in wax-like exterior layers before moving inside, making washing and removing the pesticides less effective, and the reduction in pesticide residues seen in the literature review ranged from 0 to 90% [128]. The effectiveness is influenced by the residue's location, age, water solubility, temperature, and washing method.

**7.3. Processing Food Products.** The bulk of foods go through processing procedures including washing, peeling, canning, or cooking before consumption, all of which contribute to a reduction in residues left on crops upon harvest [129]. Boiling may eliminate 35–60% of organophosphate residues and 20–25% of organochlorine residues, reducing the amount of pesticide residues in food [130]. With the exception of systemic pesticides, it has been demonstrated that peeling and trimming fruits and vegetables considerably reduces or eliminates pesticide residues, and it has been shown that after peeling, nonsystemic chlorpyrifos was eliminated while systemic disyston in potatoes was reduced by 35% [131]. According to a different study, peeling mandarins that contained the pesticides fenoxycarb, flufenoxuron, lufenuron, and pyriproxyfen eliminated any remaining residue, and the reduction after peeling potatoes treated with the systemic fungicide metalaxyl was just 11% [132]. The deposited profenofos was virtually completely removed (100%) when pepper and eggplant fruits were blanched and fried, and additionally, after one week and two weeks, the pickling process eliminated 92.58 and 95.61%, respectively, from the hot pepper fruit [133]. Studies on how pesticide residues in peaches used in infant food are affected by canning have shown that vinclozolin (14%) increased, whereas the levels of procymidone (65%), fenitrothion (63%), and chlorpyrifos-methyl (65%) decreased [134].

**7.4. Rational Use of Pesticides.** The proper choice of pesticides, dosage rates, dilutions, timing, frequency of application, treatment intervals, mode of application, precautions, and limitations are all part of the rational use of pesticides [135]. Pesticide residues in food products can be decreased through the prudent use of pesticides, and

a pesticide may not always be necessary, especially when cultural or biological techniques work well [136].

**7.5. Use of Nonsynthetic Chemicals.** Biopesticides are environmentally safe and biodegradable, leaving behind no toxic residues, and biochemical pesticides that are derived from microorganisms and other natural sources that offer protection against insect damage are referred to as biopesticides and include a wide variety of microbial pesticides [136]. Some repellents for insects can also be used to avoid the buildup of pesticide residues in cereals, vegetables, and fruits [137]. Natural insecticides, such as those derived from neem tree extracts and chemicals, are also particularly effective at preventing the buildup of pesticide residues in food products [138].

## 8. Review Gaps

Research on the short- and long-term consequences of pesticide residues sprayed on fruits and vegetables is currently lacking. The hazards associated with pesticide pollution, health impacts, and social and political ramifications have not been investigated due to the complexity of pesticide compounds. The degree of risk in fruit and vegetable residue problems has not yet been investigated. Additionally, the impact of pesticide residues in low- and middle-income nations has not been carefully examined.

## 9. Summary and Conclusion

Since they are abundant in vitamins, carbs, antioxidants, and other nutrients, fruits and vegetables are widely grown in Ethiopia and are an important source of revenue and nourishment. Due to its excellent climate and inexpensive labor for both domestic use and export, Ethiopia has a tremendous opportunity for the production of fruits and vegetables. Due to increased agricultural practices, including the use of pesticides, fruit and vegetable production has increased. In Ethiopia, pesticides have been used in agriculture to manage crop pests and reduce production loss without taking public health into account. Pesticide use among farmers has rapidly increased in both quantity and frequency every year. Additionally, this growing pattern is anticipated to intensify over the coming decades. The majority of the pesticides that are now registered and used to control fruits and vegetables are nonspecific and non-biodegradable. However, fruit and vegetables frequently have pesticide residues after harvest since persistent and nonspecific insecticides are frequently used throughout manufacturing.

It is challenging to increase output without the use of pesticides while simultaneously reducing the impact of pesticide residues in fruits and vegetables. Because most fruits and vegetables are consumed raw and greater pesticide residue levels are anticipated compared to other food groups of plant origin, it is necessary to minimize postharvest treatment of fruits and vegetables to limit the greatest pesticide residual effect on the crop. Additionally, producers and researchers should focus on creating new pesticide formulations that are

biodegradable and nonpermanent. Ethiopia has not yet made a thorough assessment of the pesticide residue in fruits and vegetables; as a result, monitoring of the pesticide residue in high pesticide-consumed fruits and vegetables is necessary in Ethiopia. In addition, fruit and vegetable pest management requires integrated pest management (IPM) combining low-toxic pesticides with integrated nonchemical control practices. To increase international trade and guarantee clean local food consumption, organic farming practices must be improved.

## Data Availability

The dataset that supports the findings of this review is included in the article.

## Conflicts of Interest

The authors declare that they have no conflicts of interest.

## Authors' Contributions

The concept of the review was developed by Yohannes Gelaye while the design, data analysis and synthesis, interpretation and drafting, and final write-up of the paper were performed by both of the authors.

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