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ASSESSMENT OF PESTICIDE RESIDUES IN CUCUMBER (*Cucumis sativa*) FRUITS FROM THREE MAJOR MARKETS IN THE AMANSIE WEST DISTRICT, GHANA

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Abstract: *Cucumber (Cucumis sativa), a widely consumed vegetable, often faces issues with pests and diseases, leading to the excessive use of pesticides during its cultivation. This study aimed to assess the presence of widely used chemicals in cucumbers sold in the major markets in the Amansie West District of Ghana and to compare these levels with the international maximum residue limits (EU MRLs). A total of 81 mature cucumber fruits were collected from three (3) local markets namely Bekwai, Dominase, and Kokofu, and subjected to pesticide residue analysis using gas chromatography-mass spectrometry (GC-MS). Results revealed that cucumbers contained traces of 13 different types of pesticides, including organochlorines, carbamates, organophosphates, and pyrethroids. In at least one market, 7 out of the 13 identified pesticides exceeded the EU MRLs, accounting for 53.8%, while the remaining 6 (46.2%) were below the limits. The presence of significant levels of pesticide residues in the cucumbers, such as chlorothalonil, aldrin, carbaryl, aldicarb, chlorpyrifos, dichlorvos, and ethion, exceeding the MRLs, raises concerns about pesticide usage, compliance with regulations, and potential health risks for consumers in the area.*
Keywords*: carbamates, health risks, organochlorines, organophosphates, pyrethriods*

1. Introduction

Cucumber, scientifically known as *Cucumis sativus*, is a popular vegetable valued for its crisp texture and health benefits [1]. In Ghana, cucumber cultivation has gained significant importance in recent years, both as a cash crop for local markets and as a potential export commodity [2]. Smallholder farmers, especially those in the southern and middle belts of the country, are the primary growers of this crop. However, like many other crops, cucumber farming faces challenges, including the presence of pests and diseases. To address these issues and ensure marketable yields, farmers often rely heavily on the use of pesticides. Pesticides play a vital role in safeguarding crops from pests, diseases, and weeds, thus preserving crop quality and enhancing productivity [3, 4]. Nevertheless, excessive and uncontrolled pesticide application can have adverse effects on human health and the environment [5]. Pesticide residues, which refer to the trace amounts of pesticides that remain on or in agricultural products, are significant sources of concern due to their potential toxicity. Inappropriate pesticide usage in farming can lead to elevated levels of residues in harvested crops such as vegetables and fruits [6]. Pesticides are categorized into several classes, including pyrethroids, carbamates, organochlorines, and organophosphates based on their chemical compositions [7]. Studies have indicated that pesticide exposure can raise the risk of cancer development, endocrine system disorders, reproductive issues, and even Parkinson's disease [8, 9]. Consumers may face potential long-term health risks from consuming foods contaminated with pesticide residues [10]. Pesticides not only pose risks to human health but also have detrimental effects on the environment by contaminating groundwater, surface water, food, air, and soil [11]. It is widely recognized that careful monitoring of pesticide use is essential to prevent harm to

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human health, groundwater sources, and the environment. The term "maximum residue limits" (MRLs) refers to the highest allowable concentrations of pesticide residues in or on food products after pesticide application. These limits are established based on scientific assessments of health risks and are specified on product labels. MRLs are set well below levels considered unsafe for humans, indicating that food with residues exceeding the MRL may not be safe to consume [12]. Currently, there is limited information available on pesticide residues in cucumbers cultivated within the Amansie West District, hindering efforts to raise awareness about potential impacts on food safety and public health. The knowledge gap is particularly concerning given the increasing consumption of cucumbers in the district and the potential for accumulation of pesticide residues in the food chain. This study hypothesizes that the levels of pesticide residues found in cucumbers cultivated in the Amansie West District exceed international maximum residue limits (MRLs), posing potential health risks to consumers and highlighting the need for improved monitoring and management of pesticide usage in the district. As a result, the study aimed to determine the levels of specific widely used chemicals in cucumber cultivation in markets within the district and assess how these levels compare to international maximum residue level (EU MRL) standards.

2. Materials and Methods

2.1 Study area

Geographically, the district is situated between longitudes 6.05 °W and 6.35 °W, and latitudes 1.40 °N and 2.05 °N. The topography is predominantly undulating, with an elevation of approximately 210 meters above sea level. The area experiences a wet semi-equatorial climate characterized by a double maxima rainfall pattern. The major rainy season spans from March to July, while a minor rainfall season occurs from September to November. The mean annual rainfall in the district varies between 855 mm and 1,500 mm, indicating significant variability in precipitation levels throughout the year.

2.2 Cucumber sampling

Fresh and mature cucumber fruits were sourced from three markets in the Amansie West District mainly: Bekwai, Domenase, and Kokofu local markets (Figure 1). In each of the markets, 27 cucumber fruits were purchased from 3 different locations. A total of 81 fruits were collected and screened for pesticides from the three markets. A simple random sampling technique was employed in selecting the 3 different locations in each of the markets. Collected samples were immediately placed on ice and kept cool during transportation to the Crop Science Laboratory at KNUST for analysis.

Data collection was carried out from May to August 2024.

2.3 Sample Preparation

The cucumber fruits were cut into thin slices using a sanitized knife to enhance the drying process. These sliced samples were then placed in a Gallenkamp oven (SLN 75 POL-EKO-APPARATURA, Slaski, Poland) for thorough dehydration at 50 °C for 72 hours. Once the samples reached a stable weight, they were removed from the oven. Finally, in the laboratory, the dried cucumber slices were crushed into a fine powder with a porcelain mortar and pestle.

2.4 Extraction of Pesticides in Cucumber

The extraction was carried out using a minor modification of the procedure outlined by [13]. was applied to the extraction process. 10 g of sodium sulfate were combined with each sample, weighing 3 g, and the mixture was then put into a 250 mL separating funnel. Hexane in the volume of 20 mL was added, and then acetonitrile saturated with hexane in the

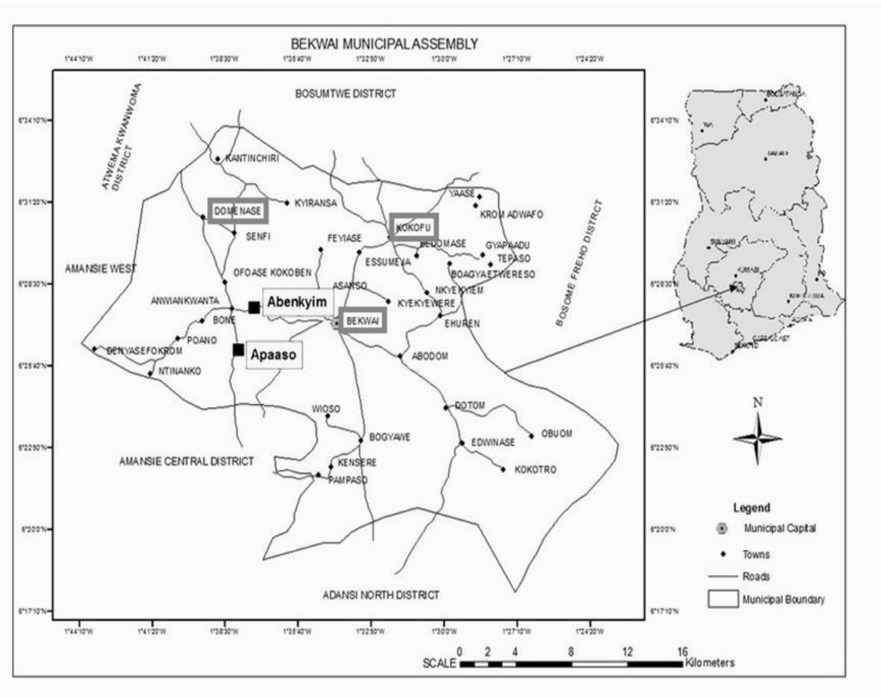

Fig. 1. Map of Amansie West District showing the 3 local markets where samples were collected

volume of 100 mL. After that, the mixture was shaken for roughly a minute. Three additional extractions of the combination were conducted using 50 mL of acetonitrile each, after the draining of the acetonitrile into a 1L separating funnel. The mixed extracts were then washed using 500 mL of distilled water, 40 mL of saturated NaCl, and 50 mL of hexane. After allowing the mixture to settle for thirty minutes, the aqueous layer was drained into a second 1L separating funnel, and 50 mL of hexane was used for extraction. The hexane extracts were combined, passed through a 10 g sodium sulfate plug, and transferred to a flask. A rotary evaporator was employed to remove the solvent. The residue was then dissolved in a solution containing 10 mL of methanol and 25 mL of distilled water. Following cleanup, a sample of 1 g of cucumber material was collected for pesticide residue analysis from a part of this solution.

2.5 Gas chromatographic Analysis

The pesticide residue analysis was carried out using a Shimadzu Model Q 2010 gas chromatograph coupled with a mass spectrometer (GC-MS) system from Shimadzu Corporation in Kyoto, Japan. A 30 m × 0.25 mm i.d., 0.25 μm film thickness HP-5MS capillary column, and helium as the carrier gas at a constant flow rate of 1.0 mL/min were used for chromatographic separation. Samples were introduced via splitless injection, with 1 μL injected per analysis. The injector temperature was maintained at 250 °C. The temperature program for the GC oven was as follows: initial temperature of 100 °C held for 2 min, ramped to 180 °C at 25 °C/min, then to 230 °C at 5 °C/min, and finally to 280 °C at 20 °C/min, with a final hold time of 10 min. The total run time was 30 minutes. The mass spectrometer operated in electron impact ionization mode at 70 eV, with the ion source temperature set at 230 °C and the interface temperature at 280 °C. Selected ion monitoring (SIM) mode was used for enhanced sensitivity, with two to three characteristic ions monitored for each pesticide. The scan range was set from m/z 50 to 550. The process of identifying pesticide residues involved comparing sample peak retention times to reference standards, as described by [14]. A total of 13 pesticides (6 organochlorines, 3 carbamates, 3 organophosphates, and 1 pyrethroid) were detected and screened using GC–MS analysis. Quantification of detected pesticides was performed using external calibration curves with matrix-matched standards. The concentrations were then evaluated against the European Union Maximum Residue Limits (EU MRLs).

2.6 Quality control measures

Quality control measures were implemented throughout the analysis process to ensure the reliability of the results. Method blanks were run with each batch of samples to check for any contamination. Matrix-matched calibration standards were prepared and analyzed alongside the samples to account for potential matrix effects. Recovery studies were conducted by spiking blank cucumber samples with known concentrations of pesticide standards, with recoveries ranging from 85% to 110% for all analytes. All analyses were performed in triplicate, and the results are reported as the mean values. The uncertainty of measurement was estimated to be ±20% for all pesticide residues, based on method validation data.

2.7 Data analysis

Pesticide residue concentrations (mg/kg) in the samples were evaluated against Maximum Residue Limits (MRLs) set by the European Commission legislation and standards [15]. The results reported are the averages of three measurements.

3. Results and discussion

The mean concentrations of pesticide residues detected in cucumber fruits sourced from 3 locations within each market were compared with the standard values of European Union Maximum Residue Limits (EU MRLs) (Table 1- 4).

Table 1.

Organochlorine's pesticide residue concentrations (mg/kg) in cucumber samples from markets in the Amansie West District, Ghana, compared to EU MRLs

Pesticide Residue	Concentration (mg/kg)			EU MRL (mg/kg)
	Bekwai market	Dominase market	Kokofu market	
Chlorothalonil	Nd	0.0367	0.0123	0.01
Imidacloprid	0.0467	0.045	Nd	0.5
Endosulfan	Nd	0.0347	0.0367	0.05
Dieldrin	Nd	Nd	0.0074	0.02
Aldrin	0.0422	Nd	0.05	0.02
DDT	0.0442	Nd	Nd	0.05

Where Nd = not detected, mean concentration=3, EU MRL= European Union Maximum Residue Limits (mg/kg).

Table 2.

Carbamate's pesticide residue concentrations (mg/kg) in cucumber samples from markets in the Amansie West District, Ghana, compared to EU MRLs

Pesticide Residue	Concentration (mg/kg)			EU MRL (mg/kg)
	Bekwai market	Dominase market	Kokofu market	
Carbaryl (mg/kg)	0.034	0.023	Nd	0.01
Aldicarb	Nd	0.05	Nd	0.02
Carbofuran	Nd	Nd	0.0018	0.002

Where nd = not detected, mean concentration =3, EU MRL= European Union Maximum Residue Limits (mg/kg).

Table 3.
Organophosphate's pesticide residue concentrations (mg/kg) in cucumber samples from markets in the Amansie West District, Ghana, compared to EU MRLs

Pesticide Residue	Concentration (mg/kg)			EU MRL (mg/kg)
	Bekwai market	Dominase market	Kokofu market	
Chlorpyrifos	Nd	0.0467	0.0126	0.01
Dichlorvos	Nd	0.0234	0.0054	0.01
Ethion	0.0122	Nd	0.0345	0.01

Where nd=not detected, mean concentration= 3, EU MRL= European Union Maximum Residue Limits (mg/kg).

Table 4.
Pyrethroid pesticide residue concentration (mg/kg) in cucumber samples from markets in the Amansie West District, Ghana, compared to EU MRLs

Pesticide Residue	Concentration (mg/kg)			EU MRL (mg/kg)
	Bekwai market	Dominase market	Kokofu market	
Permethrin	Nd	0.0467	0.0345	0.05

Where Nd= not detected, mean concentration=3, EU MRL= European Union Maximum Residue Limits (mg/kg).

3.1 Organochlorine residues

Cucumber samples from two of the three markets tested positive for chlorothalonil. The Dominase market had the highest concentration (0.0367 mg/kg), followed by the Kokofu market (0.0123 mg/kg), and no detectable levels were found in the Bekwai market (Table 1). Both measured amounts greatly exceeded the EU MRL of 0.01 mg/kg for chlorothalonil. The pesticide could be seen to be heavily used in the area as per the results from the two markets. Chlorothalonil is a broad-spectrum organochlorine fungicide known for effectively combating various fungal infections that affect vegetables [16]. Due to concerns about its potential to cause cancer, persist in the environment, and impact ecosystems, many countries have restricted the use of chlorothalonil [17]. According to certain reports [18, 19], it has been proven to be toxic to various aquatic organisms, such as fish, amphibians, and invertebrates. In terrestrial ecosystems, it has negative effects on soil microbial communities and earthworms, potentially disrupting soil health and nutrient cycling [20]. The contamination levels found in the study exceed the EU MRL by 1.23 to 3.67 times, posing risks to human health and increasing the potential for environmental contamination. According to reports by [21], the potential of chlorothalonil to accumulate in food chain may affect higher trophic levels, including birds and mammals that feed on contaminated insects or plants. In addition to these concerns, the ecological impact of chlorothalonil highlights the need for sustainable pest management practices that minimize environmental risks while maintaining crop productivity. Imidacloprid was found in samples from the Bekwai (0.0467 mg/kg) and Dominase (0.045 mg/kg) markets (Table 1). These levels are below the EU MRL of 0.5 mg/kg, indicating compliance with this standard. The absence of imidacloprid in samples from the Kokofu market suggests variability in pesticide use practices across the farming communities. While the detected levels are within acceptable limits, it is worth noting that imidacloprid, has faced restrictions in some countries due to its potential impact on pollinators [22, 23]. Continued monitoring of its use and residue levels is advisable.

Endosulfan residues were found in samples from Kokofu (0.0367 mg/kg) and

Dominase (0.0347 mg/kg) markets (Table 1). Both levels were below the EU MRL of 0.05 mg/kg, indicating compliance with this standard. However, the presence of endosulfan is worrisome due to its classification as a persistent organic pollutant (POP) [24]. A study by [25] revealed the detection of endosulfan residue in 108 fresh and dried kola nuts at concentrations ranging from 2.0 to 99.00 mg/kg, posing potential health risks to cucumber consumers. In a related study by [26], 4% of tea samples were found to exceed the EU MRL of 0.05 mg/kg for endosulfan, with the highest value being 0.34 mg/kg, potentially impacting tea exports to countries with strict MRL enforcement. Endosulfan has been shown to have significant negative impacts on aquatic ecosystems, with studies demonstrating its toxicity to fish and other marine organisms [27].

Dieldrin was found at levels lower than the EU MRL of 0.02 mg/kg, particularly in the Kokofu market sample (0.0074 mg/kg) (Table 1). Many countries have prohibited the use of this persistent organic pollutant in agriculture due to its potential for bioaccumulation and environmental persistence [28]. Its detection, even at low levels, is concerning and may indicate historical contamination or illegal use. Furthermore, research has shown that dieldrin can build up in the food chain, posing a threat to top predators like birds of prey [29, 30].

Aldrin was detected in the Bekwai market sample (0.0422 mg/kg) and the Kokofu market sample (0.05 mg/kg), both exceeding the EU MRL of 0.02 mg/kg (Table 1). Like dieldrin, aldrin is a banned persistent organic pollutant. Its presence above MRLs is alarming and suggests an urgent need for investigation into potential sources and enforcement of regulations, as cucumber consumers in the area could face health problems such as nervous system damage and cancer. As per [31], the harmful level of aldrin might stem from its direct use in controlling pests that affect fruits and vegetables. Aldrin has been linked to significant ecological impacts, such as reduced biodiversity in soil ecosystems [32] and potential endocrine disruption in wildlife [33]. Its persistence in the environment can result in long-term contamination of water bodies and sediments, affecting aquatic organisms for decades after its use has stopped [34].

DDT was found in samples from the Bekwai market at a concentration of 0.0442 mg/kg, which is below the EU MRL of 0.05 mg/kg (Table 1). Although below the MRL, the presence of DDT is concerning due to its global ban in agriculture, attributed to its persistent environmental effects and health implications [35, 36]. This persistence is further supported by [37], who discovered DDT residues in cucumber fruits below the MRL, indicating the chemical's accumulation in air, soil, and water [38]. According to reports by [39], higher DDT concentrations negatively affected seed germination rates and seedling vigor in crops such as pepper, garden egg, and okra. Exposure to the chemical can have a detrimental impact on bee populations, potentially disrupting pollination activities crucial for both wild plants and crops [40].

3.2 Carbamate residues

Levels of carbaryl exceeding the EU MRL of 0.01 mg/kg were detected in samples from the Bekwai (0.034 mg/kg) and Dominase (0.023 mg/kg) markets (Table 2). This suggests widespread use of this pesticide in cucumber cultivation across the surveyed areas. Carbaryl, a broad-spectrum carbamate pesticide, is known for its effectiveness against various pests [41, 42]. However, its extensive use raises concerns about potential health risks for consumers due to its association with neurological effects and possible carcinogenicity from chronic exposure [43]. Additionally, carbaryl has been shown to have negative impacts on non-target organisms, particularly beneficial insects such as honeybees [44]. A study by [45] found that organic produce contained significantly lower carbaryl levels compared to conventionally grown fruits and vegetables. This suggests that adopting organic farming practices could reduce carbaryl's presence in vegetables, potentially offering a safer option for consumers concerned about pesticide exposure and mitigating ecological impacts.

Aldicarb was exclusively found in the Dominase market samples, with a level of 0.05 mg/kg, exceeding the EU MRL of 0.02 mg/kg by 2.5 times (Table 2). The presence of Aldicarb in one market suggests that this pesticide may be used in a specific location due to particular pest challenges or different farming methods in that market area. The detection of aldicarb above the MRL is especially concerning due to its high toxicity as a systemic insecticide. According to reports by [46], aldicarb has the potential to induce immediate cholinergic symptoms even with small amounts and has been linked to groundwater pollution in farming areas where it is applied. A comprehensive investigation on pesticide residues in fruits and vegetables as carried out by [47], revealed the maximum residue limit of aldicarb for cucumbers exceeded the 0.02 mg/kg MRL set by the EU. They advised customers not to disregard MRLs since this can shield them from potential health concerns.

The level of carbofuran detected in the Kokofu market sample was 0.0018 mg/kg, slightly below the EU MRL of 0.002 mg/kg (Table 2). Carbofuran functions as a broad-spectrum pesticide and nematicide. Since 2007, the EU has banned it due to its high acute toxicity to humans and its impact on environmental safety [48]. The presence of the pesticide in the Kokofu area might indicate a particular pest problem in the area whereas absence from other markets may suggest differences in pest control methods. Carbofuran can persist in the environment for an extended period and could potentially contaminate groundwater, posing a threat to aquatic ecosystems [49].

3.3 Organophosphate residues

Cucumber samples from two out of the three markets were found to contain chlorpyrifos (Table 3). The highest concentration of chlorpyrifos (0.0467 mg/kg) was detected in samples from the Dominase market, followed by samples from the Kokofu market (0.0126 mg/kg). No chlorpyrifos concentration was found in samples from the Bekwai market. Both detected concentrations exceeded the EU MRL of 0.01 mg/kg for chlorpyrifos in cucumbers, suggesting widespread use in local cucumber cultivation. Chlorpyrifos, a versatile organophosphate pesticide, effectively combats various pests [50]. However, its use has been restricted in several countries due to neurotoxicity concerns, especially in young children [51]. High-level exposure to chlorpyrifos can lead to abdominal cramps, diarrhea, vomiting, and delayed neurological symptoms [52]. The levels found in this study, 1.26 to 4.67 times higher than the EU MRL, are alarming. Additionally, chlorpyrifos poses significant risks to aquatic ecosystems, potentially harming fish populations and other non-target organisms [53].

Dichlorvos was found in samples from the Dominase (0.0234 mg/kg) and Kokofu (0.0054 mg/kg) markets (Table 3). The concentration in the Dominase market sample exceeded the EU MRL of 0.01 mg/kg, while the Kokofu market sample was just below but close to the limit. According to [54], dichlorvos, a highly volatile organophosphate insecticide, may have carcinogenic effects on humans. Its detection, particularly above the MRL, is alarming and suggests a need for stricter control measures. Reports by [55], revealed that, at high concentrations or improper application, dichlorvos may cause phytotoxic effects on some vegetables and fruits, including leaf burn, leaf chlorosis, and fruit distortion or growth inhibition. Furthermore, a study by [56], showed dichlorvos can have harmful effects on aquatic ecosystems, potentially leading to a reduction in the diversity and abundance of zooplankton communities in freshwater bodies. Ethion was detected in samples from two markets; Kokofu (0.0345 mg/kg) and Bekwai (0.0122 mg/kg) (Table 3). The level in Kokofu market samples exceeded the EU MRL of 0.01 mg/kg by more than three times, while the level in Bekwai market samples was just above the MRL. Ethion was not detected in samples from the Dominase market. Ethion, an organophosphate insecticide, and acaricide, is used to control varied pest populations various pests [57]. Its presence above MRLs raises concerns, despite being less acutely hazardous than some other organophosphates, especially considering the potential effects of chronic exposure. In a study by [58], it was revealed, ethion can persist in soil for several weeks, potentially affecting soil microorganisms and non-target organisms.

3.4 Pyrethroid residue

In Table 4, it is evident that the highest concentration of permethrin was found in the Dominase market at 0.0467 mg/kg, followed by samples from the Kokofu market at 0.0345 mg/kg. Samples from the Bekwai market did not have any detectable levels of the pesticide. The EU MRL for permethrin in cucumbers stands at 0.05 mg/kg, and both measured amounts fell below this threshold. The presence of permethrin residues in two markets, although below the EU MRL, suggests extensive use of this pesticide by nearby farming communities for cucumber cultivation. Unlike organophosphate and carbamate insecticides, permethrin is a broad-spectrum pyrethroid insecticide known for its low toxicity to mammals and effectiveness against various pests [59, 60]. However, it is crucial to understand that permethrin can have substantial effects on the environment, particularly on aquatic ecosystems. Research indicates that even at low concentrations, permethrin is highly toxic to numerous aquatic species, including fish and invertebrates [61, 62]. While the measured values are within the EU MRL, it is worth noting that the concentration of samples from the Dominase market is 0.0467 mg/kg, which is very close to the limit. It is advisable to exercise caution and maintain ongoing monitoring to ensure compliance, especially given the proximity to the MRL and potential environmental concerns.

4. Conclusion

The analysis of cucumber samples from markets in Bekwai, Dominase, and Kokofu revealed the presence of various pesticides, including pyrethroids, carbamates, organophosphates, and organochlorines. Several pesticides, notably chlorothalonil, aldrin, carbaryl, aldicarb, chlorpyrifos, dichlorvos, and ethion, were found to exceed the EU MRLs. The findings highlight serious concerns regarding potential health risks for consumers and environmental impacts, especially on aquatic ecosystems and beneficial insects. The differences in pesticide residues across various markets indicate varied pest management practices within the Amansie West District. This emphasizes the crucial need for comprehensive district-wide initiatives to tackle pesticide usage. These initiatives should prioritize educating farmers on proper application of pesticides, promoting integrated pest management strategies, and encouraging the adoption of sustainable agricultural practices.

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Competing Interest
The authors have declared no conflicts of interest.
Data Availability
All generated and analyzed data is included in the research article.
Conflicts of Interest
The authors declare that they have no conflicts of interest.

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