

Determination of organophosphorus and synthetic pyrethroid pesticide residues and their variability in large size fruit crops

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Abstract

BACKGROUND: Variability of pesticide residues in food item plays a key role for the evaluation of consumer food safety. However, variability factors (VFs) derived from the large size fruit crops are still scarce. Therefore, the present work was aimed to quantify pesticide residues and to estimate VFs in large size fruit crops of mango and guava.

RESULTS: A total of 140 mango and 130 guava samples from different marketplaces in Bangladesh were collected to estimate the variability of pesticide residues (acephate, diazinon, malathion, fenitrothion, chlorpyrifos, quinalphos, dimethoate and cypermethrin) by in-house validated methods based on modified QuEChERS extraction and gas chromatography coupled with electron capture detector (ECD) and flame thermionic detector (FTD). The method was validated at three fortification levels (0.01, 0.10 and 0.30 mg kg⁻¹) and satisfactory recoveries (80–111%) with relative standard deviation (RSD_r) ≤ 13% were achieved. A wide variation of residues was found in the analyzed samples. In the case of mango, the ranges of residues were 0.011–0.314, 0.015–0.04, and 0.05–0.291 mg kg⁻¹, respectively, for cypermethrin, chlorpyrifos, and dimethoate, while in the case of guava, the ranges were 0.04–0.113, and 0.03–0.290 mg kg⁻¹, respectively, for cypermethrin and acephate. The average VF for mango was 4.06 and it was 5.70 for guava.

CONCLUSION: VFs originating from the marketed samples of mango and guava are reported in this study for the first time. The estimated VFs were higher than the default value of 3, therefore, the default VFs should be reconsidered when more data are obtained regarding large size crops.

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Keywords: variability factors; pesticide residues in fruits; QuEChERS extraction; method validation; gas chromatography

INTRODUCTION

Fruits are a good source of fiber, potassium, vitamins and minerals, and also play a vital role in preventing vitamin C and vitamin A deficiency.¹ Mango is one of the principal tropical fruits and is widely acceptable in Bangladesh and other parts of the world as it has excellent flavor, delicious taste, and color. In Bangladesh, mango is called the king of fruit. Guava is a delicious source of vitamin C and it contains four times more vitamin C than oranges. This vitamin helps to improve immunity and to protect common infections and pathogens.² However, due to high temperature and high humidity in the tropical region mango is infested by more than 492 species of insects, 17 species of mites and 26 species of nematodes.³

The farmers of Bangladesh are using different types of organophosphorus and synthetic pyrethroid pesticides for the control of insect pests of fruits in order to increase the production and to reduce the economic loss. But, it is well known that the application of pesticides at the time of fruit cultivation may leave residues, which is a global concern for the consumers due to their detrimental effects on consumer's health and the environment. Therefore, it is necessary to use pesticides following Good Agricultural Practice (GAP) and it is also important to fulfill the consumer

demand of safe food by considering the issues of variation in concentration of pesticide residues remaining in the treated agricultural products as it is not possible to apply pesticides uniformly in the field even though pesticides are applied following GAP. The reason for this situation maybe because during pesticide application in the field, all areas are not receiving the same amounts of pesticides. Therefore, variations in concentrations of pesticide residues remaining in the treated crops are inevitable.

Hence, it is important to account for this variation in concentrations of residues in the agricultural products as the variability factors (VFs) are influenced by the variation of residues. There are a great variety of factors that are responsible for this variation of residues such as type of pesticide formulation, method of pesticides

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application, type of sprayers used, mode of cultivation, height and shape of plants, soil characteristics and soil dissipation factors, weather conditions, etc. Up until now, a number of field experiments have been conducted to estimate the residue variability in/on small (the individual unit weight < 25 g) and medium size (individual unit weight > 25–250 g) fruit crops,^{4–15} while only a few field experiments have been conducted so far on large size (individual unit weight > 250 g) fruit crops.^{6,12} Therefore, the estimation of VFs with the marketed samples of large, medium and small size fruit crops are very limited.^{9,16–20}

From the literature presented earlier, it appears that VFs for large size fruit crops are still scarce, and hence it was aimed to estimate VFs for two popular large size fruit crops (mango and guava). To the best of our knowledge, this is the first study to estimate VFs originating from the residue data derived from the marketed samples of mango and guava. In this study, seven organophosphorus pesticides (acephate, diazinon, malathion, fenitrothion, chlorpyrifos, quinalphos, dimethoate) and one synthetic pyrethroid pesticide (cypermethrin) were selected as pollutants caused by food, organophosphorus pesticides have become critical due to the extensive use of organic phosphorus.²¹ Gas chromatography (GC) coupled with an electron capture detector (ECD) and a flame thermionic detector (FTD) is widely used especially for the quantification of organophosphorus and synthetic pyrethroid pesticides, respectively, as the technique is very sensitive to the earlier mentioned groups of pesticides.^{22–26} Furthermore, GC-FTD and GC-ECD are cheaper and have lower maintenance costs, hence are more readily available in some countries than mass spectrometers.

Therefore, the present study was initiated to develop and validate a multi-residue analytical method using GC coupled with FTD and ECD to monitor pesticide residues and to estimate VFs originating from the residue data derived from the marketed samples of mango and guava. The outcome of the study will help the relevant stakeholders to take necessary action by employing the VFs for mango and guava estimated from this study.

MATERIALS AND METHODS

Chemicals and reagents

Eight pesticides used in this study, including acephate, diazinon, malathion, fenitrothion, chlorpyrifos, quinalphos, dimethoate and cypermethrin with purity higher than 98% were purchased from Sigma-Aldrich (St Louis, MO, USA) via SAF Scientific, Bangladesh Limited. The analytical reagents including sodium chloride (NaCl, analytical grade), anhydrous magnesium sulfate (MgSO₄, analytical grade) were purchased from Scharlau, Spain, and primary secondary amine (PSA) was obtained from Agilent (Santa Clara, CA, USA) via SAF Scientific, Bangladesh Limited.

Preparation of pesticide standard solution

An accurately weighed 10 mg individual analytical standard of acephate, dimethoate, malathion, diazinon, fenitrothion, quinalphos, chlorpyrifos and cypermethrin was dissolved in a 10 mL volumetric flask using acetonitrile (MeCN) to prepare a standard stock solution of 1000 mg L⁻¹ and stored at -20 °C until use. Then, a multiple standard solution of 50 mg L⁻¹ in MeCN containing all the selected pesticides was prepared by adding the appropriate volume of each individual stock solution in a 50 mL volumetric flask and made to volume by addition of MeCN. An intermediate multiple standard solution of 10 mg L⁻¹ in MeCN was prepared from the multiple standard solution of

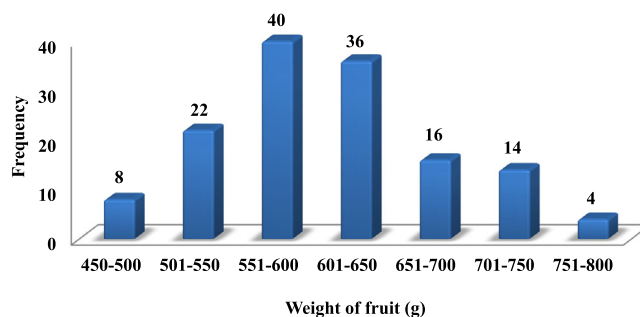


Figure 1. Frequency distribution of the weight of individual mango sample.

50 mg L⁻¹. Afterwards, working standard solutions of 0.1, 0.2, 0.5, 1.0, 2.0, 3.0, and 5.0 mg L⁻¹ in MeCN were prepared by transferring the appropriate amount from 10 mg L⁻¹ intermediate multiple standard solution into eight separate 10-mL volumetric flasks. Matrix-matched standard for preparing the calibration curve were made by adding multiple standard working solution in the blank extracts of both matrices separately to reach the desired concentrations (0.01, 0.05, 0.1, 0.2 and 0.3 mg kg⁻¹) and stored at -20°C.

Sampling and sample preparation

A total of 270 samples (140 mangos and 130 guavas) were purchased from 10 different locations (Bogura, Barishal, Cumilla, Dhaka, Gazipur, Dinajpur, Jamalpur, Jashore, Narsingdi and Rajshahi) in Bangladesh. For both of the fruit, the individual unit was considered as one sample. The frequency distribution of the weight of individual mango samples is presented in Fig. 1. Among 140 samples of mango, 76 were in the range of 551 g to 650 g. The mean weight of the collected samples of mango was 611 g [relative standard deviation (RSD) was 11%] and the median was 600 g. The frequency distribution of the weight of individual guava samples is presented in Fig. 2. Among 130 samples of guava, 80 were in the range of 351 g to 450 g. The mean weight of the collected samples of guava was 398 g (RSD was 16%) and the median was 400 g. In the case of guava, the whole unit was chopped while for mango, the peel and the seed were discarded and the pulp was taken for chopping. After chopping, the samples were stored at -20°C until homogenization.

Extraction and cleanup of the desired pesticides from the selected fruit matrices were carried out using the modified QuE-ChERS extraction technique.²⁷ At first, the chopped samples were homogenized thoroughly with a fruit blender. Representative thoroughly homogenized fruit samples (10-g) were weighed in a 50 mL polypropylene centrifuge tube and 10 mL of MeCN was added into the tube. Then, the tube was shaken properly for 30 s. Hereafter, 4 g of anhydrous MgSO₄ and 1 g of NaCl were added into the centrifuge tube, and the tube was shaken immediately for 1 min using a vortex mixer. Afterwards, the tube containing the extract was centrifuged for 5 min at 1957 × g. An aliquot of 3 mL of the MeCN layer was transferred into a 15 mL micro centrifuge tube containing 600 mg anhydrous MgSO₄ and 120 mg PSA. Then it was thoroughly mixed by vortex for 30 s and centrifuged for 5 min at 1252 × g. (Laboratory Centrifuges, Sigma-3 K30, 37520 Osterode am Harz, Germany). After centrifuging, a 1 mL supernatant was filtered by a 0.2 µm PTFE filter, and then it was taken in a clean GC vial for injection.

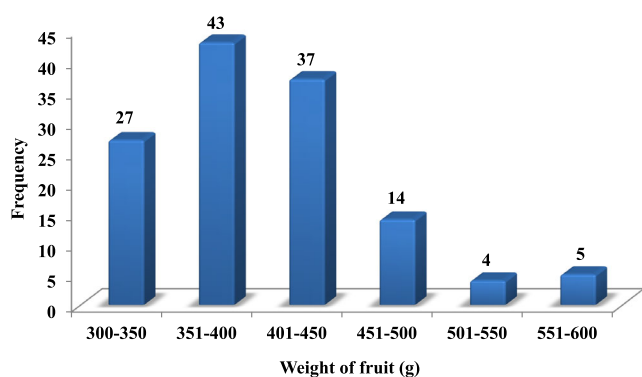


Figure 2. Frequency distribution of the weight of individual guava sample.

Instrumental analysis

The concentrations of the extracted organophosphorus pesticides (acephate, malathion, diazinon, chlorpyrifos, quinalphos, fenitrothion, and dimethoate) were detected by GC-FTD (Shimadzu GC-2010, Shimadzu corporation, Nakagyo-ku, Kyoto 604-8511, Japan), coupled with a capillary column of 30 m long \times 0.32 mm inner diameter (ID) \times 0.32 μ m film thicknesses (Rtx-OPPesticides2). The GC-FTD was operated in split mode and the injector and detector temperatures were set to 250 $^{\circ}$ C and 280 $^{\circ}$ C, respectively, and the column oven temperature program consisted of two steps: started from 160 $^{\circ}$ C (1 min hold) and ramped from 160 to 240 $^{\circ}$ C with incremental rate 8 $^{\circ}$ C (1 min hold). So, the total run time was 12 min. Helium was used as carrier (column flow rate 2.27 mL min $^{-1}$) and make up gas (flow rate 30 mL min $^{-1}$). While, the concentrations of the extracted pyrethroid pesticide (cypermethrin) was detected by GC-ECD (Shimadzu GC-2010, Shimadzu corporation, Nakagyo-ku, Kyoto 604-8511, Japan), coupled with a capillary column of 30 m long \times 0.32 mm ID \times 0.25 μ m film thicknesses (Rtx-CLPesticides2). The GC-ECD was handled in split mode and the injector and detector temperatures were set to 280 $^{\circ}$ C and 300 $^{\circ}$ C, respectively, and the column oven temperature was programmed as follows: initial temperature of 160 $^{\circ}$ C was held for 1 min and ramped to 270 $^{\circ}$ C with incremental rate of 10 $^{\circ}$ C was held for 8 min, resulting in a total run time of 20 min. Nitrogen was used as carrier (column flow rate 2.71 mL min $^{-1}$) and make up gas (flow rate 15 mL min $^{-1}$). Identification of the analyte in the extracted samples was done by comparing the retention time of the corresponding matrix matched calibration standard and quantification was done by the external calibration curves made up of a five point matrix matched calibration standard.

Method validation

The method was tested to assess for validation parameters and criteria in terms of accuracy, precision, linearity, limit of detection (LOD), and limit of quantification (LOQ) for both of the matrices of mango and guava separately. The blank samples of mango and guava were collected from the experimental fruit orchard under Pomology Division of Bangladesh Agricultural Research Institute (BARI), Gazipur, Bangladesh. In this study, the matrix effect was also evaluated according to the procedure described by Gilbert-Lopez *et al.*²⁸

In order to determine the potential interferences and cross contamination, the blank and spiked samples were analyzed. The accuracy of the method was expressed in terms of average

recovery of pesticides from fortified samples. The recovery analyses were carried out at three fortification levels (0.01, 0.1, and 0.3 mg kg $^{-1}$) for both of the matrices separately following the European Commission (EC) document no. SANTE/12682/2019.²⁹ Prior to the extraction procedure, the homogenized sample (10-g) was spiked by the addition of multiple standard working solutions in order to prepare the desired fortification levels mentioned earlier. In every fortification level, five replicates were analyzed. At the end of fortification, the sample was shaken properly for equilibration and it was kept for 30 min ensuring the proper contact of the analytes with the whole matrix. Afterwards, the desired analytes were extracted from the matrix following the extraction and clean up procedure described earlier. Precision [relative standard deviation (RSD_r)] was also estimated at the similar fortification levels along with five replicates.

The LOD and LOQ was estimated for both mango and guava matrices separately. To determine the LOD of all analytes, initially 10 blank samples were spiked to prepare the lowest acceptable concentration (0.01 mg kg $^{-1}$), after that they were injected and finally the LOD was calculated as the analyte concentration equivalent to three times the standard deviation.³⁰ The LOQ was determined following the SANTE/12682/2019 document,²⁹ which was the lowest fortification level for each analyte providing satisfactory accuracy (average recoveries for individual analyte ranged from 70 to 120%) and precision (RSD_r \leq 20%).

RESULTS AND DISCUSSION

Method validation

The accuracy and precision of the method were performed for mango and guava separately. For both of the matrices, the acceptable accuracy and precision was obtained for all of the selected analytes at three fortification levels (0.01, 0.1, and 0.30 mg kg $^{-1}$). For mango, the mean recoveries were in the range from 86 to 111% with RSD_r \leq 10% for all of the selected pesticides (Table 1), and in the case of guava, the mean recoveries were in the range from 80 to 109% with RSD_r \leq 13% for all of the selected pesticides (Table 2).

Calibration curves were prepared for individual matrices using matrix matched calibration standards at concentration levels of 0.01, 0.05, 0.1, 0.2, and 0.3 mg kg $^{-1}$. Linearity was found very good and coefficients of determinations were \geq 0.996 for all of the selected pesticides with matrix matched calibration standards prepared with mango and guava. The correlation coefficients for all of the selected pesticides are summarized in Table 1 (for mango) and in Table 2 (for guava).

The LOD was estimated for mango and guava separately. The LOD of each analyte is presented in Table 1 (for mango) and in Table 2 (for guava). The LOD ranged from 0.002 to 0.004 mg kg $^{-1}$. The LOQ for all of the selected pesticides was set to 0.01 mg kg $^{-1}$, which achieved acceptable accuracy (mean recoveries for individual pesticides ranged from 88% to 111% for mango, and 81% to 109% for guava) and precision (RSD_r \leq 8% for mango and RSD_r \leq 10% for guava) (Tables 1 and 2, respectively).

Matrix effects

The matrix effect was evaluated for all the selected pesticides in both of the matrices. Matrix effects were determined between the ratio of the slopes of the calibration curves made with matrix matched standards and solvent based standards.²⁸ Therefore, the

Table 1. Mean recovery (%) with % relative standard deviation (RSD) at different fortification levels, limit of detection (LOD), limit of quantification (LOQ) and coefficient of determination (R^2) of the selected pesticides in mango

Pesticides	Fortification levels						LOD	LOQ	R^2
	0.01 mg kg ⁻¹		0.1 mg kg ⁻¹		0.3 mg kg ⁻¹				
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)			
Acephate	103.2	5.3	94.0	4.1	97.6	4.0	0.003	0.01	0.997
Chlorpyrifos	99.2	7.4	95.0	4.9	96.0	5.6	0.003		0.996
Diazinon	104.8	4.4	96.0	4.7	98.6	4.7	0.004		0.997
Dimethoate	92.4	4.4	87.0	3.0	94.2	10.1	0.002		0.998
Fenitrothion	106.8	7.6	97.6	3.7	102.6	5.2	0.003		0.996
Malathion	98.4	6.7	91.4	3.3	95.0	4.3	0.003		0.998
Quinalphos	88.4	6.6	90.2	2.9	86.0	6.3	0.003		0.997
Cypermethrin	111.2	8.4	108.2	7.0	106.2	4.6	0.004		0.996

Table 2. Mean recovery (%) with % relative standard deviation (RSD) at different fortification levels, limit of detection (LOD), limit of quantification (LOQ) and coefficient of determination (R^2) of the selected pesticides in guava

Pesticides	Fortification levels						LOD	LOQ	R^2
	0.01 mg kg ⁻¹		0.1 mg kg ⁻¹		0.3 mg kg ⁻¹				
	Mean (%)	RSD (%)	Mean (%)	RSD (%)	Mean (%)	RSD (%)			
Acephate	95.4	6.3	100.6	6.1	105.0	5.6	0.003	0.01	0.996
Chlorpyrifos	93.2	9.9	90.0	10.1	87.2	11.1	0.002		0.996
Diazinon	108.0	5.8	102.0	6.1	97.8	9.4	0.003		0.996
Dimethoate	99.6	6.9	90.6	6.9	96.2	6.4	0.003		0.997
Fenitrothion	101.2	5.5	105.0	4.4	95.0	5.5	0.004		0.997
Malathion	85.0	7.9	80.0	8.7	82.8	7.3	0.003		0.996
Quinalphos	80.6	8.8	87.0	12.6	93.8	10.1	0.002		0.997
Cypermethrin	109.2	6.6	105.0	8.1	101.6	8.9	0.004		0.997

percent matrix effect would be classified into three categories as presented in Table 3: no matrix effect, medium matrix effect and strong matrix effect.³¹ Matrix effects of mango and guava with the selected pesticides are presented in Figs 3 and 4, respectively. Percent matrix effect was in the range of -19% (dimethoate) to 92% (cypermethrin) for mango while in the case of guava it was 4% (dimethoate) to 58% (cypermethrin). However, no matrix effect was found for most of the selected pesticides, showing suppression or enhancement ranging from -19% to 13% for mango and 4% to 17% for guava. The strong matrix effect was found only for cypermethrin in both of the matrices (92% for mango and 58% for guava). The strong matrix effect for cypermethrin in cauliflower has been reported by Prodhan *et al.*³² The findings of the present study are in good agreement with Menkissoglu-Spiroudi

and Fotopoulou.³³ They showed that GC-ECD detected pesticides with pronounced matrix effect.

Monitoring of pesticide residues in the fresh fruit samples

A total of 140 samples of mango and 130 samples of guava was collected from different retail markets of Barishal, Bogura, Cumilla,

Category	Percent matrix effect	
	Positive value	Negative value
No matrix effect	Less than 20	Higher than -20
Medium matrix effect	20-50	-20 to -50
Strong matrix effect	More than 50	Less than -50

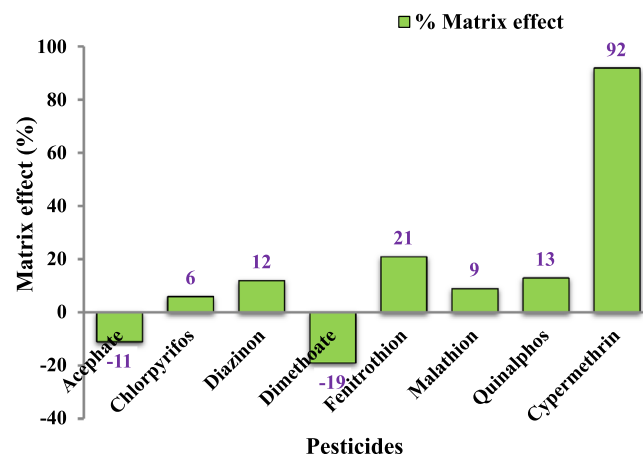


Figure 3. Effect of matrix on the selected pesticides in mango.

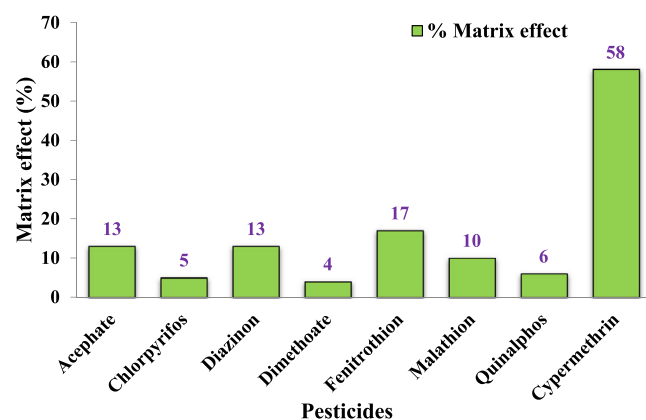


Figure 4. Effect of matrix on the selected pesticides in guava.

Dhaka, Dinajpur, Gazipur, Jamalpur, Jashore, Narsingdi and Rajshahi district of Bangladesh and were analyzed. The levels of detected pesticide residues in the analyzed samples and their maximum residue levels are outlined in Table 4.

Out of 140 analyzed mango samples, 127 (90.7% of the total number of samples) contained no detectable residues of the sought pesticides and 13 (9.3% of the total number of samples) contained detectable levels of cypermethrin, chlorpyrifos and dimethoate residues, of them only six samples (4.3% of the total number of samples) contained residue of chlorpyrifos (0.015, 0.019, and 0.04 mg kg⁻¹) and dimethoate (0.05, 0.062, and 0.291 mg kg⁻¹) at a level above the European Union maximum residue levels (EU-MRLs).³⁴ Cypermethrin (0.011, 0.016, 0.02, 0.028, 0.092, 0.185, and 0.314 mg kg⁻¹) was detected in seven samples at a level being below the EU-MRLs. The results of the present study are supported by Pingping *et al.*³⁵ They found that among the 45 analyzed mango samples, four had chlorpyrifos residues at a level above the EU-MRLs. The findings of the present study indicate that the farmers are now using cypermethrin, chlorpyrifos and dimethoate for the control of insect pests of mango. The percentage of contaminated samples collected from different locations is presented in Fig. 5. From Fig. 5, it can be seen that most of the samples containing residues were from Dinajpur (20%), Jamalpur (20%) and Rajshahi (13%). The samples collected from Barishal, and Narsingdi did not contain any residues of the targeted analytes.

Of 130 analyzed guava samples, 122 (93.8%) were free from detectable residues. Eight (6.2%) samples had detectable levels of cypermethrin (0.04, 0.056, 0.068, 0.104, and 0.113 mg kg⁻¹) and acephate residues (0.03, 0.045, and 0.290 mg kg⁻¹), of which seven (5.4%) samples were found contaminated with cypermethrin and acephate at a level above the EU-MRLs. Only one sample contained cypermethrin residue being below the EU-MRLs. The percentage of contaminated samples purchased from different districts of Bangladesh is presented in Fig. 6. Figure 6 indicates that most of the contaminated samples were purchased from Barishal (13%), Narsingdi (10%), Jamalpur (10%) and Jashore (10%). The samples purchased from Bogura, Cumilla, Dhaka, Gazipur, Rajshahi, and Dinajpur did not contain any residues of the sought pesticides.

Although, the numbers of contaminated samples were in a small percentage (9.3% for mango and 6.2% for guava) in the case of guava, almost all the contaminated samples (5.4%) contained residues above EU-MRLs. Regarding the issue of food safety, it is undoubtedly of great concern for the consumers as mango and guava are consumed fresh. Therefore, it is necessary to account for these findings and recommend that the policy planners and the respective stakeholders take proper action in order to control the indiscriminate use of pesticides for the management of insect pests and diseases of mango and guava.

Variability factors obtained from the marketed samples

VFs were estimated for individual pesticides in mango and guava. VFs were estimated following the guidelines stated on the Food and Agriculture Organization of the United Nations (FAO) plant production and protection report. They were calculated on the 97.5th percentile of the residue levels in the samples divided by the average residue of that lot through the SPSS software.³⁶ The samples that had no detectable residues were supposed to contain half of the quantification limit, this technique is suggested by Caldas *et al.*¹² In order to estimate the VFs, in total 140 samples of mango and 130 samples of guava were analyzed. The estimated VFs for mango and guava are presented in Table 4. The estimated VFs derived from the marketed samples ranged from 2.00 to 6.44 for mango and from 3.29 to 8.12 for guava. The average VF for mango was 4.06, while for guava it was 5.70. From the current study, a wide range of VFs were found due to the following reasons: the collected samples of mango and guava came into

Table 4. Residue levels (mg kg⁻¹) found in mango and guava and the variability factor (VF) estimated from the marketed samples with the detected pesticides

Fruits	Pesticides	Number of positive samples (> LOQ)	Maximum residue concentration (mg kg ⁻¹)	Minimum residue concentration (mg kg ⁻¹)	Mean residue concentration (mg kg ⁻¹)	Median residue concentration (mg kg ⁻¹)	EU MRLs (mg kg ⁻¹)	97.5th percentiles residue concentration (mg kg ⁻¹)	VFs
Mango	Cypermethrin	7	0.314	0.011	0.009	0.006	0.7	0.058	6.44
	Chlorpyrifos	3	0.04	0.015	0.005	0.005	0.01	0.01	2.00
	Dimethoate	3	0.291	0.05	0.008	0.006	0.01	0.03	3.75
	Average	13							4.06
Guava	Cypermethrin	5	0.113	0.04	0.008	0.006	0.05	0.065	8.12
	Acephate	3	0.290	0.03	0.007	0.005	0.01	0.023	3.29
	Average	8							5.70

LOQ, limit of quantification; EU MRLs, European Union maximum residue levels.

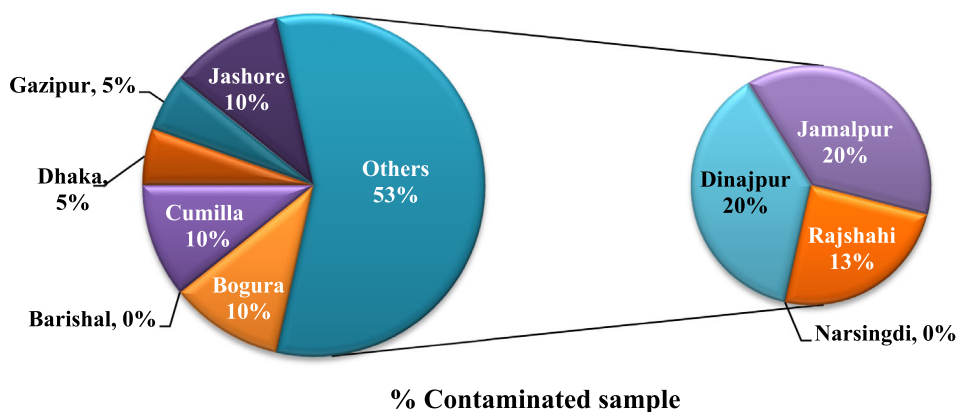


Figure 5. Contaminated samples (%) of mango found from different market places of Bangladesh.

the market from different lots and different fields and that is why different VFs were found.

The VFs derived from the marketed samples of mango and guava estimated in this study are found for the first time, that is why it is not possible to compare the present findings with previously published data. However, the findings of the current study are in good agreement with the findings found by a number of researchers. Hill and Reynolds estimated VFs for kiwi fruit, banana and apple. They found VFs ranging from 1.6 to 8.7 for several pesticides, including diazinon, fenitrothion and quinalphos in kiwi fruit; VFs ranging from 2.0 to 3.2 for chlorpyrifos in banana; and VFs ranging from 2.0 to 3.8 for several pesticides, including chlorpyrifos and triazophos in apple.¹⁶

The European Food Safety Authority (EFSA) reported VFs for peach, palm and orange. They reported VFs ranging from 3.3 to 5.9 for dimethoate and acephate in peach; VFs ranging from 2.2 to 10.4 for different pesticides, including chlorpyrifos, acephate, and fenitrothion in palm; and VFs ranging from 2.8 to 8.7 for malathion in orange.⁹

VFs ranging from 3 to 11 were reported for several pesticides, including diazinon, and fenitrothion in kiwi fruit¹⁹ and a VF value of 2.9 was reported for several pesticides, including chlorpyrifos in palm.¹⁸ VFs ranging from 3 to 12 were reported for several pesticides, including chlorpyrifos, dimethoate, and malathion in orange; and VFs ranging from 5 to 7 were reported for several pesticides, including acephate, and dimethoate in peach.¹⁷ A VF value of 3 for diazinon, and 5 for quinalphos in kiwi fruit; and a

VF value ranging from 3 to 5 for acephate, and 5 for fenitrothion was found in palm.²⁰

From the earlier discussions, it is assumed that the average VFs (4.06 for mango and 5.70 for guava) reported in the current study are in good agreement with the findings reported by several researchers and it is also supported by the proposed default VF of 5 for large-size commodities,³⁷ however, they were higher than the default VF of 3, which is presently used for the estimation of acute dietary intake.³⁶ The panel on Plant Protection Products and their Residues (PPR) of the EFSA evaluated that the VFs derived from the data of market surveys will exceed the proposed default value of 3 in about 65% of cases.⁹

CONCLUSIONS

In this study, VFs derived from the marketed samples of mango and guava were estimated for the first time. The estimated VFs ranged from 2.00 to 6.44 for mango and 3.29 to 8.12 for guava. The average VF for mango was 4.06 and for guava it was 5.70. A wide range of VFs was found in this study as the marketed samples were originated from different lots and different fields and thus different VFs were found. In order to estimate residue variability, a precise and an effective multi-residue method for the quantification of selected organophosphorus and synthetic pyrethroid pesticides has been developed using GC-FTD and GC-ECD for mango and guava. In the method, acceptable accuracy (mean recoveries ranged from 86 - 111% for mango and

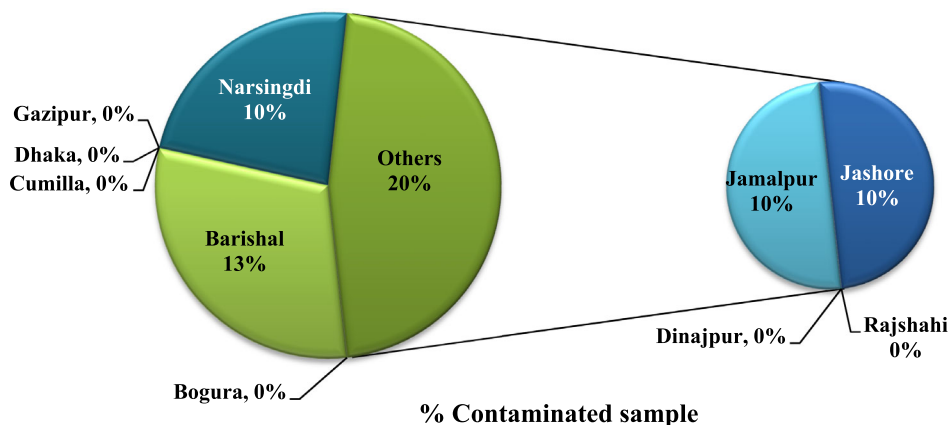


Figure 6. Contaminated samples (%) of guava found from different market places of Bangladesh.

80–109% for guava) and precision ($RSD_r \leq 10\%$ for mango and $\leq 13\%$ for guava) were found for all the analytes. The strong matrix effect was observed only for cypermethrin in mango (92%) and in guava (58%).

Moreover, monitoring of selected pesticides in 270 fresh fruit samples (140 mangos and 130 guavas) has been done successfully using the developed method. Out of 140 analyzed mango samples, 13 (9.3% of the total number of samples) contained detectable levels of cypermethrin, chlorpyrifos and dimethoate residues, of which only six samples (4.3% of the total number of samples) were found contaminated with chlorpyrifos and dimethoate at a level above EU-MRLs.³⁴ However, of 130 analyzed samples of guava, eight (6.2%) samples had detectable levels of cypermethrin and acephate residues, of which seven (5.4%) samples were found contaminated with cypermethrin and acephate at levels above the EU-MRLs. The outcome of the present study will help to increase public awareness and also help the policy planners to take necessary steps for the reduction of residue load in mango and guava.

Finally, it is suggested that a VF value should be reassessed when more data are obtained, mainly data regarding large size crops as the average VFs (4.06 for mango and 5.70 for guava) reported in this study were higher than the default VF of 3, which is presently used for the estimation of acute dietary intake.³⁶ However, they were supported by the proposed default VF of 5 for large-size commodities.³⁷

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CONFLICT OF INTEREST

The authors declare that they have no competing interests in the research.

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