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Research Article

Evaluation of integrated pest management modulation for mitigation of pesticide residues in mango[1]

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ABSTRACT

The increase of pesticide residues in food is extremely dangerous for humans. This research aimed to determine the concentrations of left-over pesticides residues on mangoes after they were exposed to pesticide residue mitigation modules (PRMM). Among these, four modules were used as candidate for integrated pest management approaches, while the fifth was traditional and served as a control. Residues of the lambda-cyhalothrin, cypermethrin, indoxacarb, imidacloprid, pyriproxyfen, acetamiprid, buprofezin and chlorpyrifos pesticides were assessed from mangoes taken from orchards. The QuEChERS technique was used to extract the residue samples and the GC-MS for their quantification. A significant increase in the percentage of contaminated samples was recorded during the 2019-2020 and 2020-2021 growing seasons. Samples belonging to PRMM-I showed 16.67 % (2019-2020) and 25.29 % (2020-2021) of contamination over the control. The samples collected during 2019-2020 and 2020-2021 from PRMM-II showed, respectively, 58.13 and 53.13 % of contamination. During 2020-2021, 66.67 and 67.00 % of the samples were contaminated for PRMM-III and PRMM-IV, respectively. Recoveries ranged from 88.37 to 99.02 %, with 1.07 to 3.97 % relative standard deviation, for all samples, in both seasons. PRMM-IV showed a greater contamination than the other modules and the control.

KEYWORDS: *Mangifera indica* (L.) Lam., pest control, pesticide residue mitigation modules.

RESUMO

Avaliação da modulação do manejo integrado de pragas para mitigação de resíduos de pesticidas em manga

O aumento de resíduos de pesticidas em alimentos é extremamente perigoso para os seres humanos. Objetivou-se determinar as concentrações de resíduos de pesticidas remanescentes em mangas, após serem expostas a vários módulos de mitigação de resíduos de pesticidas (MMRP). Dentre estes, quatro módulos foram utilizados como candidatos a abordagens de manejo integrado de pragas, enquanto o quinto era tradicional e serviu como controle. Resíduos dos pesticidas lambda-cialotrina, cipermetrina, indoxacarbe, imidaclopride, piriproxifeno, acetamipride, buprofezina e clorpirifós foram avaliados em mangas colhidas em pomares. A técnica QuEChERS foi utilizada para extrair as amostras de resíduos e a GC-MS para a sua quantificação. Um aumento significativo na porcentagem de amostras contaminadas foi registrado durante as safras de 2019-2020 e 2020-2021. As amostras do MMRP-I apresentaram 16,67 % (2019-2020) e 25,29 % (2020-2021) de contaminação, em relação ao controle. As amostras do MMRP-II coletadas durante 2019-2020 e 2020-2021 mostraram, respectivamente, 58,13 e 53,13 % de contaminação. Durante 2020-2021, 66,67 e 67,00 % das amostras foram contaminadas no MMRP-III e MMRP-IV, respectivamente. As recuperações variaram de 88,37 a 99,02 %, com desvio padrão relativo de 1,07 a 3,97 % para todas as amostras, em ambas as safras. O MMRP-IV apresentou nível de contaminação maior do que os outros módulos e o controle.

PALAVRAS-CHAVE: *Mangifera indica* (L.) Lam., controle de pragas, módulos de mitigação de resíduos de pesticidas.

INTRODUCTION

Fruits from tropical and subtropical regions are valuable sources of nutrition and energy (Akhtar et al. 2013, Zia-ud-Din et al. 2019). The nutritional profile of many fruits, along with their antioxidant potential, helps in the prevention of chronic human diseases (Baliga et al. 2018, Van Breda & Kok 2018).

Mango [*Mangifera indica* (L.) Lam.], ranked fifth after banana, apple, grape and orange, is one of the most produced fruits in the world, with annual yield of 55.6 million metric tons (Brahmeet et al.

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2023). Mango also dominates the local fruit market of Pakistan (Badar et al. 2019) and is substantially exported due to its high quality, unique taste, aroma and production (Memon 2016, Musharraf et al. 2016, Ayyaz et al. 2019). However, many biotic and abiotic factors limit the normal functioning and growth of mango plants and affect their final yield (Ahmad et al. 2019). Among the biotic constraints, weeds, diseases and insect pest are of prime importance (Affandi et al. 2017, Shahbaz et al. 2017, Malik et al. 2018).

In order to keep the crop output at a demanding level, the use of pesticides have become an integral part of modern farming intensive agricultural production systems (Masud & Akhtar 1997). In Pakistan, the Punjab province receives the highest percentage of pesticide applications (88.3 %) (Hayat et al. 2019), of which 11.9 % are being applied solely on fruits and vegetables, resulting in the accumulation of pesticide residues at concentrations above their maximum residual limits (Mehmood et al. 2021).

The problem of pesticide residues in different food items have become a global concern for human health. The scenario is even worse in the case of fruits that receive little or no postharvest treatment before use (Phan et al. 2018, Albaseer 2019). Agrochemicals, especially pesticides, can pose serious health hazards to humans, including certain skin diseases, paralysis, Parkinson's disease, blindness and even cancer (Margni et al. 2002, Kim et al. 2019). The outcomes of pesticide applications become even more catastrophic due to lack of education and awareness among farming communities, regarding their judicious and precise use (Koch et al. 2017).

The mitigation of pesticide residues from agroecosystems requires time, which may be achieved by the implementation of integrated pest management approaches in field crops, whose goal is to successfully manage insect pests while minimizing the use of pesticides by using a combination of biological, cultural and non-chemical control strategies. The integrated pest management models are sustainable because they promote the cautious use of pesticides and encourage farmers to consider alternative methods for pest control. By adopting integrated pest management strategies, farmers could easily mitigate the application frequency of pesticides, thus minimizing the potential risks to the environment and human health. Thus, the present study aimed to evaluate the effectiveness of integrated pest management control measures employed as a pesticide residue mitigation module against pesticide residues in mango fruits.

MATERIAL AND METHODS

Samples of mango fruit were collected from five small commercial orchards located in the Multan region, Pakistan, during the 2019-2020 and 2020-2021 growing seasons. They were subjected to residual analysis for calculating the concentrations of pesticides and comparing their values with the standard maximum residue limits of the Codex Alimentarius Commission (FAO 2023) or the European Union (EUC 2023).

A total of 150 samples of mango fruit were collected from five orchards, out of which four pesticide residue mitigation modules (PRMM) were integrated pest management based. For PRMM-I, a combination of cultural, mechanical and attraction and killing techniques was used to manage insect pests. Plastic sheets (LDPE) were wrapped around the trunk with plant debris, as a source to collect egg-carrying females. As a cultural control practice, fallen fruits were collected on a daily basis to minimize further infestation. Plastic sheets wrapped around the tree trunk were greased at every 15 days to disrupt the upward movement of the female mealybugs, as a mechanical control. Furthermore, repeated applications of GF-120 solution (0.5 L ha^{-1} in 4.5 L of water) and methyl eugenol + Tracer® 240SC (Spinosad) were used as attraction and killing traps with no insecticide applications. Similarly, PRMM-II included all practices mentioned for PRMM-I along with foliar application of Tracer® 240SC (Spinosad), at the rate of 10 mL ha^{-1} in 100 L of water. The PRMM-III module included applications of methyl eugenol + Tracer® 240SC (Spinosad) with 6 traps ha^{-1}. The used concentration of chemicals included 6-8 drops of M.E and 3-4 drops of Tracer® 240SC (Spinosad) sprayed on cotton pluck and placed in each trap. Each attraction and killing trap was refreshed after 12-15 days. Confidor® 20 % SL (Imidacloprid) at 200 mL ha^{-1} in 100 L of water, Jatar® 10 % EC (Bifenthrin) at 20 mL ha^{-1} in 100 L of water, and Mospilan® 20 SP (Acetameprid) at 150 gm ha^{-1} in 100 L of water were used as chemical treatments. No cultural or mechanical practices were used for pest suppression for PRMM-III. For PRMM-IV, repeated applications of Confidor® 20 % SL (Imidacloprid)

at 200 mL ha^{-1} and Jatar® 10 % EC (Bifenthrin) at 20 mL ha^{-1} were used in 100 L of water, followed by Diptrex® 80 % WP (Trichlorofon) at 250 g ha^{-1} + 100 L of water and Mospilan® 20 SP (acetamiprid) at 150 gm ha^{-1} + 100 L of water as chemical control measures. No other control tactic was used for PRMM-IV and the orchard was given the name of conventional pest control method. All the PRMM were devised to mitigate the pest population on mango trees and compared with a control module where no measures were applied for pest control. All other agronomic practices, such as irrigation and fertilizers, were applied in the same way as in the other PRMM.

The fruits were randomly collected at the end of both seasons (2019-2020 and 2020-2021). The procedures for collecting and transporting the samples followed the standards established by the Commission Directive 2002/63/EC (Wang et al. 2018). Each sample weighed 3 kg, and consisted of 3 sub-samples of 1 kg each, collected in polyethene zippers and placed in refrigerated containers for transportation. All the samples were homogenized in the laboratory and stored at -80 ºC for latter analysis.

The high-performance liquid chromatography (HPLC) technique was used to grade the amount of anhydrous magnesium sulphate ($MgSO_4$), acetonitrile (MeCN), primary secondary amines and anhydrous sodium acetate (NaAc), and the insecticide reference standards were purchased from SIGMA-ALDRICH Pvt. Ltd. (Qin et al. 2015). Lambda-cyhalothrin, cypermethrin, indoxacarb, imidacloprid, pyriproxyfen, acetamiprid, buprofezine and chlorpyrifos were used as insecticide reference standards. Each individual stock solution was prepared at a concentration of 2,000 mg L^{-1} in acetonitrile and then frozen at -18 ºC. On the day of the analysis, acetonitrile dilutions were made to the calibration and working standards. For dispersive solid-phase extraction (dSPE), Agilent Technologies (USA) supplied the necessary QuEChERS kits (Part nº. 5982-5755 + 5982-5058) containing 6 g of magnesium sulphate, 1.5 g of sodium acetate and 15 mL centrifuge tubes containing 1,200 mg of magnesium sulphate and 400 mg of primary-secondary amine.

The collected fruit samples belonging to the PRMM modules were thoroughly checked for quantification of pesticide residues. In each PRMM, multiple tactics were used for suppressing the pest population. These PRMM were compared for pesticide residue concentration. The percentage of contaminated samples, or exceeding maximum residual limits, was noted.

The fruit samples (1 kg) were homogenized by mixing 1 g of fruit with 4 mL of acetonitrile using Precelly's 24® (Model P002391-P24T0-A.0, Bertin France) at 6,500 rpm for 20 sec, followed by 90 sec of downtime cooling. Following three such cycles, 6 mL of acetonitrile (ACN) were added to the samples in a 15 mL vial/tube (Evard et al. 2015, Polyiem et al. 2018).

The QuEChERS (AOAC) method developed by Agilent Technologies was chosen for extraction and cleanup because of its selectivity, sensitivity and flexibility (Zhao et al. 2009, Malhat 2017). The homogenized sample was added to a 15 mL vial with 100 µL of respective internal standard, followed by 1.05 g of sodium acetate (NaOAc) and 6 g of magnesium sulphate. The mixture was then vortexed or shaken by hand for 1 min to ensure that all the solid and liquid components were thoroughly mixed. About 1.05 mL of supernatant from the centrifuged sample (at 4,695 g, for 5 min) was placed in a vial for dispersive SPE with 2 mL of primary and secondary amides and $MgSO_4$. The mixture was shaken by hand and then centrifuged at 10,285 g for 5 min. A supernatant after shaking without any solid particles was poured into a lid vial and placed in a centrifuge overnight. The overnight dried sample was added with 100 µL of acetonitrile for re-suspension by the vortex. The samples were centrifuged for 1 min to separate any possible solid particles and were transferred to liquid chromatography vials (LC) for analysis (Anastassiades et al. 2003, Adam et al. 2018, Faraji et al. 2018).

A gas chromatograph (model 8890) and a mass spectrometer (model 5977B) by Agilent Technologies® were used with the following parameters: the injector temperature was 220 ºC, the injection volume was 1 µL split less, the column used was 25 methyl silicon, I.D. 0.53 mm at a temperature of 250 ºC, 2.0 µm of film thickness, the G.C detector was a mass spectrometry detector at 300 ºC, N2 (30-32 mL mL^{-1}) used as carrier gas (Wang et al. 2018), the oven temperature was 60 ºC for 0.5 min, the flow rate was 17 mL min^{-1} and the injection method was the solvent flush technique (auto-sample injection). Recoveries and linearity of the samples were calculated from calibration curves, while detection and quantification limits were

calculated by determining the minimum values using the signal-to-noise ratio method (Darko & Akoto 2008, Jovanov et al. 2013).

The method was validated by testing its linearity, recovery, accuracy and specificity of peak regions. Both the detection and quantification limits were measured experimentally from fortified samples, with the signal equal to 3 and 10 times the noise ratio, respectively (EUC 2019). The matrix-matched calibration standards in the acetonitrile extracts of mango were prepared using multi-residue working solutions and blank sample extracts. The effect of the matrix was evaluated by comparing the slopes of calibration curves based on an eight-point matrix match to those based on mangoes. A coefficient of determination greater than 0.990 indicating a good linearity was attained across the board. Relative standard deviation values were below 20 % across the board, when testing various concentrations. Analytical performance metrics, including detection and quantification limits, linearity, matrix effect, selectivity, precision and recovery, were examined to guarantee that the suggested method was appropriately optimized for practical use in routine analysis.

RESULTS AND DISCUSSION

The results showed that the quantified pesticide residue levels ranged 91-99 % at 0.01 mg kg^{-1} and 91-98 % at 0.05 mg kg^{-1} for the fortification level in 2019-2020 (Table 1), as well as 85-95 % at 0.01 mg kg^{-1} and 92-98 % at 0.05 mg kg^{-1} in 2020-2021, showing the reproducibility of the procedure (Table 2). Similar results were reported by Arora et al. (2006), who monitored pesticide residues in mango and observed that, out of five samples, four were found contaminated with pesticides like cypermethrin, dichlorvos, malathion, monochrotophos and hexaconazole.

The operating conditions of gas chromatography were sensitive to the analytes indicated by the limit of detection (0.001-0.0014 mg kg^{-1}), while the number of replicates was 5. The relative standard deviation was less than 20 % in the result of the repeatability of the study for all the fruits and pesticides in both seasons. The mass to charge ratio (m/z) for different pesticides was lambda-cyhalothrin (181, 197, 208), cypermethrin (181, 209), indoxacarb (297), imidacloprid (256), pyriproxyfen (136, 226), buprofezin (116), acetamiprid (223) and chlorpyriphos (97, 314). Recoveries ranged from 91.48 to 99.02 %, with relative standard deviation of 1.03-3.97 %, in 2019-2020 (Figures 1 and 2), while it ranged 88.37-99.18 %, with relative standard deviation of 1.17-3.58 %, in 2020-2021. Recoveries also ranged 88.37-99.02 %, with relative standard deviation of 1.07-3.97 %, for all samples in both seasons, what is directly aligned with the results of a previous study by Rodrigues et al. (2007). However, these findings contradicted the results of Masud & Akhtar (1997), who tested food and water samples from Gadoon Amazai and found no traces of pesticides. The difference can be attributed to the fact that pesticides in that region were being applied properly and judiciously.

In 2019-2020, the pesticide residues were detected in the range of 0.0021-0.1350 mg kg^{-1} for PRMM-I, 0.0017-0.2514 mg kg^{-1} for PRMM-II, 0.0019-0.1524 mg kg^{-1} for PRMM-III and 0.0025-

Table 1. Concentration of pesticide residues quantified in mango samples collected from pesticide residue mitigation modules (PRMM) in the 2019-2020 season (maximum-minimum).

Pesticide	PRMM-I	PRMM-II	PRMM-III	PRMM-IV	Control	LOD	LOQ	Recoveries ± RSD (%)		
								Fortification levels (mg kg^{-1})		
	mg kg^{-1}							0.01	0.05	0.10
Lambda-cyhalothrin	0.0021-0.0651	0.0037-0.2514	0.0019-0.0365	0.0065-0.3651	ND-0.0023	0.002	0.004	96.32 ± 2.09	95.23 ± 2.77	93.00 ± 2.96
Cypermethrin	0.0052-0.0325	0.0062-0.0694	0.0095-0.1524	0.0074-0.2583	0.0145-0.0203	0.002	0.006	97.26 ± 3.03	94.91 ± 1.10	96.70 ± 2.82
Indoxacarb	0.0066-ND	0.0035-0.0784	0.0048-0.0618	0.0057-0.0817	ND-ND	0.001	0.002	99.02 ± 1.23	96.16 ± 1.03	95.34 ± 1.23
Imidacloprid	0.0095-0.0175	0.0021-0.0184	0.0089-0.0584	0.0041-0.0351	ND-0.0109	0.003	0.004	94.72 ± 1.82	92.34 ± 2.97	92.49 ± 1.03
Pyriproxyfen	0.0035-0.0115	0.0078-0.0245	0.0036-0.0321	0.0058-0.0215	ND-ND	0.002	0.005	95.64 ± 2.09	91.87 ± 1.23	98.65 ± 2.96
Acetamiprid	0.0041-0.0231	0.0017-0.0788	0.0057-0.0458	0.0036-0.1246	ND-0.0145	0.001	0.003	91.48 ± 3.03	93.27 ± 1.10	95.24 ± 1.75
Buprofezin	0.0036-0.0266	0.0127-0.1825	0.0066-0.1354	0.0025-0.0584	ND-ND	0.006	0.009	97.59 ± 2.75	97.39 ± 3.84	99.10 ± 2.09
Chlorpyrifos	0.0085-0.1350	0.0045-0.0548	0.0079-0.0258	0.0057-0.0651	0.0075-0.0096	0.003	0.005	93.33 ± 1.96	98.61 ± 3.97	94.73 ± 1.16

LOD: limit of detection; LOQ: limit of quantification: RSD: relative standard deviation; ND: not detected.

Table 2. Concentration of pesticide residues quantified in mango samples collected from pesticide residue mitigation modules (PRMM) in the 2020-2021 season (maximum-minimum).

Pesticide	PRMM-I	PRMM-II	PRMM-III	PRMM-IV	Control	LOD	LOQ	Recoveries ± RSD (%)		
								Fortification levels (mg kg^{-1})		
	mg kg^{-1}							0.01	0.05	0.10
Lambda-cyhalothrin	0.0055-0.3152	0.0021-ND	0.0036-0.0538	0.0019-0.0415	0.0015-ND	0.002	0.003	90.16 ± 1.32	92.45 ± 1.42	93.38 ± 1.07
Cypermethrin	0.0056-0.2496	0.0074-0.3145	0.0061-0.0258	0.0024-0.0652	0.0103-0.0132	0.001	0.004	91.37 ± 1.15	93.39 ± 2.75	95.22 ± 2.80
Indoxacarb	ND-ND	0.0018-ND	0.0052-0.0624	0.0031-0.0625	ND-ND	0.002	0.006	94.54 ± 2.99	94.17 ± 1.25	99.18 ± 1.13
Imidacloprid	0.0063-0.3251	0.0071-0.4523	0.0084-0.1562	0.0082-0.2153	0.0129-ND	0.007	0.008	92.62 ± 1.24	96.06 ± 2.67	91.86 ± 2.87
Pyriproxyfen	ND-ND	ND-ND	0.0081-0.0652	0.0065-0.0892	ND-ND	0.004	0.007	95.81 ± 2.66	97.35 ± 1.33	97.24 ± 1.93
Acetamiprid	0.0036-0.2561	0.0084-0.0412	0.0032-0.0241	0.0094-0.0521	0.0207-ND	0.002	0.005	89.93 ± 3.32	95.61 ± 1.17	93.17 ± 3.20
Buprofezin	0.0062-0.0724	0.0062-0.6512	0.0041-0.1452	0.0043-0.2540	ND-ND	0.002	0.003	88.37 ± 2.74	98.48 ± 3.50	94.61 ± 1.27
Chlorpyrifos	0.0061-0.1240	0.0051-0.0510	0.0081-0.0851	0.0060-0.0562	0.0086-0.0065	0.001	0.004	95.10 ± 3.58	92.26 ± 1.92	96.84 ± 2.73

LOD: limit of detection; LOQ: limit of quantification: RSD: relative standard deviation; ND: not detected.

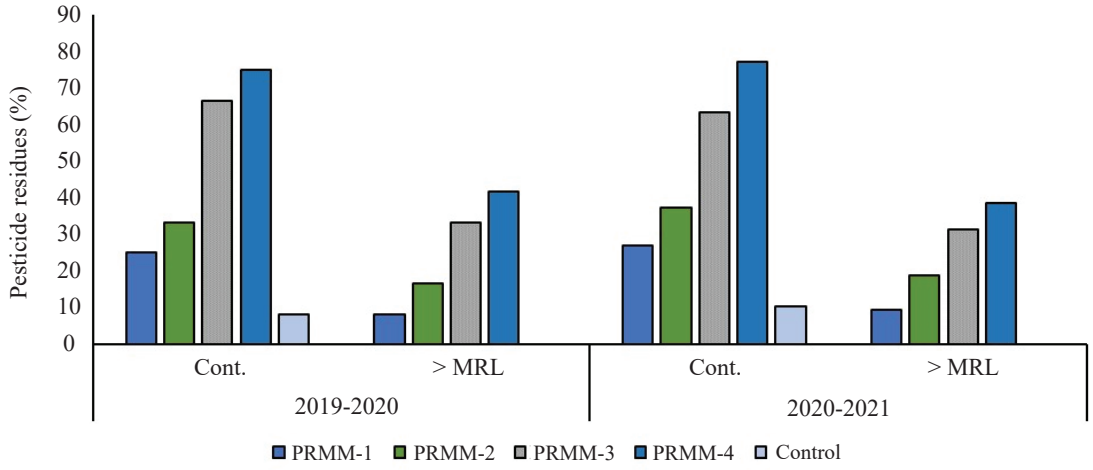

Figure 1. Comparison of pesticides residue mitigation modules (PRMM) contamination in the 2019-2020 and 2020-2021 seasons. Cont.: contaminated samples; > MRL: samples with pesticide residues above the maximum residue limit.

0.3651 mg kg^{-1} for PRMM-IV, in comparison to the control (0.0075-0.0203 mg kg^{-1}) (Table 1). In 2019-2020, they ranged 0.0036-0.3251 mg kg^{-1} for PRMM-I, 0.0018-0.6512 mg kg^{-1} for PRMM-II, 0.0032-0.1562 mg kg^{-1} for PRMM-III and 0.0019-0.2540 mg kg^{-1} for PRMM-IV, while the control module expressed a relatively shorter concentration range (0.0015-0.0132 mg kg^{-1}) (Table 2). These results are also in line with the findings of Kumari et al. (2002), who monitored 60 samples of market vegetables and reported that the tested samples showed 100 % of contamination with low, but measurable, amounts of residues.

Among the four chemical groups, the organophosphates were dominant and about 23 % of the samples showed contamination above their respective maximum residue limit values. The findings of Bhattacherjee (2013) were also in harmony with our findings. The researchers sprayed imidacloprid on mango at a dose rate of 0.3 mL L^{-1} of water during the pre-blooming stage to control hoppers and reported residues of imidacloprid in the peel (1.21 mg kg^{-1}), pulp (0.56 mg kg^{-1}) and fruit (1.77 mg kg^{-1}), even after 30 days of spraying.

A comparison of the percentages of the samples contaminated and exceeding maximum residual limits revealed that no significant difference was recorded between the 2019-2020 and 2020-2021 seasons, while a significant difference was recorded among different PRMM, in comparison to each other and the control. Samples collected from all the PRMM in 2019-2020 were analyzed for pesticide residues and revealed that 25 % of the samples from PRMM-I were contaminated, among which 8.33 % were above the maximum residue limits, while 16.66 % of the samples from PRMM-II

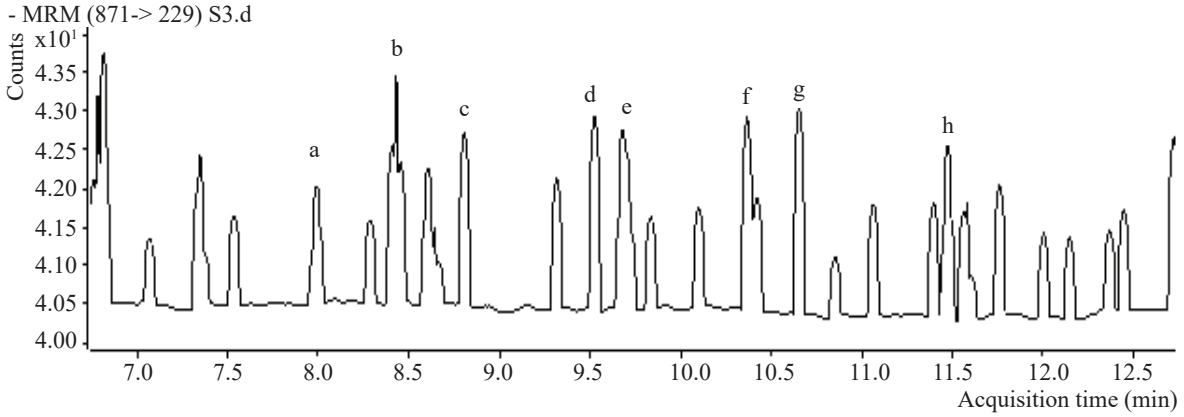

Figure 2. Total ion chromatogram obtained from a GC-MS of blank sample (standards) with maximum residue limit, in mg kg^{-1}. a: imidacloprid (0.2); b: acetameprid (0.01); c: pyriproxifin (0.5); d: buprofezine (0.09); e: chlorpyrifos (0.05); f: cypermethrin (0.7); g: indoxacarb (0.02); h: lambda-cyhalothrin (0.2).

were contaminated, for a total of 33.33 %. Similarly, 66.66 % were contaminated for PRMM-III, among which 33.33 % were above the maximum residue limits, and PRMM-IV showed a maximum (75 %) contamination level with a 41.66 % violation rate, while the control module showed 8.33 % for sample contamination, with no sample exceeding the maximum residue limits (Figure 1).

Samples collected in the 2019-2020 season depicted almost similar results, with 27.08 % of contamination, among which 9.37 % were above the maximum residue limits for PRMM-I, while 18.75 % of the samples violated the maximum residue limits, among 37.5 % of contaminated samples. Similarly, 63.54 and 31.25 % of the samples were found contaminated and above the maximum residue limits, respectively, for PRMM-III, while 38.54 % of the samples exceeded the maximum residue limits, from a total of 77.08 % contaminated for PRMM-IV. In comparison to these PRMM, only 10.41 % of the samples were found with residues, with no samples violating the maximum limit in the control module (Figure 1). The current results were further verified by surveys conducted in Pakistan, which reported that fruit and vegetable samples present at the Karachi farmers' market were found contaminated with traces of organochlorine, organophosphate and pyrethroid insecticides (Hussain et al. 2002, Masud & Hasan 2002). Similarly, Hussain et al. (2002) also supported our results, as they screened residues of commonly used pesticides, viz. cypermethrin, methamidophos, monochrotophos, cyfluthrin, dieldrin and methyl parathion, in mango fruit samples collected from the grower fields in the Multan division. They reported that all the samples were contaminated with a degree of variation regarding pesticides residues.

Higher levels of organochlorine and organophosphate pesticide residues can be attributed to the fact that several organochlorine and organophosphate insecticides have been classified as persistent organic pollutants, owing to their bulk (intensive) properties, including persistence and biomagnification (Fremlin et al. 2020). So, even a little use of these pesticides can result in higher levels of residues after a prolonged time (Giesy et al. 2014). Contrarily, neonicotinoids and pyrethroids are mostly favored by commercial growers for sucking insect-pest management in mango crops (Karar et al. 2021, Zahid et al. 2022).

The base for the lambda-cyhalothrin ion peaked at m/z 181, followed by m/z197 and m/z 208, for cypermethrin, indoxacarb, imidacloprid, pyriproxyfen, buprofezin, acetamiprid and chlorpyriphos.

Lambda-cyhalothrin was detected in 43.75 % of the samples, among which 23.33 % were above the maximum residue limits, while 45 % were detected with cypermethrin, with a 24.16 % violation rate. Indoxacarb occurred in 31.25 % of the samples, with 5.41 % of them exceeding the maximum residue limits. Similarly, 44.16 % of the samples were found with imidacloprid, while 25 % violated the maximum limit. Pyriproxyfen occurred in 33.33 % of the samples, with an 8.33 % violation rate among the contaminated ones, while 43.75 % of the samples

owned acetamiprid, with 22.91 % of them above the maximum residue limits. Similarly, 37.08 % of the samples showed contamination of buprofezin, with a 4.16 % violation of the safe limit, while chlorpyriphos was determined in 44.58 % of the samples, with 22.92 % of them above the maximum residue limits.

The linearity of the samples was calculated on the basis of two fortification levels to calculate the correlation coefficient (R^2), and the regression equation was generated (Table 3). The limit of detection for all the pesticides was less than the minimum concentration that was quantified in the samples, while the standard deviation was calculated as less than 20 % (Tables 1 and 2). Similar results were reported by Sinha et al. (2012), where the limit of detection ranged 0.0006-0.091, while the relative standard deviation was less than 10 %, with less than 10 % for R^2. Differences were attributed to the equipment used, which was an LC-MSMS in the latter case, while the method accuracy was above 99 % in both studies.

Overall, the pest population reduction efficiency of the modules was compared, resulting in the PRMM-II reducing the pest population up to 90.79 %, followed by PRMM-I, with 83.61 %. Similarly, PRMM-III reduced the pest population up to 75.78 %, while 72.18 % was reduced by PRMM-IV, as already reported by Bana et al. (2015). In their study, Bana et al. (2015) formulated five modules to mitigate the population of mango hopper in mango orchards. The module-V in their study considered integrated pest management based on insecticides and botanicals application. Although the maximum mango production was recorded from the tested integrated pest management module, they did not detect pesticide residues from mango samples. After the mango seasons of 2019-2020 and 2020-2021 were completed, the average yield of 5 modules showed a considerable difference. The fruit production loss was measured both qualitatively and quantitatively, because not all the pests cause a quantity loss, such as meallybug and mango hopper, but fruit fly does it. PRMM-II gave a maximum yield of 47,211.954 kg ha^{-1}, from which 85.24 % were marketable, followed by PRMM-I, with 45,321.59 kg ha^{-1} and 81.12 % of marketable yield. PRMM-III produced 42,699.81 kg ha^{-1}, with 77.96 % of marketable fruits, followed by PRMM-IV, with 41,323.43 kg ha^{-1} and 71.42 % of marketable yield, and all these modules were compared with a control module, where the yield was calculated as much as 35,941.47 kg ha^{-1}, while only 59.95 % were marketable yield. PRMM-II produced 25.29 % more marketable fruits, in comparison to the control module, while PRMM-I produced 21.17 % more marketable fruits over the control. In the case of PRMM-III and PRMM-IV, the surplus marketable fruits over the control was calculated as 17.21 and 11.47 %, respectively. Similar differences were reported by Karar et al. (2020), in a study where they evaluated three modules and checked the efficacy of insecticides on mango production. The highest production and minimum pest population were observed in module-III, where the maximum number of pesticides was applied, but unlike in the current study, since the focus of their study was a higher production and minimum pest population, and pesticide residues were not determined in their study. However, in their experiment, Farooq et al. (2019) reported that the integrated pest management

Table 3. Linearity of pesticides in mango samples collected from modules in the 2019-2020 and 2021 crop seasons.

Pesticide	2019-2020					2020-2021				
	1 mL dispersive SPE regression equation	R^2	8 mL dispersive SPE regression equation	R^2	Linear range (µg mL^{-1})	1 mL dispersive SPE regression equation	R^2	8 mL dispersive SPE regression equation	R^2	Linear range (µg mL^{-1})
Lambda-cyhalothrin	y = 0.3256x - 0.0016	0.9826	y = 0.2951x - 0.0019	0.9584	0.220-15.4	y = 0.2654x - 0.0047	0.9984	y = 0.3162x - 0.0019	0.9715	0.200-15.0
Cypermethrin	y = 0.2751x - 0.0014	0.9957	y = 0.3861x - 0.0052	0.9925	0.190-17.2	y = 0.2351x - 0.0052	0.9684	y = 0.0878x - 0.0057	0.9925	0.170-16.8
Indoxacarb	y = 0.0865x - 0.0058	0.9938	y = 0.2831x - 0.0061	0.9862	0.200-22.3	y = 0.3182x - 0.0061	0.9845	y = 0.2387x - 0.0062	0.9932	0.210-21.0
Imidacloprid	y = 0.3175x - 0.0024	0.9601	y = 0.4213x - 0.0008	0.9951	0.230-17.0	y = 0.6122x - 0.0080	0.9685	y = 0.9155x - 0.0091	0.9624	0.160-16.2
Pyriproxifen	y = 0.6540x - 0.0013	0.9709	y = 0.2152x - 0.0018	0.9604	0.210-17.9	y = 0.3341x - 0.0073	0.9735	y = 0.7899x - 0.0008	0.9807	0.170-17.1
Acetamiprid	y = 0.6523x - 0.0008	0.9948	y = 0.0985x - 0.0095	0.9750	0.230-19.3	y = 0.6281x - 0.0009	0.9958	y = 0.5234x - 0.0092	0.9713	0.190-18.9
Buprofezin	y = 0.8741x - 0.0051	0.9761	y = 0.2741x - 0.0042	0.9765	0.210-18.6	y = 0.7361x - 0.0018	0.9868	y = 0.0323x - 0.0064	0.9662	0.170-17.4
Chlorpyrifos	y = 0.1721x - 0.0004	0.9802	y = 0.3942x - 0.0060	0.9909	0.230-19.3	y = 0.6808x - 0.0023	0.9710	y = 0.2264x - 0.0032	0.9579	0.190-18.7

R^2: correlation coefficient.

module with minimum use of insecticides was more effective, in terms of pest population reduction and reduced pesticide residues.

A better cropping and legislative approach to minimize the injudicious use of pesticides is required, and more efficient eco-friendly approaches should be joined in integrated pest management modules to manage insect pests, especially in the case of fruit crops.

CONCLUSIONS

After exposed to pesticide residue mitigation modules (PRMM), minimum pesticide residues of 16.67 % were observed in the mango samples for PRMM-I, followed by 53.13 % for PRMM-II, 66.67 % for PRMM-III and 67.00 % for PRMM-IV, while the maximum production was recorded for PRMM-II, followed by PRMM-I, PRMM-III and PRMM-IV.

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