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Research Article

Pesticide Residues in Fruit and Vegetables available in the Local Market in Riyadh, Saudi Arabia

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Abstract

This study evaluated the presence of pesticides in fruit and vegetables available in the local market in Riyadh, Saudi Arabia. A total of 777 of samples were analysed, 283 fruits and 494 vegetables, using LC-MS/MS as the preferred method. Results showed that 10.5% of sampled exceeded the MRL requirements with acetamiprid, imidacloprid, carbendazim, and methomyl being predominant. In addition, some imported products contained pesticides that are banned. Despite the years of monitoring for pesticides, breaches of MRLs continue to be reported. Recommendation for more stringent approaches to the management of pesticide along the supply chain are suggested.

Introduction

The Food and Agricultural Organisation (FAO) define pesticides as "any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies [1]. Pesticide use is common in the agricultural and horticultural industry [2]. A number of authors [3-5] have reported that the increased use of chemical pesticides has resulted in environmental contamination and degradation leading to human as well as animal health concerns. Pesticides have been implicated in a spectrum of human health hazards ranging from short-term headaches and nausea to chronic impacts like cancer, endocrine disruption and reproductive disorders [6]. Consumption of foods such as fruit and vegetables is the main exposure route to pesticide residues. In addition, they are largely consumed raw or semi-processed and sometimes may be unwashed. Thus, for these reasons, it is essential to limit the amount of pesticide residues in food. Maximum Residue Limits (MRL) have been set by agencies such as the European Parliament [7] and the FAO/WHO [8].

According to a report by Trading Economics [9], Saudi Arabia spent US$1.58Billion in 2018 importing approximately 70% of its fruits and vegetables. In developing countries, poor pesticide handling practices as well as inadequate management and regulation [10] has given rise to greater pesticide poisoning incidences compared to developed countries [11]. Controls in developing countries is often limited to resource availability and legislative rigour. Due to high market demand and low perception of toxicity, some farmers may not wait long enough for the residue to wash off [12]. Developed countries are not immune to such problems either. A report from Belgium [4] indicated that out of 1413 samples, 72% contained pesticides and 6% exceeded the MRLs while a more recent report from Poland [11] using 123 fruit samples found pesticide residues in 63% of samples with 13% above the MRLs. The Eatwell Guide [12] to consume at least 5 fruit and vegetables per day is a policy recommendation by the UK government on eating healthily and achieving a balanced diet. However, children are a vulnerable group of fruit and vegetable consumers as their lower body weight renders them susceptible to health-related issues when pesticide levels are higher than legislated requirements [4,13]. The authors [2] of a research report evaluating pesticides in the Al-Qassim region, Saudi Arabia, recommend a frequent monitoring programme for pesticide residues, in particular for vegetables grown under greenhouse conditions at a national level.

This work forms part of a preliminary study which will be expanded across all regions in Saudi Arabia and investigate additional pesticides. The objective of this study is to analyse, present and discuss the findings obtained for selected pesticides in fruit and vegetables marketed in Riyadh, Saudi Arabia using a relatively new method of analysis. In addition, recommendations for food safety schemes such as Good Agricultural Practice (GAP) that incorporate HACCP are highlighted.

Materials and Methods

Sample Collection

Our approach utilises the sampling method in [14] according to Codex Alimentarius Commission, 2000. A total of 777 samples (283 fruits and 494 vegetables) were collected for a 4 month period from Jan 2018 to April 2018. The samples were purchased from various open markets and supermarkets from each of the 17 districts in Riyadh city. The sampling was performed by authorized food control inspectors. All samples were a minimum of 2Kg, placed in plastic bags and labelled. The samples were then transported under refrigerated conditions at 4^{o}C to the ISO 17025:2005 certified analytical laboratory where extraction occurred within 24 hours of delivery. The fresh fruit samples analysed in this study included dates, apple, orange, lemon, mango, grape, pomegranate, banana, cantaloupe, watermelon, peach, strawberry, apricot, cherries, and guava while the fresh vegetable samples included onion, eggplant, pumpkin, potato, okra, capsicum, eggplant, cabbage, coriander, spinach, garlic, jute mallow, watercress, carrot, beans, cucumber, mint, broccoli, lettuce, celery, cauliflower, zucchini, parsley and tomato.

Reagents and Standards

Pesticide-grade acetonitrile, methanol, hexane ammonium acetate and hydrous sodium sulphate were obtained from Merck (Darmstadt, Germany). Thirty two pesticide standards (99% purity) (acetamiprid, imidacloprid, carbendazim, methomyl, metalaxyl, pyridaben, indoxacarb, azoxystrobin, difenoconazole, tebuconazole, boscolid, linuron, ethion, metalaxl-m, chlorpyrifos, thiamethoxam, mycobutanil, hexythiazox, chinomethionat, biphenyl, phenthoate, quinalphos, pyrimethanil, malathion, bifenthrin, pyriproxyfen, iprodione, oxadiazon, lamda-cyhalothrin, imazalil, permethrin, and fipronil) were obtained from Dr.Ehrenstofer GmbH (Germany) and stored in the freezer at -18°C to minimize degradation. Stock solutions of each pesticide were made up by dissolving 25mg of each compound in 25ml of methanol and stored in a dark glass-stoppered bottle at 4°C.

Extraction Procedure

Accurate sample weights of 10±0.1g were measures and then samples were transferred into a 50ml PTFE tube (extraction kits). To this 10ml acetonitrile was added and shaken vigorously for 1 min. Buffer salt was added. The mixture was then shaken vigorously for 1 min and centrifuged at 10 000 RPM for 10 min. The upper clear solution was transferred into dispersive solid phase extraction tubes (15ml Polyethylene tube) containing 150mg primary secondary amine (PSA) and 900mg anhydrous magnesium sulphate. The tube was capped and the extract was mixed with sorbent and vigorously mixed for 1 min followed by centrifugation at 4000 RPM for 5 min. Two millilitres of the clear extract was transferred into stoppered vials.

Analytical Procedure

The preferred technique for determination of multiresidue methods reported for fruits and vegetables are based mostly on the use of liquid chromatography coupled with tandem mass spectrometry (LC-MS/MS). LC-MS/MS was performed with an Agilent 1200 series HPLC instrument coupled to an API 3200 Qtrap MS/MS from Applied Biosystems with electrospray ionization interface (ESI) (AB SCIEX, Dublin, CA, USA) and operated under unit mass resolution. The pesticide analysis procedure was conducted as reported in [15] by Sanchez et al (2010). The samples were extracted following the quick, easy, cheap, effective, rugged and safe method known as QuEChERS.

A 20μl sample extract was injected for chromatography into a C18 column ZORBAX Eclipse XDB-C18 4.6×150 mm, 5 μm particle size (Agilent, Santa Clara, CA, USA), in which Mobile Phase A contained 5mm ammonium formate and Mobile Phase B was methanol. An ESI source was used in the positive mode, with nitrogen as the nebulizer curtain gas. Other gas settings were optimized according to recommendations made by the manufacturer; source temperature was 300 °C, gradient elution programme was 0.3ml/min flow, ion spray potential: 5500 V, de-cluster potential and collision energy were optimized using a syringe pump by introducing individual pesticide solutions into the MS instrument to allow optimization of the MS/MS conditions.

Identification and Quantification

The selected reaction monitoring (SRM) mode was used in which one transition ion product was used for quantification and the other for confirmation. The identification of a pesticide residue was considered to be confirmed when the retention time of the pesticide matched with that of the pesticide in the pure standard in and the appearance of two product ion transitions that matched the relative intensity criterion under SRM conditions. Once the presence of a pesticide residue was confirmed in an extract, the concentration of the residue was obtained from the appropriate calibration function which corresponds to the matrix-matched calibration standards. Calibration standard curves were produced by plotting the peak areas for each pesticide versus its concentration with the matrix-matched standard solution and used for the quantification of each pesticide in the sample extract. All sample analyses were conducted in triplicate. The standard curves were linear in the range 0.005–0.100 μg/g with correlation coefficients greater than 0.998. The concentration of the pesticide in the sample extract, Cs (μg/g), was calculated using the following formula:

$$C_s = C_i \times V_{tot} / V_e \times V_f / W$$

Where:

C_s = sample concentration (μg/g)

C_i= injection concentration (μg/ml)

V_{tot} = total volume of extraction (ml)

V_e = volume for evaporation (ml)

V_f= final volume (ml)

W = sample weight (g)

Statistical Analyses

Data analysis was performed using SPSS software, version 19.0 (IBM Corporation, Armonk, NY). Descriptive statistics for frequencies, ranges and means were used to summarise the variables of interest.

Results and Discussion

Evaluation by Commodity

Table 1 provides an overview of the data obtained after analysis of 777 samples. Of the 34 commodities tested, 447 (57.5%) had no detectable pesticide residues. While 82 samples (10.5%) exceeded the MRLs, 248 (32.0%) of analysed samples contained pesticide residues below or equal to the level cited in SFDA.FD standard No. 2019/382 “Maximum Limits of Pesticide Residues in Agricultural & Food Products” [16] or Codex Maximum Residue Limits for Pesticide (2019) [17], whichever is lower.

Table 1: Frequency of samples with and without detected pesticides residues and samples containing residues above MRL for fruit and vegetables collected from Riyadh, Saudi Arabia.

Commodity	No. of Samples Analysed	No. of samples without Detectable Residues (%)	No. of Samples ≤ MRL (%)	No. of Samples >MRL (%)
Dates	62	46 (74.2)	8 (12.9)	8 (12.9)
Apple	14	9 (64.3)	4 (28.6)	1 (7.1)
Orange	13	8 (61.5)	4 (30.7)	1 (7.6)
Lemon	24	7 (29.2)	14 (58.3)	3 (12.5)
Mango	16	13 (81.3)	3 (18.8)	0 (0.0)
Grape	19	5 (26.3)	14 (73.7)	0 (0.0)
Pomegranate	21	12 (57.1)	5 (23.8)	4 (19.10
Banana	11	6 (54.6)	5 (45.5)	0 (0.0)
Cantaloupe	31	14 (45.2)	17 (54.8)	0 (0.0)
Watermelon	27	16 (59.3)	10 (37.0)	1 (2.7)
Peach	8	3 (37.5)	5 (62.5)	0 (0.0)
Strawberry	12	3 (25.0)	8 (66.7)	1 (8.3)
Apricot	8	1 (12.5)	7 (87.5)	0 (0.0)
Cherries	7	3 (42.9)	4 (57.1)	0 (0.0)
Guava	10	2 (20.0)	3 (30.0)	5 (50.0)
Onion	42	35 (83.3)	5 (11.9)	2 (4.8)
Eggplant	34	22 (64.7)	11 (32.3)	1 (2.9)
Pumpkin	37	32 (86.5)	5 (13.5)	0 (0.0)
Tomato	37	16 (43.2)	16 (43.2)	5 (13.5)
Potato	36	25 (69.4)	8 (22.2)	3 (8.3)
Cucumber	33	11 (33.3)	18 (54.6)	4 (12.1)
Lettuce	20	13 (65.0)	7 (35.0)	0 (0.0)
Capsicum	21	8 (38.1)	9 (42.9)	4 (19.0)
Garlic	11	11 (100.0)	0 (0.0)	0 (0.0)
Okra	31	21 (67.7)	10 (32.3)	0 (0.0)
Parsley	30	17 (56.7)	5 (16.7)	8 (26.6)
Zucchini	24	14 (58.3)	10 (41.7)	0 (0.0)
Carrot	20	8 (40.0)	12 (60.0)	0 (0.0)
Watercress	23	19 (82.6)	3 (13.0)	1 (4.4)
Mint	23	8 (34.8)	5 (21.7)	10 (43.5)
Coriander	19	8 (42.1)	4 (21.1)	7 (36.8)
Beans	16	9 (56.3)	4 (25.0)	3 (18.7)
Spinach	20	14 (70.0)	4 (20.0)	2 (10.0)
Jute Mallow	17	8 (47.0)	1 (5.9)	8 (47.1)
Total	777	447 (57.5)	248 (32.0)	82 (10.5)

The MRL breached most often was for guava in which 50% of samples were above the limit followed by jute mallow 47.1%, mint 43.5% and coriander 36.8%. There were no breaches in MRL for mango, grape, banana, cantaloupe, peach, apricot, cherry, pumpkin, lettuce, garlic, okra, zucchini and carrot.

Evaluation by Pesticide

In this work, we found that of the 32 different pesticides monitored, 19 exceed the MRL, see Table 2. Acetamiprid was above the limit in 19 samples followed by imidacloprid 11, carbendazim 9, and methomyl 12 samples. The four pesticides accounted for 62.2% of the pesticides violating the MRL. The level of exceedance can be seen in the range exhibited for the aforementioned pesticides. The maximum values for acetamiprid, imidacloprid, carbendazim, and methomyl were 9.885mg/kg, 4.092mg/kg, 2.979mk/kg and 2.917mg/kg respectively. The remaining 14 samples represented 37.8% of the breached residue levels. Results obtained in this study as well as exceeded tolerances are of the same order as other published studies conducted elsewhere [3,5].

Table 2: Pesticides detected in fruit and vegetables from Riyadh, Saudi Arabia.

Pesticide	Mean Value (mg/kg)	Range (min-max)	No. of Detectable Samples	No. of Samples >MRL
Acetamiprid	0.037	<DL[a]- 9.885	45	19
Imidacloprid	0.09	<DL - 4.092	36	11
Carbendazim	0.033	<DL - 2.979	27	9
Methomyl	0.036	<DL - 2.917	12	12
Metalaxyl	0.053	<DL - 1.049	12	2
Pyridaben	0.067	<DL - 2.077	12	1
Indoxacarb	0.013	<DL - 1.089	12	3
Azoxystrobin	0.009	<DL - 1.121	10	2
Difenoconazole	0.044	<DL - 2.051	4	0
Tebuconazole	0.031	<DL - 2.033	8	1
Boscalid	0.012	<DL - 0.766	8	0
Linuron	0.011	<DL - 1.301	10	2
Ethion	0.078	<DL - 1.783	6	4
Metalaxyl-M	0.044	<DL - 1.051	8	2
Chlorpyrifos	0.013	<DL - 2.545	4	1
Thiamethoxam	0.071	<DL - 1.103	5	0
Mycobutanil	0.012	<DL - 1.809	1	0
Hexythiazox	0.043	<DL - 2.127	8	1
Chinomethionat	0	<DL - 0.001	0	0
Biphenyl	0	<DL - O.003	0	0
Phenthoate	0.013	<DL - 1.412	6	3
Quinalphos	0.012	<DL - 2.006	5	4
Pyrimethanil	0.011	<DL - 1.438	5	0
Malathion	0.092	<DL – 0.052	4	1
Bifenthrin	0.007	<DL - 0.909	6	0
Pyriproxyfen	0.097	<DL - 0.029	3	0
Iprodione	0.011	<DL - 0.890	2	0
Oxadiazon	0.025	<DL - 0.601	3	3
λ- cyhalothrin	0.004	<DL - 0.491	4	1
Imazalil	0.054	<DL - 0.220	1	0
Permethrin	0	<DL - 0.012	3	0
Fipronil	0.013	<DL - 0.002	1	0

[a]Detection Limit.

Some of the samples analysed contained multiple pesticide residues. This is common in horticulture especially when cultivation takes place under greenhouse conditions [2]. Different pesticides are applied ineluctably during the growth cycle due to insects, pathogens and pests. Knowledge and training regarding use and best practice and well as legal requirements is lacking [18,19] within developing countries. The need to provide adequate training and practical use for dosing and withdrawal is required. The training must be verified by evaluation methods suitable for the level of delivery and for the objectives required.

Imported Fruit and Vegetables

Figure 1 displays the counties that have exported their produce and is available in the local market in Riyadh at the time of sampling. The pesticides of concern are hexythiazox and carbendazim (from Egypt), carbendazim and quinalphos (from Republic of South Africa), malathion and ethion (from Yemen), acetamiprid and carbendazim (from Turkey) and imazalil (from Italy). A total of 13 samples were detected with MRLs above the regulatory requirements. It is important to note that ethion, acetamiprid, carbendazim and imazalilare banned in Saudi Arabia and thus such products should not be imported in to the country.

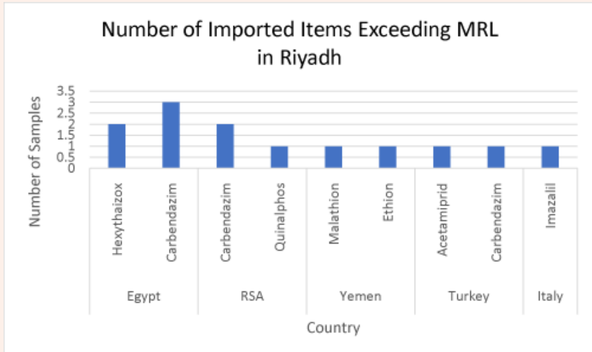

Figure 1: Number of samples exceeding MRL from Exporting country.

The problems experienced with pesticide MRLs are a global problem. They occur in both developing and developed countries [2-5,11]. In order to reduce pesticide residues, a stringent approach to the management of pesticide application, use and regulatory compliance must be implemented and adhered to. Thus, the use Good Agricultural Practice (GAP) standards which incorporate the Hazard Analysis and Critical Control Point (HACCP) scheme is critical for the long-term sustainability of the environment as well as for human health and well-being. We recommend as a minimum the following:

a) Audit schemes that institute programmes for pre-inspection on farm and post-harvest quality assurance

b) Training for all individuals concerned with specified objectives

c) HACCP requirements on farm in line with GAP

d) Elimination of corrupt practices (e.g. falsification of results)

e) Development of public and private partnerships. Such relationships in business provide clear benefits to understanding of issues and assist in alleviating concerns in the supply chain

f) Formulating rigid specifications by importing countries as part of pre-inspection protocols. A clear understanding is needed between importing and exporting bodies as well as importing country legislation by the exporter.

g) Review penalties in the supply chain to act as a deterrent so that compliance is met

Conclusion

This study revealed that 57.5% of samples of fruit and vegetables analysed for pesticide residues contained no residues. Of the remainder, 32.0% contained pesticide residues below or equal to the MRLs stipulated. In addition, 10.5% of samples exceeded the regulatory MRLs. The presence of acetamiprid, imidacloprid, carbendazim, and methomyl accounted for 62.2% of the pesticide violations. Furthermore, imported products from five countries also breached the MRLs and in some cases, with pesticides that have been banned.

Routine monitoring programmes for pesticides of food can assist in the prevention, control and reduction of pollution as well as minimise risks to health. However, more rigid approaches to the management of pesticide along the supply chain are necessary. These include training for all individuals concerned with specified objectives and under different farming circumstances, audit schemes on farm and post-harvest, understanding of legal requirements and specifications in domestic and international trade as well as cooperation between competent authorities and exporting countries.

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