MONITORING OF PESTICIDE CONTAMNATION OF SELECTED LEGUME CROPS IMPORTED IN UAE

ABSTRACT

Food contamination with pesticide residues is a serious concern. In United Arab Emirates, ministry of climate change and environment (MOCCAE) carries out incidence/level monitoring in order to acquire data on the presence and amounts of pesticide residues in particular commodity/chemical combinations. This monitoring aimed to provide the necessary information on quantitative and qualitative pesticide multiresidues in imported legume crops

Sampling plan of 2375 selected legume imported into the UAE has been examined as part of an official surveillance program, these samples include beans, peas, peanuts, lupine and lentils, they were collected from across United Arab Emirates (UAE) ports of entry during 2020 and 2021 by certified staff. These samples were analyzed by modified QuEChERS method for pesticide residue screening based on multi-reaction monitoring (MRM) mode with gas and/or liquid chromatography tandem mass spectrometry for monitoring more than 400 pesticides residues in these legume crops. The method used in this study was validated following the European Commission guidelines achieving good recovery values in the range 70–120% with relative standard deviation values lower than 20% and providing limits of quantification of the method in the low mg/kg range, in accordance with the maximum residue limits set by European policies and CODEX.

The results showed that the majority (98.8%) of legume crops samples analyzed had compliance with the legislation in force in UAE and 29 samples (1.2%) contained residues above MRLs established by the Codex Committee on pesticide residues as well as by the European Union. This monitoring is a part of a surveillance study for pesticide control in food samples.

CONCLUSION: based on the results current monitoring program provide a valuable source of information for estimating dietary exposure of UAE consumers to pesticide residues, and to check compliance with the national maximum residue levels in legume samples.

Keywords: legumes, MRL, monitoring, multiresidue, pesticides, QuEChERS, UAE.

1. INTRODUCTION

“Legumes are plants that belong to the family, *Fabaceae* or *Leguminosae*, very diverse with nearly 20,000 species worldwide, Legumes come in a variety of shapes, colors, and sizes” [1]. They can be found in many formats including dried, canned, cooked, frozen, split, or ground into flour, these legume include beans, peas, peanuts, lentils, and lupines [2]. “According to the FAO, pulse is a type of legume that is exclusively harvested for the dry grain and therefore excludes peanuts and soybeans, which are harvested for their oil”[3]. Pulses are also sometimes referred to as grain legumes or pulse grains. The published literature often refers to the *Phaseolus vulgaris* species; these include kidney beans, haricot beans, pinto beans, and navy beans.

“Legumes has highly nutritious value and they are important sources of protein, carbohydrates, fats and dietary fiber, low glycemic index (GI), rich in potassium, magnesium, and fiber, all nutrients that have a positive impact on blood pressure management” [4] “and can be consumed as food by human beings and animals” [5]. “They are thought to have unique health effects due to their high content of certain phytoestrogens such as isoflavones and other bioactive compounds” [6]. “On account of their high nutritive value, they would play an important role in ensuring nutritional security especially for the developing countries” [7].

“The contamination of legumes with pesticides in various parts of the world has been reported in scientific literature. Many of these literature highlight on the acute and chronic health risks that human beings may be exposed to as a result of the ingestion of legumes polluted with pesticides” [8]. “Pesticides cause short-term health effects including hypersensitivity and mortality, some chronic untoward effects of pesticides are congenital disabilities and neurological damage as well as their persistence in the bionetwork” [9]. To ensure food safety and protect consumer health, international organizations such as the Codex Alimentarius Commission, established by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO), and the European Union (EU), as well as many individual countries have established maximum residue limits (MRLs) to regulate pesticide residue levels in foods.

Nowadays, gas chromatography coupled to mass spectrometry (GC-MS, GC-MS/MS) with electron impact ionization (EI) and liquid chromatography-tandem mass spectrometry (LC-MS/MS) with electrospray ionization (ESI) are techniques most often employed for multiresidue

pesticides analysis in food due to their high sensitivity and selectivity, ability to screen many pesticides from various chemical classes in very complex matrixes in a single run. GC-MS is a method of choice for less polar pesticides; for more polar compounds, LC-MS is more suitable.

As part of keeping imported food under constant control, the pesticide residue monitoring program, a compliance program, is used by the MOCCAE at UAE to monitor the level of pesticide residues in imported foods and to ensure that they do not exceed the allowable limits (MRLs) according to UAE Mandatory Standard (UAE.S MRL 1:2019) by cabinet resolution No. (4) In 2020, held on (2/1/2020). considering this monitoring study will help to generate residue data in establishment of national MRLs. The aim of this work to monitor the level of pesticide residues in consignments of imported legume crops during the period 2020-2021 for the purpose of verifying compliance with national legislation.

2. MATERIAL AND METHODS

Chemicals and standard solutions

Certified reference material (CRM) were purchased from Dr. Ehrenstofer GmbH (Germany), with purity between 92.0 and 99.5%, LC-MS grade acetonitrile (Merk, Germany), methanol (LC-MS CHROMASOLV^{TM}, Ethyl acetate (LC-MS grade, Scharlab) (≥99.9%), Formic acid (Honeywell, Germany). Ready-made QuECHERS kits were purchased from Suplco; Supel™ QuE citrate extraction tube (contains 4.0 g $MgSO_4$, 1.0 g NaCl, 0.5 g NaCitrate dibasic sesquihydrate, 1.0 g NaCitrate tribasic dehydrate), Supel™ QuE PSA/C18 (EN) Tube, 15 mL clean up Tube (contains 150 mg Supelclean PSA, 150 mg Discovery DSC-18, 900.0 mg $MgSO_4$.) The solutions were prepared with Ultrapure demineralized water Milli-Q plus system (Merck-Millipore Corporations, USA).

The monitoring program

2375 of legume samples included beans such as Beans (1170), Peas (165), peanuts (3), lupines (5) and Lentils (1032) were collected as a part of the national monitoring program for pesticide residues. The sampling was performed by authorized personnel across United Arab Emirates (UAE) ports of entry during 2020 and 2021. Samples were mainly taken according to sampling method outlined Codex guidelines to determine pesticide residues to comply with MRLs [10].

All samples barcoded with unique identification numbers, transported to the laboratory and stored at 4ºC until analyzed.

Analytical procedure

Extraction and clean-up of legume crops samples were carried out according QuEChERS method commonly used in the multi-residue analysis of food matrices [10,11] pesticide residues laboratory, Ministry of Climate Change and Environment, UAE with slight modifications. Each sample (approx. 50 g) was ground to powder, precisely 5.0 g of powder was weighed into a 50 mL Teflon capped centrifuge tube, 5.0 mL of Milli-Q water followed by 10 mL of acetonitrile was added, and the mixture was vigorously shaken for 1.0 min. to hydrate the sample. A mixture of 4.0 g MgSO4, 1.0 g NaCL, 0.5 g NaCitrate dibasic sesquihydrate, 1.0 g NaCitrate tribasic dehydrate were added to the extract in the tube, which was agitated for 3.0 min at 500 rpm on a shaker. The sample was centrifuged for 5.0 min at 3,000 rpm and the supernatant was collected. Samples required clean-up to remove any organic acids, polar pigments, and other compounds that could interfere with the analysis. For clean-up, 8.0 mL of the supernatant was pipetted into a 15 mL d-SPE tube packed with 150 mg Supelclean PSA, 150 mg Discovery DSC-18, 900.0 mg $MgSO_4$, the content of the tube was then vortex for 1 min, centrifuged for 5.0 min at 3000 rpm. Finally, for LC-MS/MS analysis, 1.0 mL of the supernatant was collected while GCMSMS analysis, 1.0 mL of supernatant was evaporated at 40 °C until dryness, replaced by ethyl acetate in auto sampler vial for analysis.

Calibration curve:

Individual analytical stock solutions (1000 mg L^{-1}) for each pesticide were prepared considering the purity of each pesticide standard in methanol and ethyl acetate into a 10.0 mL calibrated volumetric flask and made up to 10.0 mL with methanol and ethyl acetate for LC and GC amenable pesticides, respectively and stored in the dark at −20°C. A standard mixed stock solution were prepared in methanol and ethyl acetate to 10 mg L^{-1}. Afterwards, a mixture with the concentration of 10.0 mg L^{-1} containing all pesticides was diluted to 1.0 mg L^{-1}. A stock solution of triphenyl phosphate (TPP) at concentration of 1.0 mg mL^{-1} was used as internal standard. Matrix-matched calibration was prepared using 5 concentration levels of 0.01, 0.02, 0.05, 0.1 and 0.2 mg kg^{-1}which were mixed with an ISTD solution and filled the volume with extracts from blank samples.

Instrumental analysis

- **GC–MS/MS analysis**

GC–MS/MS analysis was performed using Agilent 7890A GC equipped with a 7693B. coupled to a Triple quadrupole (QQQ) mass spectrometer detector 7000 Series with electron impact ionization (EI) equipped with auto sampler (Agilent Technologies, Santa Clara, CA, USA), MSD system (Agilent, USA). An Agilent Ultra Inert GC column, HP-5MSUI, was used to provide a highly inert flow path into the detector. The oven temperature was programmed from 70^0C (hold 3.0min) to 180^0C by a rate of 20^0C/min and finally increased to 300 ^{0}C (hold 2.5 min) by a rate of 5°C/min, the injection volume was 5.0 µL with splitless mode. Helium carrier gas (99.999%) flowed constantly at 0.5mL/min. The mass spectrometry detector (MSD) used electron impact ionization mode (ionization energy 70 eV). The temperature of ion source and quadrupole were set at 250^0C and 150^0C, respectively. The multiple reaction monitoring (MRM) mode with minimum two ions for each pesticide was used for detection and quantification of analyzed pesticides. The Agilent Mass Hunter Workstation software B.07.00SP2was used for data analysis. The analyzed pesticides are presented in Table 1.

- **LC–MS/MS analysis**

Detection and quantification were performed using QTRAP 5500® 5500 LC/MS/MS system (AB SCIEX, Foster City, CA, USA) equipped with an electrospray ionization (ESI) source working simultaneously in both positive and negative modes (ESI+ and ESI−). two ion transitions were selected for analyzed compound, a quantifier and a qualifier MRM. In terms of chromatographic conditions, a column Luna® Omega 3 µm Polar C18 100 Å, LC Column 100 x 2.1 mm, Ea was used and kept at 40^0C, the auto sampler was maintained at 10 ^{0}C to refrigerate the samples and a volume of 5 µL of sample extract was injected in the column. The mobile phase using 0.1% formic acid in ultrapure water as mobile phase [A] and formic acid 0.1% in methanol as mobile phase [B] with a flow rate of 0.5 mL/min. The analyzed pesticides are presented in Table 2

Method validation and Acceptability Criteria

The acceptability of used method for the analysis of target pesticides was validated following the SANTE/2021/11312 guidelines [12]. Linearity was determined using matrix-matched calibration curves with spiked blank samples at five concentrations (0.01, 0.02, 0.05, 0.1 and 0.2 mg kg^{-1}). All coefficients of determination ($R^2 > 0.99$) were acceptable. Recoveries (%) and precisions, in

terms of repeatability and reproducibility, were determined by analysis of blank samples spiked with standard solutions at two concentrations (0.01 and 0.1 mg kg^{-1}), with trueness or mean recovery (accuracy) for tested pesticides all within the acceptable recovery range of 70–120%. The mean RSD less than 10% considered acceptable and fulfill the criteria for quantitative methods [12]. These results indicate that the analytical method applied to this study is appropriate for the analysis of targeted pesticide residues legume crops.

Table 1. list of analyzed pesticides using GCMSMS

Acetamiprid	Chlorpropham	Endosulfan- alpha	Fosthiazate	Omethoate	Pyridaben
Acrinathrin	Chlorpyrifos ethyl	Endosulfan beta	Gamma HCH (Lindane)	Oxadixyl	Pyrimethanil
Aldicarb- sulfone	Chlorpyrifos methyl	Endosulfan Sulfate	Heptachlor	Oxyfluorfen	Pyriproxyfen
Aldrin	Chlorthal-dimethyl	Endrin	endo epoxide	Paclobutrazol	Quinoxyfen
Atrazine	Cyfluthrin	Ethion	Hexaconazole	Paraoxon methyl	Tebufenpyrad
Azinphos methyl	Cyhalothrin Lambda	Ethoprophos	Imazilil	Parathion ethyl	Tecnazene
Azoxystrobin	Cypermethrin	Fenamiphos	Indoxacarb	Parathion methyl	Tefluthrin
Bifenthrin	Cyproconazole	Fenarimol	Iprodione	Penconazole	Tetraconazole
Bitertanol	DDD 4,4	Fenazaquin	Iprovalicarb	Pencycuron1	Tetradifon
Boscalid	DDE 4,4	Fenitrothion	Isofenphos methyl	Pendimethalin	Thiabendazole
Bromopropylate	DDT 2,4	Fenoxycarb	Kresoxim methyl	Permethrin	Tolclofos methyl
Bromuconazole	DDT 4,4	Fenpropathrin	Lenacil	Phosalone	Tolyfluanid
Bupirimate	Deltamethrin	Fenpropimorph	Linuron	Pirimicarb	Triadimefon
Buprofezin	Diazinon	Fenthion	Metalaxyl	Pirimiphos-Methyl	Triazophos
Cadusafos	Dichlofluanid	Fenvalerat I	Metconazole	Prochloraz	Trifloxystrobin
Carbaryl	Dichlorvos	Fenvalerate II	Methiocarb	Procymidone	Trifluralin
Carbofuran	Dicloran	Fipronil	Methoxychlor	Profenofos	Triticonazole
Chlordane cis (alpha)	Dicrotophos	Fludixonil	Metribuzin	Propargite	Vinclozolin
Chlordane trans (gamma)	Difenoconazole	Fluquinconazole	Monocrotophos	Propoxur	Zoxamide
Chlorfenapyr	Dimethoate	Flusilazole	Myclobutanil	Prothiophos	
Chlorfenvinphos	Dimethomorph	Flutriafol	Nonachlor cis	Pyraclostrobin	
Chlorobenzilate	Diphenylamine	Folpet	Nonachlor trans	Pyrazophos	

Table 2. list of analyzed pesticides using LCMSMS

Abamectin	Bromacil	Dimethenamid	Etrimfos	Isocarbophos	Methamidophos	Propamocarb
Acephate	Bromoxynil	Dimethoate	Famoxadon	Isofenphos	Methiocarb	Propanil
Acetamiprid	Bromucanozole	Dimethomorph	Fenamidone	Isoprocarb	Methiocarb sulfone	Propaquizafop
Acibenzolar-S-methyl	Bupirimate	Dimoxystrobin	Fenamiphos	Isoproturon	Methomyl	Propargite
Alachlor	Buprofezin	Diniconazole	Fenarimol	Isoxadifen-ethyl	Methoprotryne	Propazine
Alanycarb	Butafenacil	Dinotefuran	Fenazaquin	Ivermectin	Methoxyfenozide	Propetamphos
Aldicarb	Butocarboxim	Dioxacarb	Fenbuconazole	Kresoxim-methyl	Metobromuron	Propham
Aldicarb sulfone	Butoxycarboxim	Dioxathion	Fenhexamid	Lenacil	Metribuzin	Propiconazole
Aldicarb sulfoxide	Buturon	Diuron	Fenobucarb	Linuron	Mevinphos	Propoxur
Ametryn	Cadusafos	Emamectin-benzoate	Fenpiclonil	Lufenuron	Mexacarbate	Propyzamide
Aminocarb	Carbaryl	Endosulfan Sulfate	Fenpropathrin	Malaoxon	Molinate	Prosulfocarb
Azaconazole	Carbendazim	EPN impurity	Fenpropimorph	Malathion	Monocrotophos	Prothioconazole
Azinphos ethyl	Carbetamide	Epoxiconazole	Fenpyroximate	Mandipropamid	Monolinuron	Pymetrozine
Azinphos methyl	Carbofuran	Eprinomectin	Fenthion	Mecarbam	Monuron	Pyracarbolid
Azoxystrobin	Carbofuran 3 hydroxy	EPTC	Fenuron	Mefenacet	Moxidectin	Pyraclostrobin
Beflubutamid	Carboxin	Etaconazole	Fipronil	Mefenpyr-diethyl	Myclobutanil	Pyraflufen-ethyl
Benalaxyl	Carfentrazone-ethyl	Ethiofencarb	Flamprop-methyl	Mepanipyrim	Napropamide	Pyrazophos
Bendiocarb	Chlorantraniliprole	Ethion	Flonicamid	Mepronil	Neburon	Pyridaben
Benfuracarb	Chlorfluazuron	Ethiprole	Fluazifop-butyl	Mesotrione	Nitenpyram	Pyrifenox
Benomyl	Chloridazon	Ethirimol	Fluazinam	Metaflumizone	Novaluron	Pyrimethanil
Benzoximate	Chloroxuron	Ethofumesate	Flubendimide	Metalaxyl	Nuarimol	Pyriproxyfen
Bifenazate	Chlorpyrifos ethyl	Ethoprophos	Fludioxonil	Metamitron	Ofurace	Pyrudaphenthion
Bifenthrin	Chlortoluron	Ethoxyquin	Flufenacet	Metazachlor	Omethoate	Quinoxyfen
Bitertanol	Clethodim	Etofenprox	Flufenoxuron	Metconazole	Oxadiazon	Quizalofop-ethyl

Table 2. Cont.

Boscalid	Dichlofluanid	Formetanate	Methabenzthiazuron	Pirimicarb	Spiroxamine	Thiobencarb
Clodinafop-propargyl ester	Dichlorvos	Fosthiazate	Oxadixyl	Pirimiphos-ethyl	Sulfentrazone	Thiodicarb
Clofentezine	Diclobutrazol	Fuberidazole	Oxamyl	Pirimiphos-Methyl	Sulfotep	Thiofanox
Clomazone	Dicloran	Furalaxyl	Oxyfluorfen	Prochloraz	Tebuconazole	Thiophanate-methyl
Clothianidin	Dicrotophos	Furathiocarb	Paclobutrazol	Profenofos	Tebufenozide	Tolyfluanid
Coumaphos	Diethofencarb	Halofenozide	Paraoxon ethyl	Promecarb	Tebufenpyrad	Triadimefon
Cyanazine	Difenoconazole	Heptenophos	Paraoxon methyl	Prometon	Tebutam	Triadimenol
Cyazofamid	Diflubenzuron	Hexaconazole	Penconazole	Prometryne	Tebuthiuron	Tri-allate
Cycloxidim	Diflufenician	Hexaflumuron	Pencycuron	Propachlor	Teflubenzuron	Triazamate
Cycluron	Etoxazole	Hexazinone	Pendimethalin	Rotenone	Temephos	Triazophos
Cymoxanil	Fluometuron	Hexythiazox	Permethrin	Secbumeton	Terbumeton	Trichlorfon
Cyproconazole	Fluoxastrobin	Hydramethylnon	Phenmedipham	Siduron	Terbutryne	Tricyclazole
Cyprodinil	Fluquinconazole	Imazalil	Phenthoate	Silthiofam	Tetrachlorvinphos	Tridemorph
Cyromazine	Flusilazole	Imidacloprid	Phosalone	Simazine	Tetraconazole	Trifloxystrobin
Deltamethrin	Flutolanil	Indoxacarb	Phosmet	Simetryn	Tetramethrin	Triflumizole
Demeton S methyl	Flutriafol	Ipconazole	Phosphamidon	Spinetoram	Thiabendazole	Triflumuron
Demeton S methyl sulfone	Foramsulfuron	Iprobenfos	Picolinafen	Spinosad	Thiacloprid	Triticonazole
Desmedipham	Forchlorfenuron	Iprodione	Picoxystrobin	Spirodiclofen	Thiamethoxam	Uniconazole
Diazinon	Dichlofluanid	Iprovalicarb	Piperonyl butoxide	Spirotetramat	Thidiazuron	Vamidothion
						Zoxamide

Quality Assurance:

The pesticide residues laboratory was audited as part of a laboratory quality assurance system by UKAS (United Kingdom Accreditation Service).and its accreditation status to the ISO/IEC 17025:2017 standard was confirmed and extended. The pesticides in the scope of the accreditation may be viewed on the United Kingdom Accreditation Service website at 2572Testing Multiple (ukas.com).

The method is applicable for determination of pesticide residues in legume samples with high starch and/or protein content and low water and fat content. The average recoveries of these pesticides at different concentration levels varied between 70-120 %. The reproducibility expressed as relative standard deviation was less than 25%. The limit of quantification started at 0.01 $mg\ kg^{-1}$ and up depending on the pesticide type and detection module. The measurement uncertainty expressed as expanded uncertainty and in terms of relative standard deviation (at 95 % confidence level) is lower than the default value set by the EU (± 50 %). Blank samples were fortified with the pesticides mixture and analyzed as a normal sample with each set of samples. The results were recorded on control charts. Repeated analysis of old samples was regularly carried out to control reproducibility.

Trueness Inter-Laboratory Comparison Proficiency Tests:

The method trueness was confirmed by participation in Inter-Laboratory comparison with Food Analysis Performance Assessment Scheme (FAPAS) at the Food and Environment Research Agency. Proficiency test were analyzed using the developed method. The z-scores were calculated by FAPAS laboratory using the spike level as true. In all cases z-score are below 2 and this met requirements of the organization. The result supported accuracy of the improved method for quantification of pesticides.

3. RESULTS AND DISCUSSION

The food supply is monitored to check compliance with national legislation for pesticide residues in food and ensure consumers are not being exposed to concentrations of pesticides that are harmful to their health. Unexpected residues can occur through deliberate misuse; the illegal use of allowed or banned pesticides; the use of sub-standard or counterfeit pesticide formulations; or

contamination from various sources including spray drift from adjacent fields and transfer during storage and/or packing. The monitoring strategy consisting of the random sampling of food commodities; and an enforcement strategy involving the sampling of food commodities or specific sources where non-compliance with pesticide legislation was suspected or had been detected previously. The current monitoring pesticide residues from each shipment of legumes for any food safety risks and rejecting any unfit shipment for this purpose.

A total of 2375 samples from imported legumes in UAE were analyzed for pesticide residues during monitoring period for up to 400 pesticides, the pesticides to be examined were selected based on the list of registered agricultural pesticides authorized in the UAE and the list of prohibited compounds in the country, developed by the Ministry of Climate Change and Environment. Samples were analyzed for pesticide residues at national laboratories, ministry of climate change and environment (pesticide residues laboratory has continued to maintain and extend its accreditation status with the National Accreditation Body for the United Kingdom (UKAS).

Monitoring results in analyzed samples:

The objective of pesticide current monitoring programme is to ensure that imported legumes shipments comply with the maximum residue levels (MRLs) allowed under the mandatory UAE standard (UAE). MRL S 1:2019), and in cases where a pesticide is not authorized to use or exceeds the permissible limit, tighten control over pesticides that are not allowed to be used or above the permissible limit rejecting any unfit shipments for this purpose. Moreover, the combination of monitoring data with food consumption data provides exposure estimate that can be used in toxicological appreciation.

The total 2375 selected and examined imported legume samples were analyzed within current monitoring programme. from 2094 analyzed legume samples (88.16%), showed no detectable residues, while pesticide residues were detected in 281 samples (11.83%); the overall compliance with the legislation in force was 2346 samples (98.77 %). The 29 samples (1.22%) contained residues above MRLs established by the Codex Committee on Pesticide Residues [13], as well as by the European Union [14] as shown in Table 3.

Table 3. Summary of Results of analyzed samples during monitoring program

Commodity	Sample Analyzed	Free Samples	Contaminated Samples		No. of Samples Within MRL		No. of Samples Above MRL	
			No.	%	No.	%	No.	%
Beans	1170	1081	89	7.6	78	66.67	11	0.94
Peas	165	30	135	81.81	119	72.12	16	9.69
Peanuts	3	2	1	33.33	1	33.33	0.0	0
Lupin	5	4	1	20	1	20	0.0	0
Lentils	1032	977	55	53.32	53	51.35	2	0.019
Total	2375	2094	281		252		29	
%		88.16		11.83		10.61		1.22

Out of 1170 beans samples analyzed, 7.60% were found contaminated with pesticide residues, and about 0.94% of the total contaminated samples contained pesticide residues above the maximum permissible limit, while the remaining 92.39% did not contain any pesticide residue. A percentage of 18.18% on 165 peas samples showed no trace of residues and 72.12% had quantifiable pesticide levels, but lower than MRLs. A further percentage of 9.69% was associated with samples containing residues above MRLs.

The 1032 lentils samples analyzed showed, 94.67% to be compliant and associated with non-quantifiable residue levels. A percentage of 5.13% showed residue contents higher than the quantification limits but lower than the MRL, two samples contained pesticides at concentrations above MRLs.

The analyses performed on 3 samples of Peanuts showed a percentage of 66.66% for the residue-free samples, 33.33% with residues below the MRLs was detected in one peanut sample and no residues of the pesticides had detected higher residues than the corresponding MRLs.

According to pesticide residues observed in the lupine samples, 20% (1 out of 5 samples) containing pesticide residues below MRLs and no residues had detected higher residues than the corresponding MRLs laid down by CODEX and EU. “Previous literature reveals that legumes are more susceptible to pest infestation; these are likely to be contaminated with certain chemical pesticides right from the crop growth to grain storage which may affect the food safety” [15]. legumes are usually stored for long periods in warehouses where various pesticides are intensively and successively applied many times resulting in their bioaccumulation. Many studies have shown that pesticide residues penetrate the grains and accumulate over time, thus indirectly exceeding the recommended doses. High amounts of organophosphorus pesticide residues were found in stored cowpea and two by-products [16], revealing a potential human dietary risk related to consumption of these grains. The most contaminated commodity was pea

samples (9.69%) containing residues above MRLs. mainly chickpea which consider one of the widely consumed pulses in many countries. It is used in preparing a variety of snacks, sweets and condiments. Fresh green seeds are also consumed as green vegetable. **MRL Exceedances and Detection Frequencies of Pesticides in Analyzed Samples**

The Exceedances detected pesticides, frequency and Status of registration for each crop analyzed under monitoring programs are presented in Table 4. The residue concentration is referred to the maximum residue limits (MRLs) of the Codex Committee on Pesticide Residues (CODEX MRLs) and EU which is adopted and applied in UAE. The results revealed that 20 pesticides were detected in the analyzed legume samples above the permissible limits, referring to the number of pesticide residues detected exceed the permissible limits were black-eyed bean samples (6), Toor dal/yellow pigeon peas (5), Chickpeas (5), Chickpeas Black (3), Chickpeas White (2), Moong dal (2), while the following samples only one pesticides in each above the limit Chana Dal / Split Chickpeas, Matar Dal/ split peas, Yellow split peas, Soybean, Fava Beans, Moong whole, Green whole Lentils, Urad dal. As shown in Table 4 in pea samples 18 different pesticides were detected, Fenpropathrin was the most frequency (8) of total samples analyze which were at the same time above the permissible limits (0.01 mg Kg^{-1}) as the following, in yellow pigeon pea samples the pesticide residues were 0.04-0.378 mg Kg^{-1} with average 0.209 mg Kg^{-1}. In Chick-peas two samples the pesticide residues were 0.05-0.2 mg Kg^{-1} with average 0.125 mg Kg^{-1}. In Chickpeas White, Fenpropathrin monitored only in one samples with the residues 0.08 mg Kg^{-1}. Also in Chickpeas Black, monitored with the residues 0.05 mg Kg^{-1}.

Chlorpyrifos with frequency (10) of total samples analyze and (5 out of 10) were detected above the permissible limits 0.01 mg Kg^{-1}. The results indicate that 1 out 4 of yellow pigeon pea sample (0.04 mg kg^{-1}) violated the MRL, in Chickpea sample (0.1 mg kg^{-1}) above the permissible limits. All the analyzed white chick pea samples contaminated (0.07-0.16 mg Kg^{-1}) with the average (0.115 mg Kg^{-1}), also in Black chick pea (0.05mg Kg^{-1}).Pirimiphos-Methyl with the frequency (3) of total samples analyze and (2 out of 3) were detected above the permissible limits in yellow pigeon peas (0.04-0.378 mg Kg^{-1}) and Chick-peas (0.04 mg Kg^{-1}), moreover, (5) samples contaminated with Acephate, Bitertanol, Dimethoate, Myclobutanil and Phenthoate 0.04, 0.48, 0.09, 0.22 and 0.15 mg Kg^{-1}, respectively which were at the same time above the permissible limits (0.01 mg Kg^{-1}), Malathion (0.1 mg Kg^{-1}) was monitored in Chickpeas Black

within the limits of the permissible (2 mg Kg^{-1}). Previous studies mentioned that, pesticide "Chlorpyrifos is one of the world's most widely used organophosphorus pesticides for various applications including grain storage system. The use of chlorpyrifos has been restricted in UAE, US and some European countries but it is still in use in some developing countries. Also during a survey in National Capital Region (NCR) in 2009, it was found that chlorpyrifos is the most consumed pesticides" [17].

Table 4. Summary of MRL Exceedances and Detection Frequencies of Pesticides in Analyzed Samples.

Commodity	No. of samples over MRLs	Pesticide Detected	Freq.	No. of pesticides over MRLs	Pesticide residue $mgKg^{-1}$	Average $mgKg^{-1}$	MRL $mgKg^{-1}$	*Status of registration
Toor dal/yellow pigeon peas	5	Fenpropathrin	4	4	0.04-0.378	0.209	0.01	Banned
		Pirimiphos-Methyl	2	1	0.16	0.16	0.01	Banned
		Chlorpyrifos	4	1	0.04	0.04	0.01	Restricted
Chick-peas	5	Acephate	1	1	0.04	0.04	0.01	Banned
		Acibenzolar-S-methyl	1		0.01	0.01	0.01	Unregistered
		Bitertanol	1	1	0.48	0.48	0.01	Unregistered
		Chlorpyrifos	3	1	0.01-0.1	0.06	0.01	Restricted
		Dimethoate	1	1	0.09	0.09	0.01	Banned
		Fenpropathrin	2	2	0.05-0.2	0.125	0.01	Banned
		Myclobutanil	1	1	0.22	0.22	0.01	Banned
		Pirimiphos-Methyl	1	1	0.04	0.04	0.01	Banned
		Thiamethoxam	1		0.01	0.01	0.04	Allowed
Chickpeas White	2	Chlorpyrifos	2	2	0.07-0.16	0.115	0.01	Restricted
		Phenthoate	1	1	0.15	0.15	0.01	Banned
		Fenpropathrin	1	1	0.08	0.08	0.01	Banned
Chickpeas Black	3	Chlorpyrifos	1	1	0.05	0.05	0.01	Restricted
		Fenpropathrin	1	1	0.05	0.05	0.01	Banned
		Malathion	1		0.1	0.1	2	Banned
Chana Dal / Split Chickpeas	1	Carbendazim	1	1	0.22	0.22	0.1	Banned
		Thiophanate-methyl	1	1	0.533	0.533	0.1	Banned
		Lufenuron	1	1	0.05	0.05	0.01	Allowed
Matar Dal/ split peas	1	Fenpropathrin	1	1	0.1	0.1	0.01	Banned
Yellow split peas	1	2-Phenylphenol	1	1	0.06	0.06	0.01	Unregistered
Black-eyed bean	6	Acetamiprid	1		0.02	0.02	0.15	Allowed
		Carbaryl	3	3	0.13-1.566	0.767	0.05	Banned
		Chlorpyrifos	2	2	0.04-0.067	0.053	0.01	Restricted
		Dimethoate	1	1	0.02	0.02	0.01	Banned
		Fenpropathrin	2	2	0.045-0.085	0.065	0.01	Banned
		Malathion	2		0.03-0.341	0.185	2	Banned
		Methomyl	1		0.02	0.02	0.05	Banned
Soybean	1	Imidacloprid	1		0.03	0.03	3	Restricted
		Propiconazole	1		0.02	0.02	0.07	Allowed
		Tebuconazole	1		0.06	0.06	0.15	Allowed
		Thiamethoxam	1	1	0.2	0.2	0.04	Allowed
		Tricyclazole	1	1	0.09	0.09	0.01	Banned
		Tridemorph	1	1	0.4	0.4	0.02	Unregistered
Fava Beans	1	Metalaxyl	1	1	0.05	0.05	0.02	Allowed
Moong whole	1	Indoxacarb	1	1	0.05	0.05	0.001	Allowed
Moong dal	2	Acetamiprid	1	1	0.18	0.18	0.01	Allowed
		Fluthiacet-methyl	1	1	0.13	0.13	0.01	Banned
Green whole Lentils	1	Chlorpyrifos	1	1	0.1	0.01	0.01	Restricted
		Fenpropathrin	1	1	0.04	0.04	0.01	Banned
Urad dal	1	Chlorpyrifos	1		0.09	0.09	0.01	Restricted
		Fenpropathrin	1	1	0.08	0.08	0.01	Banned
		Thiacloprid	1	1	0.05	0.05	0.01	Restricted

*Status of registration according to List of registered pesticides in the Ministry (MOCCAE)-Last update 17 -11- 2021[18].

In all 1170 examined bean samples, 15 different pesticide residues were monitored as shown in Table 4, Carbaryl was the most frequency (3) of total samples analyze (0.13-1.566 mg Kg^{-1}) which were at the same time above the permissible limits (0.05 mg Kg^{-1}), followed by Fenpropathrin with frequency (2) of total analyzed samples (0.045-0.085 mg Kg^{-1}) and above the permissible limits (0.01 mg Kg^{-1}), Chlorpyrifos (0.04-0.067 mg Kg^{-1}) in analyzed black eye bean samples violated the MRL (0.01 mg Kg^{-1}). Dimethoate detected in black eye bean sample with the residue (0.02 mg Kg^{-1}) above the permissible limits (0.01 mg Kg^{-1}). At the same time results mentioned that Thiamethoxam, Tricyclazole, Tridemorph and Metalaxyl all detected with the concentration 0.2, 0.9, 0.4 and 0.05 mg Kg^{-1}, respectively and at the same time all above the permissible limits. On the other hand, residues of 5 pesticides were detected within the permissible limits each with the frequency (1 samples) as follows Methomyl, Imidacloprid, Propiconazole, Tebuconazole with 0.02, 0.03, 0.2,. 0.06 and 0.02 mg Kg^{-1}, respectively.

With regard to pesticide residues observed in lentil samples (1032), the number of contaminated samples detected above the permissible limits was negligible, as only two samples contained pesticides above the permissible limits as mentioned (Table 4). Fenpropathrin was detected in Green whole Lentils and Urad dal with residues 0.04 and 0.08 mg Kg^{-1}, respectively) and at the same time all above the permissible limits (0.01 mg Kg^{-1}).

Moreover, in beans samples (1170), five different pesticide residues were monitored, Tebuconazole, Indoxacarb, Metalaxyl Thiamethoxam and Acetamiprid are allowed / registered and authorized for use in accordance with UAE regulations of banned and restricted pesticides as mentioned in Table 4. At the same time monitoring program detected residues of 7 banned pesticides mainly Carbaryl, Fenpropathrin, Fluthiacet-methyl, Tricyclazole, Malathion, Dimethoate and Methomyl according to UAE regulations of banned and restricted pesticides.

Restricted pesticides Chlorpyrifos, Propiconazole and Imidacloprid were monitored all within the permissible limits. While, Tridemorph observed above the permissible limits, which is currently unregistered in the UAE regulations of banned and restricted pesticides.

Same context in peas samples (165), observed 16 samples (9.690%) were contained pesticide residues above the permissible limits. the following banned pesticides were detected Fenpropathrin, Pirimiphos- Methyl, Acephate, Dimethoate, Myclobutanil, Phenthoate, Carbendazim, Thiophanate-methyl and Malathion, all above the permissible limits except Malathion within the limit. Only Chlorpyrifos, restricted for use was observed in the total

samples analyzed (10). Referring to Table 4, Bitertanol and 2-Phenylphenol that are not registered for use in the UAE, were detected and all above the permissible limits. Except Lufenuron and Thiamethoxam were monitored, which is currently authorized in the UAE to use, Lufenuron was above the permissible limits.

Contaminated lentil samples (1032) was negligible (2), Fenpropathrin (banned pesticide) monitored only in two samples (0.04 and 0.08 mg Kg^{-1})with concentration above the permissible limits (0.01 mg Kg^{-1}). The results demonstrates the miss use of pesticides where most of the detected pesticide residues are either not registered for use on the crop contaminated with it or not registered for use at all in the country. These can be justified by lack of Good Agricultural Practices (GAP) leading to appropriate applications of pesticides by farmers, because of insufficient training and deficient assistance from agricultural extension agents, hence the necessity of actions to be taken by regulatory authorities to regulate usage of agrochemicals in the country.

Co-occurrence of Multiple Pesticide Residues

Multiple pesticide residues (up to sex in a single sample) were detected from analyzed legume samples, as shown in Table 5

Table 5. The number of analyzed samples, contaminated, having 1, 2 and more than two pesticides

Commodity	Sample Analyzed	Contaminated Samples	No. of samples with one pesticide		No. of samples with two pesticides		No. of samples with more than two pesticides	
			No.	%	No.	%	No.	%
Beans	1170	89	65	73.03	13	14.60	11	12.35
Peas	165	135	108	80.0	20	14.81	7	5.18
Peanuts	3	1	0.0	0.0	1	33.33	0.0	0.0
Lupin	5	1	0.0	0.0	1	20.0	0.0	0.0
Lentils	1032	55	43	78.18	6	10.9	6	10.90
Total	2375	281	216		41		24	
%		11.83		76.86		14.59		8.18

In bean samples, 73.03% (65) of the analyzed samples contained residues of one insecticide while two pesticides were detected in 14.60% (13) of samples and 12.35% (11) contained three or more different types of pesticide residues, Additionally, beans were the crop with highest

number of samples with multiple residues, compared with peas and lentils. The multiple residues were found most frequently in soybean and black-eyed bean) have contamination of more than two pesticide residues including Acetamiprid, Carbaryl, Chlorpyrifos, Dimethoate, Fenpropathrin, Imidacloprid, Profenofos, Propiconazole, Tebuconazole, Thiamethoxam, Tricyclazole and Tridemorph indicating the co-occurrence of multiple pesticide residues in bean samples. Similar results have been detected in lentils 10.90% (6) samples contained 6 different pesticides including Chlorpyrifos, Thiamethoxam, Tolclofos-methyl, Deltamethrin, Imidacloprid and Piperonyl butoxide. The occurrence of multi-residue pesticide contamination in different commodities has also been reported in other investigations [19, 20, 21] mentioned occurrence of multiple residues is likely to be a consequence of the application of different types of pesticides to protect a crop against different insect pests and diseases, where the incidence of pests can be extremely high. Consequently, a follow-up investigation is needed to determine risk assessment for multiple residues.

4. CONCLUSION

This monitoring program quantified the amount pesticide residues in imported some legume crops, which indicated that regulation of pesticide maximum residue limits (MRLs) fully enforced in UAE. Risks were mainly associated with the residues of pesticides. Due to multiple pesticide residues exceeding the MRLs for single residue concentrations, the consumers are exposed to pesticides.

Data obtained from this monitoring program is considered important source of information for estimating the potential health risks associated with the exposures to these pesticides' contaminants since it is based on fully validated and accredited analytical procedures, and it provides accurate data related to 2375 samples of widely consumed legume types.

The results from this monitoring program, are a valuable source of information for estimating dietary exposure of UAE consumers to pesticide residues and to contribute to the knowledge of food pesticide contamination. Moreover, it is providing information that makes it possible to take the appropriate measures to reduce health risk potential.

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