

MONITORING OF PESTICIDE MULTI RESIDUES IN SELECTED CEREALS CROP GRAINS IN UNITED ARAB EMIRATES

ABSTRACT

Assessing the contamination of cereals and their manufactured products with pesticide residues is a topic of global importance, and monitoring studies are needed to analyze multiple residues at trace levels. Current study was conducted to monitor pesticide residues in various cereals (corn, oats, rice, barley, sorghum and wheat) imported into the UAE as part of official surveillance. A total of 1,440 samples were collected during 2020 and 2021.

Modified QuEChERS method for pesticide residue screening based on multi-reaction monitoring (MRM) mode with advanced gas and/or liquid chromatography tandem mass spectrometry were optimized for monitoring 400 pesticides residues in cereals, and the method was validated for oats, rice, barley and corn matrices, 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 to the maximum residue limits set by European policies and CODEX.

Results from monitoring showed that among the Cereals Grains samples, 903 samples (62.7%) were free from detectable residues, while 419 samples (29.09%) contained residues and 121 samples (8.4%) had residues exceeded the MRLs allowed by the EU legislation and/or CODEX. Tricyclazole, Thiamethoxam, Carbendazim and Buprofesin were the most frequently detected exceeded the MRLs in samples.

Keywords: Cereal grains, MRL, Monitoring, Multi residue, Pesticides, QuEChERS, UAE.

INTRODUCTION

“Cereals are annual grasses grown for their grain. They include wheat (*Triticum aestivum*), durum wheat (*Triticum durum*), barley (*Hordeum vulgare*), oats (*Avena sativa*), rye (*Secale cereale*), triticale (cross between durum wheat and rye), maize (*Zea mays*), sorghum (*Sorghum bicolor*), rice (*Oryza sativa*) and common millet (*Panicum milaceum*). Cereal crops besides being an important global product and part of the human diet, it is a source of energy, essential fatty acids, nutritious proteins and dietary fiber. Grains also provide important minerals, vitamins and other micronutrients needed to maintain optimal health” [1].

“In 2020, cereals production for World was 2,996 million tons. Cereals production of World increased from 1,299 million tons in 1971 to 2,996 million tons in 2020 growing at an average annual rate of 1.79%”. [2]. “Among cereals, rice is one of the world's three main grains and serves as a staple food for nearly half of the world's population Global rice consumption has seen a slight increase over the past few years. In the 2021/2022 crop year, about 509.87 million metric tons of rice were consumed worldwide” [3].

Cereals constitute one of the most important imports of the UAE from agricultural food crops, starting with wheat and barley, passing through corn and rice, and ending with oats. In addition to the domestic consumption of grain and flour, Wheat milling, and package is driven by both re-export demand and local consumption. In 2020, cereals import quantity for United Arab Emirates was 3.2 million tons, wheat imports quantity was 1,500 thousand tons, rice imports quantity was 900 thousand tons, barley imports quantity was 470 thousand tons, maize imports quantity was 600 thousand tons [4].

“Pesticide residue levels and risk monitoring are important aspects of agricultural product quality in many countries. The consumption of pesticide-contaminated food product may become potential health risk for human body. Some investigations illustrate that pesticide via polluted agricultural crops may cause toxicity” [5], “Moreover, it may be associated with chronic illnesses such as cancers, genetic mutation, and blood and reproductive disorders” [6]. “These negative effects indicate that extensive studies on agricultural products are necessary, and the World Health Organization (WHO) considers them as a severe public health problem”. [7].

“Pesticide application to cereal crops is regulated by international organizations, and maximum residue levels (MRLs) are set for each pesticide/commodity combination to reduce the levels of harmful pesticides. In the EU, if no substantive MRL has been set, a default MRL value of 0.01 mg/kg is usually applied” [8].

“Different guidelines have been established around the world, restricting the pesticide residues in food, as a way to ensure the safe consumption of food by the population [9], so governments and agencies establish national pesticide MRLs (Maximum Residue Limits (CODEX ALIMENTARIUS FAO-WHO)”. “MRLs [6], that are specified by each country’s federal legislation for each analyte and matrix These legislations also establish the interval of the safety of each active pesticide ingredient for each crop”.

“The MRL is an index that represents the highest concentration (expressed in mg kg⁻¹) of pesticide or related residues (metabolites and coadjutants) residue that is legally allowed or accepted in a food or animal feed after the use of pesticides according to standards set by various regulatory bodies, to minimize consumer exposure to harmful or unnecessary pesticide ingestion around the world. A consumer exposure is of concern if the estimated dietary exposure to a pesticide exceeds the ADI” [10].

“Considering the potential health risks of contaminated cereals crop grains, it is necessary to monitor the concentration of pesticides cereals periodically, and to create strict rules and regulations for proper use of pesticides”, [11, 12],

In this regard, the surveillance program is designed to enable the regulatory authorities to check that pesticides are being found at levels, as expected, under the MRLs. This confirms that the regulatory processes are working correctly. In addition, checks that dietary intakes of residues are within acceptable limits. Also, consider as a key tool to verify that no unexpected residues occur in crops (this supports the legal approvals process for pesticides)

The Gulf Food Rapid Alert System (GCC-RASFF) aims to facilitate and accelerate the exchange of information between the relevant government agencies of the GCC regarding reports and warnings related to food safety and surfaces in contact with food, to prevent the entry of foodstuffs that pose a risk to consumer health into the markets and to take the necessary

preventive measures either by retrieving them or withdrawing them from the markets to ensure that consumer health is protected from unsafe food (Regulatory Regulations for Rapid Alert System for Food and Feed for Gulf Cooperation Council Countries (GCC-RASFF based on The unified food system (law) of the countries of the Cooperation Council for the Arab States of the Gulf).

The UAE Ministry of Climate Change and Environment (MOCCA) implements the National Pesticide Residue Monitoring Program in both export consignments, which includes the collection of representative samples from each shipment prior to export "The result of the residue test is compared with the maximum limits of the national residue" and also local compliance samples in addition to the examination of imported consignments, in which based on the risk statement, the commodity is allowed to enter the country according to test results.

The results of this monitoring represent proven scientific facts that can be relied upon in taking action, decisions and legislation to enhance the safety and quality of foodstuffs traded in the UAE market, in addition to providing a reference database for the concerned national authorities in this regard. The research reviews the results of monitoring the level of pesticide residues in imported grain consignments during the period 2020-2021 and comparing them with the maximum permissible limits of pesticide residues for the purpose of verifying compliance with national legislation.

MATERIALS AND METHODS

Chemicals and standard solutions

Certified reference material (CRM) were purchased from Dr Ehrenstorfer GmbH (Germany), with purity between 92.0 and 99.5%, LC-MS grade acetonitrile (Merk, Germany), methanol (LC-MS CHROMASOLV™, Ethyl acetate (LC-MS grade, Scharlab) ($\geq 99.9\%$), Formic acid (Honeywell, Germany). Ready-made QuEChERS kits were purchased from Suplco; Supel™ QuE citrate extraction tube (contains 4.0 g MgSO₄, 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 MgSO₄.) The solutions were

prepared with Ultrapure demineralized water Milli-Q plus system (Merck-Millipore Corporations, USA).

Sampling

The samples were collected and analyzed within UAE pesticide residue monitoring programs. In this study, 1,440 grain samples of cereal crops (rice, wheat, oats, barley, corn, bulgur, millet, harees and quinoa) were collected across United Arab Emirates (UAE) ports of entry during 2020 and 2021 by certified staff. Samples were taken using the sampling method outlined Codex guidelines to determine pesticide residues to comply with MRLs [13], At least 1.0 kg of grain sample is taken from a shipment, stamped with unique identification numbers of the samples and brought to pesticide residues laboratory, National Laboratories Department, ALAin, Ministry of climate change and environment

Analytical procedure

“The complexity of cereal matrices owing to their dry nature and fat content makes necessary some modifications in the original QuEChERS method in order to achieve a good extraction efficiency and avoid co-extracted compounds” [14, 15]. “In this case, the addition of water swells the sample and facilitates the access of ACN and, consequently, improves analyte recovery” [16]

To extract multi-classes pesticide residues from high-fat matrices such as cereal crops (rice, wheat, oats, barley, corn, millet and quinoa) and their processed products samples, briefly, 5.00 ± 0.05 g of milled sample were weighted accurately in a 50 mL polypropylene PP tube, 250ng g^{-1} of TPP solution added. Ceramic homogenizers were inserted in each tube before adding 10 mL of cold water and 10.0 mL of acetonitrile. Samples were mechanically shaken for 5 minutes by Eberbach’s Wrist Motion Shaker. Prepared mixture of salts, containing 4.0 g MgSO_4 , 1.0 g NaCl, 1.0 g Na_3 citrate dihydrate and 0.5 g Na_2H citrate sesquihydrate, were added to the samples. Tubes were shaken mechanically for another minute and then centrifuged at 4000 rpm for 5 min. Eight milliliter of organic phase was separated as clear solution (upper layer) from the surface of the aqueous phase (bottom layer), transferred in a clean tube and placed in -80°C freezer for at least 1 hour. After freezing-out the samples were removed from freezer, thawed and centrifuged at 5°C for 10 minutes at 4500 rpm. Appropriate amount of extract was transfer for the LC analyses and another 6 mL extract were transferred to a 15.0 ml single use centrifuge

tube containing 150 mg Supelclean PSA, 150 mg Discovery DSC-18, 900.0 mg MgSO₄, shaken 30 seconds and centrifuged five minutes at 4500 rpm. After centrifugation step sample analyzed on GC.

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 10.0 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 10, 20, 50, 100 and 200 ng g⁻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 autosampler (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°C (hold 3min) to 180°C by a rate of 20°C/min and finally increased to 300 °C (hold 2.5 min) by a rate of 5C/min, the injection volume was 5 µL with spitless 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°C and 150°C, respectively. The multiple reaction monitoring (MRM) mode with minimum two ions for each pesticide was used for detection and quantification of pesticides. The Agilent Mass Hunter Workstation software B.07.00SP2 was used for data analysis.

- 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 each 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°C, the autosampler was maintained at 10 °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.

Method validation and Acceptability Criteria

The acceptability of used method for the analysis of target pesticides was validated following the SANTE/2019/12682 guidelines [17]. Linearity was determined using matrix-matched calibration curves with spiked blank samples at five concentrations (0.005, 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) in the range 70–120%. Precision was expressed as the relative standard deviation ($RSD \leq 20\%$) of replicate analyses.

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 \(ukas.com\)](https://www.ukas.com/2572Testing/Multiple). The method is applicable for determination of pesticide residues in cereal crops 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 0.01mg/kg 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 ($\pm 50\%$). 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.

RESULTS AND DISCUSSION

This monitoring program during the period 2020-2021, planned for the analysis of 1,440 consignments of the most consumed cereal crops in the UAE which collected from ports, UAE, these cereal crops included rice, barley, oats, corn, wheat, quinoa, sorghum and harees. for up to 400 pesticides to check for compliance with national legislation for pesticide residues in food. The surveillance 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 cereal grain for any food safety risks and rejecting any unfit shipment for this purpose.

The samples were analyzed for pesticide residues at national laboratories, ministry of climate change and environment. The pesticide residues laboratory has continued to maintain and extend its accreditation status with the National Accreditation Body for the United Kingdom (UKAS).

Following efficient extraction methods and determination with a sensitive technique such as liquid chromatography-tandem mass spectrometry (LC-MS/MS) and gas chromatography tandem mass spectrometry (GC-MS/MS) could meet the regulatory requirements. The active ingredients 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.

Method validation

“As recommended by the European regulations (European Commission SANTE/2019/12682, the method validation is an essential prerequisite to provide accurate and reliable results during the official monitoring studies, the used method was validated under optimized conditions by determining the limits of detection (LOD) and quantitation (LOQ), the recovery and precision at different fortification levels. The recovery for all tested pesticides within the acceptable recovery range of 70–120% and the RSD of less than 10% considered acceptable and fulfill the criteria for quantitative methods (SANTE/2019/12682)”, [17]. These results indicate that the analytical method applied to this study is appropriate for the analysis of targeted pesticide residues cereal grain.

Compliance of the quantified pesticides with MRL

The national pesticide residues monitoring is according to a nation-wide sampling plan designed by ministry of climate change and environment. In this monitoring, 1,440 samples of cereal grains such as rice, corn, wheat, barley, oats, Quinoa, sorghum, milled, and bulgur were collected and analyzed up to 400 different pesticides contamination to ensure that consumers are not exposed to unacceptable risks from pesticide residues.

Table 1. Cereal samples analyzed results during years of monitoring program by MOCCAE

Commodity	Sample Analyzed	Free Samples	Contaminated Samples		No. of Samples Within MRL		No. of Samples Above MRL	
			No.	%	No.	%	No.	%
Rice	1012	615	397	39.22	285	28.16	112	11.06

Wheat	139	104	35	25.17	32	23.02	3	2.15
Barley	118	40	78	66.10	77	65.25	1	0.8
Corn	97	91	6	6.18	5	5.15	1	1.03
Bulgur	27	23	4	14.81	3	11.11	1	3.7
Oats	24	16	8	33.33	7	29.16	1	4.16
Quinoa	12	6	6	50.00	5	41.66	1	8.33
Sorghum	8	6	2	25.00	1	12.5	1	12.5
Millet	3	3	0.0	0.0	0.0	0.0	0.0	0.0
Total	1440	904		536		415		121
%		62.777%		37.22%		28.819%		8.40%

During this year's monitoring program, out of 904 analyzed cereal grain samples (62.777%), no detectable residues were found, while pesticide residues were detected in 415 samples (28.819%); the overall compliance with the legislation in force was 91.59 %. Out of 121 samples only (8.40%) contained residues above MRLs established by the Codex Committee on Pesticide Residues [18], as well as by the European Union [19] as shown in Table 1.

A total of 1012 rice samples were analyzed, 39.22% of the total samples were contaminated with pesticide residues, and about 11.06% of the total contaminated samples contained pesticide residues above the maximum permissible limit, while the remaining 60.77% did not contain any pesticide residue.

A percentage of 93.81% on 97 corn samples showed no trace of residues and 5.15% had quantifiable pesticide levels, but lower than MRLs. A further percentage of 1.03% was associated with samples containing residues above MRLs. The analyses performed of 139 samples of wheat showed a percentage of 76.47% for the residue-free samples, 23.02% with residues below the MRLs and 2.15% contain higher residues than the corresponding MRLs.

Of the 118 barley samples, 33.89% were found to be compliant, associated with non-quantifiable residue levels. A percentage of 65.25% showed residue contents higher than the quantification limits but lower than the MRL; one samples contained pesticides at concentrations above MRLs. On a total of 24 samples of oats analyzed, 66.66% were found to be residue-free and 29.16% with residues below the MRL, 4.16% contain higher residues than the corresponding MRLs.

According to pesticide residues observed in the Quinoa samples, 8.33% (1 out of 12 samples) exceeded the MRL, 41.6% (5 out of 12 samples) containing pesticide residues below MRLs.

Sorghum (1 out 8 samples) contained pesticide residues at or below MRLs laid down by CODEX and EU, one sample contained pesticide residues above MRLs, and 6 samples were found to be residue-free. Out of 27 bulgur samples analyzed, 3 (11.11%) had pesticide residues below MRLs while 23 (85.18%) had none detected, one sample had residues above MRLs. All millet samples (3) were found to be residue-free. Surveillance study for pesticide control in food samples in SWEDEN 2008, revealed that a total of 279 samples of cereal grains were analyzed. Most of the samples (73%) contained no residues but five samples exceeded the MRLs [20]. The presence of pesticide residues in wheat grains and its products produced and imported in Algeria was determined in 2019 [21] showed that detectable residues were found in 62.5% of wheat samples.

Incidences and MRL violation of pesticide residues

The residues of various detected pesticides, residue amounts, frequency and Status of registration for each crop analyzed under the programs are presented in Table 2. The results revealed that the main contaminated grains were rice, referring to the number of pesticide residues detected, rice was the highest crop contains pesticide residues (41), wheat (10) Barley (10), Quinoa (7), Corn (6). Oats (6), the magnitude of contamination of the two latter (Bulgur and Sorghum) was negligible (3, 2), respectively.

In 1012 rice samples, 41 different pesticide residues were detected, of which 13 are allowed / registered and authorized for use in accordance with UAE regulations of banned and restricted pesticides [Ministerial Decree No. 36 of 2018 on Banned and Restricted Pesticides in the United Arab Emirates]. Thiamethoxam was the most frequency (132) of total samples analyze, in a range of 0.01-1.1 mgkg⁻¹, (51 out of 132) were detected above the permissible limits, Pirimiphos-Methyl with a frequency of (141) of total samples analyzed, in a range of 0.01-8.097 mgkg⁻¹ and only one sample detected above the permissible limits, Propiconazole with a frequency of (50) of total samples analyzed, in a range of 0.01-0.3 mgkg⁻¹ and (3) of detected samples above the permissible limits, Buprofezin with a frequency of (16) of total samples analyzed, in a range of 0.01-0.11 mgkg⁻¹ and (6) of detected samples above the permissible. Tebuconazole, Clothianidin and Azoxystrobin were monitored within the limits of the permissible, with a frequency of 83, 31 and 23, respectively. Some substances were misused and were banned for use due to their systemic and persistence properties [22], about 15 banned pesticides were detected, Tricyclazole was one of the most detected pesticide whose residues were monitored with a frequency of (100) of the total samples analyzed, of which 77 samples were above the permissible limits, at the same time Tricyclazole is currently not authorized in the EU, and EU MRL is 0.01 mgkg⁻¹ of a product.

In the other hand, Carbendazim highly toxic fungicide, which was banned in 2014 in the European Union because it can cause mutations in animals that are also toxic to reproduction, was detected with an observed frequency (9), all of which were above the permissible limits, then Hexaconazole was monitored frequency (6), of which (3) samples exceeded the permissible

limits. Malathion, highly toxic to bees or aquatic life, with a frequency (40), but none were detected above the permissible limits.

Table 2. Pesticides detected, Residue amounts, frequency and MRL of pesticide residues in the analyzed samples.

Commodity	Pesticides detected	Freq.	No. of pesticides over MRLs	Range mg kg ⁻¹	Average mg kg ⁻¹	MRL mg kg ⁻¹	References	*Status of registration
Rice	Pirimiphos-Methyl	141	1	0.01-8.097	4.0535	0.5	Reg. (EU) No 2016/53	Allowed
	Thiamethoxam	132	51	0.01-1.1	0.555	0.01	Reg. (EU) 2017/671	Allowed
	Tebuconazole	83		0.01-0.57	0.29	1.5	CODEX 2012	Allowed
	Propiconazole	50	3	0.01-0.3	0.155	0.01	Reg. (EU) 2021/155	Allowed
	Clothianidin	31		0.01-0.5	0.25	0.5	CODEX 2012	Allowed
	Azoxystrobin	23		0.01-0.19	0.1	5	CODEX 2009	Allowed
	Buprofezin	16	6	0.01-0.11	0.06	0.01	Reg. (EU) 2019/91	Allowed
	Acetamiprid	5	3	0.01-0.11	0.06	0.01	Reg. (EU) 2019/88	Allowed
	Difenoconazole	4		0.01-0.036	0.023	8	CODEX 2018	Allowed
	Chlorantraniliprole	2		0.02-0.03	0.025	0.4	CODEX 2014	Allowed
	Bifenazate	2	2	0.035-0.8	0.417	0.02	Reg. (EU) 2020/1565	Allowed
	Deltamethrin	1		0.01		1	Reg. (EU) 2018/832	Allowed
	Metalaxyl	1		0.01		0.01	Reg. (EU) 2017/1164	Allowed
	Tricyclazole	100	77	0.01-1.1	0.555	0.01	Reg. (EU) 2017/983	Banned
	Malathion	49		0.01-1.3	0.655	8	Reg. (EU) 2015/399	Banned
	Carbendazim	9	9	0.03-0.1	0.065	0.01	Reg. (EU) 2021/155	Banned
	Hexaconazole	6	3	0.01-0.047	0.028	0.01	Reg. (EU) No 899/2012	Banned
	Triazophos	6		0.01-0.072	0.041	0.6	CODEX 2014	Banned
	Dichlorvos	5		0.01-0.07	0.04	0.15	CODEX 2013	Banned
	Cypermethrins	3		0.02-0.14	0.07	2	CODEX 2009	Banned
	Fenpropathrin	2	2	0.05-0.14	0.095	0.01	Reg. (EC) No 839/2008	Banned
	Acephate	2	2	0.01-0.03	0.02	0.01	Reg. (EU) No 899/2012	Banned
	Bromacil	1	1	0.03		0.01	UAE.S MRL 1 :2019	Banned
	Cyproconazole	1		0.01		0.1	Reg. (EU) 2018/70	Banned
	Kresoxim-methyl	1	1	0.03		0.01	Reg. (EU) 2020/856	Banned
	Methoxychlor	1	1	0.14		0.01	Reg. (EC) No 149/2008	Banned
	Monuron	1	1	0.04		0.01	Reg. (EU) No 899/2012	Banned
	Phenthoate	1	1	0.2		0.01	UAE.S MRL 1 :2019	Banned
	Chlorpyrifos	69	1	0.01-0.81	0.42	0.5	CODEX 2005	Restricted
	Imidacloprid	54	9	0.01-1.5	0.755	0.01	Reg. (EU) 2021/1881	Restricted
	Piperonyl Butoxide	3	3	0.02-0.24	0.13	0.01	UAE.S MRL 1 :2019	Restricted
	Spirodiclofen	3	3	0.08-0.13	0.105	0.02	Reg. (EU) 2016/1902	Restricted
	Permethrin	1		0.02		0.05	Reg. (EU) 2017/623	Restricted
Isoprothiolane	69		0.01-0.29	0.15	1.5	CODEX 2018	Unregistered	
Chlorfenvinphos	2	1	0.01-0.03	0.015	0.01	Reg. (EU) 1138/2013	Unregistered	
Lenacil	1		0.02		0.1	Reg. (EC) No 149/2008	Unregistered	
Acibenzolar-S-methyl	1		0.01		0.01	Reg. (EU) 2021/1807	Unregistered	
Flutriafol	1		0.02		1.5	Reg. (EU) 2018/70	Unregistered	
Ofurace	1	1	0.03		0.01	UAE.S MRL 1 :2019	Unregistered	
Picoxystrobin	1	1	0.31		0.01	Reg. (EU) 2019/91	Unregistered	
Spiroxamine	1	1	0.32		0.01	Reg. (EU) No 2016/452	Unregistered	
Wheat	Pirimiphos-Methyl	28		0.01-0.499	0.254	5	Reg. (EU) No 2016/53	Allowed
	Deltamethrin	3		0.041-0.094	0.067	1	Reg. (EU) 2018/832	Allowed
	Tebufoenozide	2	2	0.06-0.07	0.065	0.01	Reg. (EU) 2021/1807	Allowed
	Difenoconazole	1		0.02		0.02	CODEX 2008	Allowed
	Tolclofos-methyl	1		0.01		0.01	Reg. (EU) 2022/1324	Allowed
	Tricyclazole	1		0.01		0.01	Reg. (EU) 2017/983	Banned
	Chlorpyrifos	5		0.02-0.068	0.044	0.5	CODEX 2003	Restricted
	Piperonyl Butoxide	4		0.02-0.07	0.045	30	CODEX 2004	Restricted

Cont. Table.2

Commodity	Pesticides detected	Freq.	No. of pesticides over MRLs	Range mg kg ⁻¹	Average mg kg ⁻¹	MRL mg kg ⁻¹	References	*Status of registration
Wheat	Imidacloprid	1		0.03		0.03	CODEX 2004	Restricted
	Bitertanol	1	1	0.41		0.05	CODEX 2001	Unregistered
Barley	Pirimiphos-Methyl	62		0.02-15	7.51	7	CODEX 2005	Allowed
	Deltamethrin	58		0.02-0.57	0.295	2	Reg. (EU) 2018/832	Allowed
	Spinosad	1		0.04		1	CODEX 2005	Allowed
	Azoxystrobin	1		0.02		1.5	CODEX 2014	Allowed
	Malathion	6		0.01-0.1	0.055	8	Reg. (EU) 2015/399	Banned
	Dichlorvos	1		0.01		0.01	Reg. (EC) 839/2008	Banned
	Fenpropathrin	1	1	0.2		0.01	Reg. (EC) 839/2008	Banned
	Myclobutanil	1		0.02		0.01	Reg. (EU) 2020/770	Banned
	Chlorpyrifos	49		0.01-0.5	0.255	0.5	CODEX 2003	Restricted
	Piperonyl butoxide	29		0.02-15	7.51	30	CODEX 2004	Restricted
Corn	Deltamethrin	2		0.04-0.184	0.112	2	CODEX 2004	Allowed
	Pirimiphos-Methyl	2		0.03-0.256	0.143	7	CODEX 2004	Allowed
	Fenpropathrin	1	1	0.01-0.03	0.02	0.01	Reg. (EC) 839/2008	Banned
	Piperonyl butoxide	3		0.11-0.123	0.673	30	CODEX 2004	Restricted
	Imidacloprid	2		0.01-0.02	0.015	0.2	CODEX 2004	Restricted
	Chlorpyrifos	1	1	0.01-0.03	0.02	0.01	Reg. (EU) 2020/1085	Restricted
Bulgur	Thiamethoxam	1		0.03		0.01	UAE.S MRL 1 :2019	Allowed
	Carbendazim	1	1	0.04		0.01	UAE.S MRL 1 :2019	Banned
	Piperonyl butoxide	2		0.01-0.04	0.025	7	CODEX 2005	Restricted
Oats	Pirimiphos-Methyl	6		0.02-0.63	0.325	5	Reg. (EU) 2016/53	Allowed
	Deltamethrin	4		0.1-0.3	0.2	2	Reg. (EU) 2018/832	Allowed
	Tebufenozide	1	1	0.13		0.01	Reg. (EU) 2021/1807	Allowed
	Azoxystrobin	1		0.04		1.5	CODEX 2014	Allowed
Quinoa	Chlorpyrifos	4		0.02-0.39	0.205	0.5	CODEX 2003	Restricted
	Acetamiprid	4		0.01		0.01	Reg. (EU) 2019/88	Allowed
	Pirimiphos-Methyl	1		0.02		0.5	Reg. (EU) No 2016/53	Allowed
	Metalaxyl	1		0.01		0.01	Reg. (EU) 2017/1164	Allowed
	Methomyl	3	1	0.01-0.03	0.02	0.01	Reg. (EU) 2016/1822	Banned
	Fenpropathrin	1		0.01		0.01	Reg. (EC) No 839/2008	Banned
	Phenthoate	1	1	0.01		0.01	UAE.S MRL 1 :2019	Banned
	Chlorpyrifos	3	3	0.01-0.03	0.02	0.01	Reg. (EU) 2020/1085	Restricted
Sorghum	Pirimiphos-Methyl	1		0.073		5	Reg. (EU) 2016/53	Allowed
	Chlorpyrifos	1	1	1.5		0.5	CODEX 2003	Restricted

*Status of registration according to List of registered pesticides in the Ministry (MOCCA)-Last update 17 November 2021 [20] Action on this was taken by the concerned department.

In this work results also showed the detection of residues of 5 restricted pesticides, including Spirodiclofen in 3 samples, which were at the same time above the permissible limits, followed by Chlorpyrifos with a frequency of 69, of which one sample was above the permissible limits. As for the frequently monitored restricted pesticides and none of which were detected above the Permissible limits, Imidacloprid with a frequency of 54, followed by Piperonyl Butoxide (3) and Permethrin (1). It was found residues of 8 unregistered pesticides were detected in the samples as follows, Isoprotheline (69), acebenzolar-S-methyl, picoxestrobil, linacil, flutriafol each detected

in a single sample, and the pesticides that exceeded the maximum allowable limit were Chlorfenvinphos (1 of 2), Spiroxamine (1) and Ofurace (1). Above results indicated, during the period 2020-2021, banned and restricted pesticide residues in imported rice are continuously monitored indicating that it is necessary to strengthen control over imported rice.

The MRL of rice grains among different countries varies according to the legislation of each administrative organization, and some pesticides used in this study were not registered for rice in certain countries [23]. They reported that fungicides tebuconazole, tricyclazole, isoprothiolane, propiconazol and carbendazim, which are mainly applied against the fungal rice blast, and the insecticides imidacloprid, buprofezin, chlorpyrifos and thiamethoxam were found in over 10% of the samples each, moreover, rice with high residue levels of isoprothiolane and tebuconazole is perfectly fine for the EU market while triggering import alerts in the USA. On the other hand, high levels of tricyclazole and buprofezin might cause a rapid alert in the EU RASFF, but the rice can be imported without problems into the US. Japan and Australia New Zealand tolerate carbendazim residues of 1 and 2 mg/kg respectively, whereas the default limit applies in the EU and zero tolerance in the USA. The banned and restricted pesticide residues as shown in Table 2 were detected in rice samples, therefore, it is necessary to strengthen the supervision and management of these pesticides

In 139 wheat samples, 10 different pesticide residues were detected, of which 5 are allowed / registered and authorized for use in accordance with UAE regulations of banned and restricted pesticides [20]. Pirimiphos-Methyl was the most detected (28) and within allowable limit, residues in a range 0.01-0.499 mgkg⁻¹, Tebufenozide was detected in two samples in a range mgkg⁻¹, and above the allowable limit. Tricyclazole banned pesticide detected only in one sample with a concentration within the allowable limit. Chlorpyrifos, Piperonyl Butoxide and Imidacloprid are restricted were detected within the allowable limit and with a frequency 5, 4, and 1, respectively. The contamination with Bitertanol was negligible.

Wheat is often stored for long periods of time, which entails the risk of insect infestation. Storage during transport is also a source of pest infestation, so it has become a normal agricultural practice to spray or fumigate stored grains, especially before shipping them with contact pesticides so that they reach the port of destination free of any pest infestation [24]. There are

two main sources of pesticides in wheat grains. First, spray insecticides on growing crops to prevent insect infestation, fungi and weeds. Secondly, the insecticide mixture is used on stored goods [25].

In 118 barley samples, 10 different pesticide residues were monitored, Pirimiphos-Methyl, Deltamethrin, Spinosad and Azoxystrobin are allowed / registered and authorized for use in accordance with UAE regulations of banned and restricted pesticides [Ministerial Decree No. 36 of 2018 on Banned and Restricted Pesticides in the United Arab Emirates]. Pirimiphos-Methyl and Deltamethrin detected with a concentration within the allowable limit and with a frequency 62 and 58, respectively. Malathion, Dichlorvos, Fenprothrin and Myclobutanil are banned pesticides [20], and the number of contaminated detected samples was negligible.

Chlorpyrifos and Piperonyl butoxide are Restricted pesticides [Ministerial Decree No. 36 of 2018 on Banned and Restricted Pesticides in the United Arab Emirates] which were monitored in concentration within the allowable limit and with a frequency 49 and 29, respectively

In Bulgur samples (27), both Thiamethoxam (allowed / registered) and Piperonyl butoxide (Restricted) were monitored with concentration within the allowable limit, while Carbendazim (1) (Banned) which banned also in 2014 by the EU, UK, Morocco and Switzerland was monitored with concentration above the allowable limit. the proportion of these pesticides above their MRLs were 14.81% (Table 2). In Oats samples (24), allowed / registered and authorized for use in accordance with UAE regulations of banned and restricted pesticides, Pirimiphos-Methyl, Deltamethrin, and Azoxystrobin residues were monitored with concentration within the allowable limit, while Tebufenozide monitored only in one sample above the allowable limit. the proportion of these pesticides above their MRLs were 33.33%.

In Quinoa samples (12), Three different pesticide residues were monitored with concentration within the allowable limit, Acetamiprid, Pirimiphos-Methyl, Metalaxyl are allowed / registered and authorized for use in accordance with UAE regulations of banned and restricted pesticides [Ministerial Decree No. 36 of 2018 on Banned and Restricted Pesticides in the United Arab Emirates]. Three banned pesticides in the country (Methomyl, Fenprothrin and Phenthoate) were found in the samples, Phenthoate with the concentration above their MRLs only in one

sample (Table 2). In Sorghum samples (8), Pirimiphos-Methyl, allowed pesticide was monitored with concentration above the allowable limit, more over Chlorpyrifos, Restricted was monitored above the allowable limit, the proportion of these pesticides above their MRLs were 25% (Table2).

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 were present in cereals samples, as shown in Table 3. In rice samples 16.69% (169) of the analyzed rice contained residues of one insecticide while two pesticides were detected in 9.98% (101) of samples and 12.55% (127) contained three or more pesticide residues, Additionally, rice was the crop with highest number of samples with multiple residues, compared with wheat, barley, corn, bulgur, oats, quinoa and sorghum, with two samples have contamination of 10 different pesticides including Acetamiprid, Azoxystrobin, Buprofezin, Carbendazim, Clothianidin, Dichlorvos, Difenoconazole, Imidacloprid, Malathion, Pirimiphos-Methyl, Propiconazole, Tebuconazole, Thiamethoxam, Triazophos and Tricyclazole. indicating the co-occurrence of multiple pesticide residues in rice grain.

Table 3. The number of analyzed samples, contaminated, having 1, 2 and more than two pesticides

Commodity	Samples 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.	%	No.	%
Rice	1012	397	39.22	169	16.69	101	9.98	127	12.55
Wheat	139	35	25.17	27	19.42	5	3.59	3	2.15
Barley	118	78	66.10	23	19.49	5	4.24	50	42.37
Corn	97	6	6.18	2	2.06	3	3.09	1	1.03
Bulgur	27	4	14.81	4	14.81	0.00	0.00	0.00	0.00
Oats	24	8	33.33	4	16.67	0.00	0.00	4	16.67
Quinoa	12	6	50.00	2	16.67	1	8.33	3	25

Sorghum	8	2	25.00	2	25	0.00	0.00	0.00	0.00
Millet	3	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Total	1440	536		233		115		188	
%		37.22%		16.18%		7.98%		13.05%	

The coexistence of multiple pesticide residues was detected in rice samples, and 12.55% (127) of rice samples contained two or more pesticide residues (Table 3). Similar results have been detected in Barley 42.37% (50) samples contained two or more. Cui *et al.*, [26] reported that more than 30% of rice samples contained more than three TF residues. Thus, the coexistence of multiple pesticide residues in crops is very common in China. Extensive studies have demonstrated that the coexistence of multiple residues in the same sample could cause joint toxicities to the environment and human health [27, 28]. Regulation (EC) (no. 396/2005) [29] has proposed that the cumulative and synergistic effects of multiple pesticides should be considered when establishing MRLs since 2008. However, current food safety standards from many countries only concern individual pesticides, which may underestimate the health risk of pesticides in foods. Thus, more work should be done to establish MRLs for the co-occurrence of multiple pesticide residues. The cumulative chronic and acute dietary exposures to OPs, NEOs, and TFs from rice consumption were not considered of health concern, moreover the cumulative risks of dietary exposure to pesticides for children and adolescents were higher than those for adults and the elderly due to their higher rice intake per kg body weight [30]. Barley is the second highest number of pesticides contamination, 42.37% (50) was associated with samples containing three or more pesticide residues.

The results from this monitoring program are a valuable source of information for estimating dietary exposure of UAE consumers to pesticide residues and to assess acute and chronic risk to consumer health, dietary exposure to pesticide residues was estimated and compared with health-based guidance values. Moreover, it is not only about detecting infringements in individual cases, but also about gaining general information that makes it possible to take the appropriate measures to reduce risk potential.

CONCLUSIONS

The Pesticide Residue Monitoring Program is a compliance program used to monitor the level of pesticide residues in imported grains and other products in the UAE during the period 2020-2021

to ensure that they do not exceed the MRL limits to assess the risk of consumer exposure to these residues and ensure a high level of consumer protection.

Residues exceeding the maximum residue limits (MRLs) were found in 112 (11.11%) of rice samples, which makes up 92.6% of all samples containing pesticide residues above the maximum permissible limit. Tricyclazole, Thiamethoxam and Carbendazim are the pesticides most frequently found in rice. The results revealed that pesticide residues are present in some imported rice, some of detected pesticides are above MRL and/or not authorized for use. The results provided valuable information on the current state of pesticide residues, which could serve as a reference for pesticide supervision and management.

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