scientific reports

Check for updates

OPEN

Simultaneous screening of 211 pesticide residues in date fruits in Iran and health risk assessments based on Mont Carlo simulation

Moslem Basij[1]✉, Najmeh Sheibani Tezerji[2], Mahboube Shirani[3]✉ & Vahideh Mahdavi[4]

In this study, 211 pesticides were analyzed simultaneously using a QuEChERS method coupled with GC–MS–MS and LC–MS–MS in 90 fresh date fruit samples produced in Kerman Province. Probabilistic estimates of non-carcinogenic and carcinogenic health risks were evaluated using Monte Carlo simulation-based hazard Quotient (HQ), hazard index (HI) and carcinogenic risk (CR). The linearity of 0.015–0.30 mg kg^{-1} with the coefficient of determination (R^2) values exceeding 0.9989 were achieved. The percentage of recoveries, limits of detection (LODs), limits of quantification (LOQs), Relative standard deviation (RSD %) and matrix effect (ME) were determined in the range of 77–119%, 0.001–0.003 mg kg^{-1} and 0.005–0.01 mg kg^{-1}, ≤ 15% and − 7.5 to 14.2%, respectively. Among 90 analyzed date fruits, 9 samples (10%) contained at least one pesticide residue, whereas 5 samples (5.5%) showed pesticide residues exceeding maximum residual limit (MRL) according to the national and European Commission. The obtained HQ values for the target pesticides were as cypermethrin > imazalil > permethrind > endosulfan > Fenpropathrin. The HI values for adult and child consumers with all pesticide residues were lower than 1. The CR was less than 1.0E-6 value. Thus, there was no carcinogenic risk to the consumers of date fruits.

Keywords Pesticide residues, Health risk assessments, Date fruit, Monte Carlo, GC–MS–MS, LC–MS–MS

Pesticides are chemical substances which used to control pests. Pesticides includes insecticide, molluscicide, herbicide, piscicide, avicide, rodenticide, bactericide, nematicide, insect repellent, animal repellent, microbicide, fungicide, and lampricide[1]. Target pests can include insects, weeds, molluscs, plant pathogens, birds, fish, nematodes, mammals, and microbes that destroy property, cause nuisance, or spread disease, or are disease vectors[2]. Moreover, pesticides have harmful and toxic effects on humans and other species[3,4].

Plants have the ability to absorb various pollutants such as pesticides from the environment[5]. Although in some cases very low levels of pesticides are used to control or eliminate pests, pesticide residues may be found in the soil, water, air and food chain (such as vegetables, fruit, and animal based products)[6,7]. Date fruit has high levels of nutrients and carbohydrates[8,9]. According to the FAO report, more than 7 million and 800 thousand tons of date fruits are produced in the world every year, and Iran is one of the major date producers and exporters in the world[7]. Kerman province is the second producer of date fruits in the Iran with various types of dates including Mazafati, Piarom, Shahani, Rabbi, Zahedi, Kabkab, Kaloteh, Karoot and Qhasb.

Date fruits have many products such as: date juice, date paste, alcohol, vinegar, lavash, date syrup, date powder, date coffee, date kernel powder, animal and poultry feed and agricultural fertilizer[10]. Date fruit is a strategic product due to the creation of transformation industries and job creation, helping to preserve resources and the environment, and earning currency from exports[11,12].

In order to prevent economic and health losses, the use of pesticides such as acaricides, the usage of insecticides, fungicides and herbicides is inevitable in date production[13,14] which may increase crop productivity in palm cultivation[15]. On the other hand, if these toxins remain in date fruits, there is a possibility of damage to the health of consumers[16]. Now, researchers and experts believe that it has side effects such as skin, nervous, digestive, carcinogenic, and respiratory effects due to direct or indirect connection with pesticide use or their residues in agricultural products[17]. According to the statistics published by FAO in 19 countries, it is estimated

[1]Department of Plant Protection, Faculty of Agriculture, University of Jiroft, Jiroft, Iran. [2]Iranian National Standards Organization of Kerman, Kerman, Iran. [3]Department of Chemistry, Faculty of Science, University of Jiroft, P. O. Box 7867161167, Jiroft, Iran. [4]Iranian Research Institute of Plant Protection (IRIPP), Agricultural Research, Education and Extension Organization (AREEO), Tehran, Iran. ✉email: Moslembasij@ujiroft.ac.ir; m.shirani@ujiroft.ac.ir

that 50,000 cases of poisoning and 5000 deaths are due to the use of pesticides every year. In fact, 70% of the fatal cases occur in developing countries (FAOSTAT, 2021)[7]. It is very necessary and important to measure and continuously monitor the amount of toxins in agricultural products[18].

Due to the variety of pesticides usage in date fruit production process, the general tendency is the application of multiresidue methods to enable the contingency for simultaneous analysis of a wide range of pesticides within a single run. To reach this aim, tondomn techniques particularly gas chromatography (GC) and liquid chromatography (LC) with tandem mass spectrometry (MS/ MS) i.e. GC/MS/MS and LC/MS/MS are considered as most useful and potent techniques for multiresidue analysis. In determination of trace levels of pesticides in food samples, complex matrix of food samples and large quantities of co-extracted compounds definitely influence the efficiency of the method. The quick, easy, cheap, effective, rugged, and safe (QuEChERS) method is a rapid and facile and accessible solid-phase extraction/cleanup technique for multiresidue extraction of pesticides in food products[19].

In recent years, due to the public concerns in regard with the increase in the risk of residual toxins in products, the maximum limit of pesticide residues was determined[20,21]. The Maximum Residue Limit (MRL) of pesticides has been determined in order to protect the health of the community and encourage farmers to use pesticides properly[22]. MRL is the highest allowed pesticide concentration in the product, which is actually a standard used for international food trade. The MRL values of each country are different, depending on the consumption of each pesticide for each product and the share of each product in the food basket of that country, WHO/FAO (2011)[7]. To this aim, in this study, 90 date samples were collected randomly and 211 pesticides were separated and determined via a modified QuEChERS (based on BS EN 15,662: 2018 method) method coupled with GC–MS–MS and LC–MS–MS. The health risk assessment factor was calculated and simulated using Mont Carlo Model.

Materials and methods

Chemical and reagents

All the materials were supplied by Merck Chemicals (Darmstadt, Germany) and all reagents were HPLC grade (Fisher Chemical Scientific, UK). Ultrapure water was produced by Milli-Q system (Millipore, MA, USA). Standards of 211 pesticides were purchased from Dr Ehrenstorfer (Augsburg, Germany), all with purity > 98%. Individual pesticide stock solution was prepared and stored at − 18 °C. Some adsorbents such as magnesium sulfate anhydrous ($MgSO_4$), sodium chloride (NaCl), Trisodium citrate dihydrate ($C_6H_5Na_3O_7.2H_2O$), Disodium hydrogen citrate sesquihydrate ($C_6H_8Na_2O_8$), and primary–secondary amine (PSA) were all purchased from Agilent Co. (USA) need for QuEChERS extraction.

Instrumentation

The Ultrasonic bath (Sonicator) model vCLEAN 1 -16 (Vira Tejarat Bekr Co., Tehran, Iran), centrifuge model Universal 320R (Hettich, USA), vortex shaker model Vortex 3000 (Wiggens, China), pH meter model CP-511 (Elemtron, Poland), Oven model K.M85 (Pars Azma, Iran), Nitrogen Evaporator (Royan Iran Co., Iran) were all used for sample preparation process.

Standard solutions and spiking procedures

Pesticides have a variety of pH stabilities, to cover the entire spectrum of analyzed pesticides, multiple working standard solutions containing one or more pesticides were prepared. Defined volumes of the required pesticide stock solutions were mixed to prepare these standards using certified "A" class volumetric flasks according to the compound solubility and stability requirements with the appropriate volume of acetonitrile. The spiking was carried out for two concentrations of 0.01 and 0.05 mg kg^{-1}. To this aim, 10 g of date paste sample was spiked with 75 µL and 375 µL of mixed standard solutions for 0.01 and 0.05 mg kg^{-1} respectively. In addition, an internal standard (IS) solution of triphenylphosphate (TPP) (0.01 mg kg^{-1}) was made in acetonitrile, and 75 µL was added to all solutions and samples. The standard storage was done at a temperature of − 18 °C until analysis.

Sample collection and storage

90 fresh date fruit samples were collected from different shops and local markets located in three towns of Kahnoj, Bam and Jiroft in Kerman province, between June and August 2023. Figure 1 represents the geographical location of the sampling areas. According to the Codex recommended methods for sampling of pesticide (CAC/GL 33–1999), 1 kg of each variety of date fruit (Mazafati, Piarom, Shahani, Rabbi, Zahedi, Kabkab, Kaloteh, Karoot and Qhasb) were collected to monitor pesticides. The samples were stored in a freezer (− 18 °C) until analysis (each sample was analyzed maximum 3 days after preparation).

Sample preparation and extraction procedures

A modified QuEChERS method was utilized to extract pesticides in accordance with BS EN 15,662: 2018 method with some modifications. The 90 date fruit samples (1 kg of each sample) except the seeds, which includes the exocarp, mesocarp, and endocarp were blended and homogenized as individual (spiking was done at this step before separation process). Then, 10 g of each date fruit sample was transferred into a 50 mL centrifuge tube containing 4.5 mL of water and 10 mL of acetonitrile. The mixture was vortexed for 3 min. The pesticides were allowed to penetrate into the date paste by placing the mixture in a cool and dark place for 1 h and prevent any possibility of pesticide decomposition in (day) light. 4 g of anhydrous magnesium sulfate, 1 g of sodium chloride, 1 g of trisodium citrate dihydrate and 0.5 g of disodium hydrogencitrate sesquihydrate were added into each tube and vortexed again for 3 min. Then, the mixture was centrifuged at 3000 rpm for 5 min at − 5 °C. Immediately, the upper acetonitrile phase containing pesticides were separated by a single-channel micropipette and transferred into a 15-ml centrifuge tube, which contained 150 mg PSA and 900 mg of magnesium sulfate.

Fig. 1. Sampling sites in the monitoring area (**a**) Kahnoj, Kerman; Iran (**b**) Bam, Kerman; Iran (**c**) Jiroft, Kerman; Iran[23].

The mixture was vortexed for 30 s and centrifuge for at 3000 rpm for 5 min at − 5 °C. After that, 1 mL of the extract solution was gathered and filtered through a 0.22 µm PTFE syringe filter and used for gas and liquid chromatographic analysis as illustrated in Fig. 2.

Instrumentation

Pesticide residues were analyzed simultaneously using the GC–MS–MS system (7890B, Agilent, USA) coupled to a tandem triple quadrupole mass detector and an auto-sampler (7683B). Moreover, UHPLC–MS–MS system (1200, Agilent, USA) coupled to triple quadrupole mass spectrometer (6410, Agilent, USA) with electrospray ionization (ESI) was also used for analysis. The optimal analytical performance was achieved through setting all conditions which are all summarized in Tables S1 and S2. Moreover, Table S3 shows the GC–MS/MS and LC–MS/MS parameters for the analysis of 211 pesticides.

Method validation

To consider the validation of the proposed method, the related parameters including accuracy, linearity, precision, recovery, limit of quantitation (LOQ), limit of detection (LOD) and matrix effect were investigated according to the SANTE/11,312/2021 guideline[24]. To evaluate the linearity of the method, the homogenized date fruit blank samples were spiked with target analytes at 7 concentrations of 0.015, 0.060, 0.105, 0.150, 0.195, 0.240, 0.30 mg kg^{-1}.

The LOQ and LOD were determined according to the SANTE recommendations[25] by calculating the standard deviation (SD) of the pure data matrix with the lowest additive level of 0.01 mg kg^{-1} of the pesticide mixture, ensuring perfect accuracy (77–119%) and accuracy ((RSD) ≤ 15%). The precision and the recovery of the method were obtained by a recovery study in which blank samples were spiked with the pesticides mixture at the concentrations of 0.01 and 0.05 mg kg^{-1}. The obtained data are the results of six replicates. The spiked materials were then analyzed according to the method protocol and the target analytes were quantified based on the resulting matrix-matched calibration curves. Repeatability (n = 6) (intra-day precision) and the reproducibility

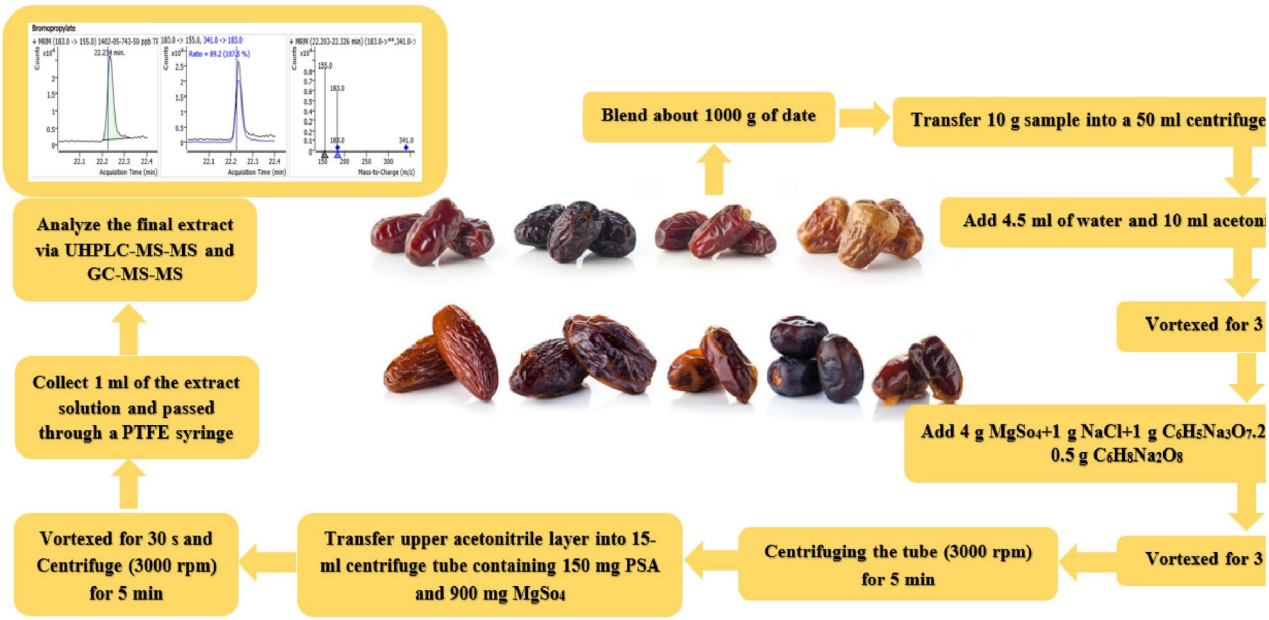

Fig. 2. Schematic representation of the QuEChERS method of pesticide residues from date fruit samples.

(inter-day precision) (n = 12) were calculated as RSD values from mirror measurements performed by one operator on the same day and by two different operators on 3 consecutive days.

Matrix effects (ME) are defined by CODEX as the influence on the measured concentration or amount of the target analyte due to the presence of other impurities in the sample. The range of ME determined by comparing the response of an analyte in pure trend solution to its response in sample extract can vary significantly[26]. ME is calculated by Eq. (1):

$$\text{Matrix effects (ME)}\ \% = ((\text{Slope of calibration curve in matrix}) / (\text{Slope of calibration curve in solvent}) - 1) \times 100 \quad (1)$$

Health risk assessment

The target hazard quotient (THQ) was obtained using Eq. 2 as follows[27]:

$$\text{THQ} = \frac{\text{EDI}}{\text{ADI}} \quad (2)$$

Acceptable daily intake (ADI) (mg day^{-1}) was presented by the Joint Meeting on Pesticide Residues (JMPR) or the European Food Safety Authority for health risk assessment.

The estimation of daily intake (EDI) was calculated using[28,29]:

$$\text{EDI} = \frac{\text{C} \times \text{IR} \times \text{EF} \times \text{ED}}{\text{BW} \times \text{AT}} \quad (3)$$

C is the quantity of pesticide (mg kg^{-1}); IR is the rate of per capital ingestion (kg/day), EF is the frequency of exposure (350 day/year), and ED is the duration of exposure for adults (70 years) and children (6 years).

BW measures body weight (children weigh 15 kg while adults weigh 70 kg) and AT measures average lifetime (2100 days for children and 10,500 days for adults).

The per capita consumption of date fruit 5.7 kg/y. Therefore, the daily date fruit would be approximately 0.015 kg/day.

Hazard quotient (HQ) is the ratio of the exposure from the specific source of interest to the respected reference values[30]. The following equation calculated by the total hazard quotient (HQ) or hazard index (HI)[31]:

$$\text{HI} = \text{HQ1} + \text{HQ2} + \cdots + \text{HQn} \quad (4)$$

When HI < 1, health risk in the consumers is acceptable, but if HQ and/or HI > 1 value, there is concern health risk for consumers[32].

Monte Carlo simulation (MCS) technique

Multiple uncertainties may arise through the estimation of health risk assessments[33]. High uncertainty is expected by using a single point value health risk calculation. Therefore, MCS was used as a probabilistic model used[34]. Based on MCS, the non-carcinogenic and carcinogenic risks are identified by Crystal Ball (version 11.1.2.4.600

(32-bit) Oracle, Inc., USA). Reproduction numbers for each equation was at least 100,000, and the standard for consumer health risk was percentile 95%[35].

Results

Analytical method validation

The method validation records for the whole date fruit matrix across the 31 LC- sensitive and 180 GC- sensitive pesticides are summarized in Tables S1 and S2, respectively. Calibrations were evaluated on a date fruit matrix and according to the guideline SANTE/11,312/2021. All compounds were found to be acceptable. A linear response was obtained for the analyte of interest in the range from 0.015 to 0.30 mg kg^{-1} ($R^2 > 0.9989$, residue ≤ 15%). For all pesticides except Cycloate, the LOQs were less than 0.01 mg kg^{-1}. For all pesticides, except for pyrimidifen, quinalphos and propargite, the LODs were at 0.001 mg kg^{-1} and the LOQs were at 0.005 mg kg^{-1}. The recoveries of pesticides obtained at the two spike levels of 0.01 and 0.05 mg Kg^{-1} in the total date fruit matrix were within the acceptable range of 77–119%. The obtained recoveries of pesticides which detected by LC were in the range of 70–117% and those detectable by GC ranged from 77 to 119%. All the results of the two spike levels in pesticides in date samples were shown in Fig. 3. The recoveries of pesticides detected at the analytical method repeatability (n = 6) and reproducibility (n = 12) were measured by injecting two spike levels from a matrix-fitted curve. RSD (%) under conditions of reproducibility ranged from 0.5- 15.0% for LC analysis and 0.2–15% for GC analysis. The ME% of the target pesticides were determined at a concentration of 0.05 mg kg^{-1} is shown in Table S4. The average ME% ranged from − 7.5 to 14.2%, with no matrix effect observed.

Pesticide residue concentration in real samples

A variety of date fruits were purchased from major supermarkets and wholesale markets in the Kerman Province to determine the current status of pesticide residues in the quantity of each product. The results of the analysis of 211 pesticides in 90 date fruit samples are presented in Table 1. From 90 analyzed date fruits, 9 samples (10%) contained at least one pesticide residue (bromopropylate, cypermethrin (I + II), fenpropathrin, permethrin (I + II), imazalil, endosulfan (I + II)), whereas, that 5 samples (5.5%) displayed pesticide residues exceeding MRL in national and European Commission. The results were compared with Iranian and European Commission regulations (Table 1). Most of the samples contained acceptable levels of pesticides. The levels of Bromopropylate and imazalil were higher than national MRLs and European Commission. The average of residue in date fruit belonged to Bromopropylate (0.250 mg kg^{-1}) and imazalil (0.101 mg kg^{-1}).

Estimation of exposure and risk assessment

Non-carcinogenic risk

The HQ average for consumers (adults and children) is shown in Fig. 4 and 5. The rank sorting of pesticides based on HQ was cypermethrin > imazalil > permethrin > endosulfan > Fenpropathrin with amounts of 1.17E-3, 2.13E-3, 2.77E-4, 3.70E-4 and 4.44E-5 for adults and 5.42E-3, 1.00E-2, 1.30E-3, 1.73E-3 and 2.08E-4 for children, respectively.

As shown in Figs. 4, 5 and 6, HI values for adult and child consumers with all pesticide residues were lower than 1. The daily fruit in take by adults and children of Hi is 0.060 and 0.280, respectively (Fig. 6). The results also tabulated in Table 2.

Carcinogenic risk

Figures 7 and 8 show that 95% (in worst scenario) percentile of CR for cypermethrin and permethrin was 6.51E-8 and 9.49E-11. The risk assessment results of this study indicated that pesticide residues in date fruits do not have carcinogenic risk (CR < 1.00E-6) (Fig. 8). The results are summarized in Table 3.

Discussion

A total of 90 samples of date were analyzed through this study to investigate the pesticides residues. A clearly diverse chance of buildup event was watched for the compared herbicides, fungicides and bug sprays from distinctive chemical classes that are authorized for date natural products development in Iran. Results of the analysis of 211 pesticides in 90 date fruit samples are presented. From 90 analyzed date fruits, 9 samples (10%) contained at least one pesticide residue, whereas 5 samples (5.5%) displayed pesticide residues exceeding MRL in national and European Commission. Bromopropylate was detected in three samples including Piarom, Zahedi and Kaloteh dates with an average of residues of 0.250 mg.kg^{-1}, Cypermethrin (I + II) was detected in Zahedi dates with an average of residues 0.042 mg.kg^{-1}, Fenpropathrin in Zahedi dates with an average of residues 0.005 mg.kg^{-1}, Permethrine (I + II) was detected in Piarom dates with an average of residues 0.05 mg.kg^{-1}, Imazalil was detected in two samples including Kaloteh dates with an average of residues 0.101 mg.kg^{-1}, and Endosulfan (I + II) was detected in Kaloteh dates with an average of residues 0.008 mg.kg^{-1}. The results were compared with Iranian and European Commission regulations (Table 1). Most of the samples contained acceptable levels of pesticides. MRL National for Bromopropylate, Cypermethrin (I + II), Fenpropathrin, Permethrine (I + II), Imazalil and Endosulfan (I + II) are 0.05 mg.kg^{-1}. MRL in European Commission for Bromopropylate, Cypermethrin (I + II), Fenpropathrin, Permethrine (I + II), Imazalil and Endosulfan (I + II) respectively are 0.01 mg.kg^{-1}, 0.05 mg.kg^{-1}, 0.01 mg.kg^{-1}, 0.05 mg.kg^{-1}, 0.01 mg.kg^{-1} and 0.05 mg.kg^{-1}. The levels of Bromopropylate and imazalil were higher than national MRLs and European Commission.

Then non-carcinogenic risk and carcinogenic risk assessment of the identified pesticides was carried out. The results of HQ values for pesticides were as follow cypermethrin > imazalil > permethrind > endosulfan > Fenpropathrin. The results were compared with Iranian and European Commission regulations (Table 1). Most of the samples contained acceptable levels of pesticides. The levels of Bromopropylate and imazalil were higher than national

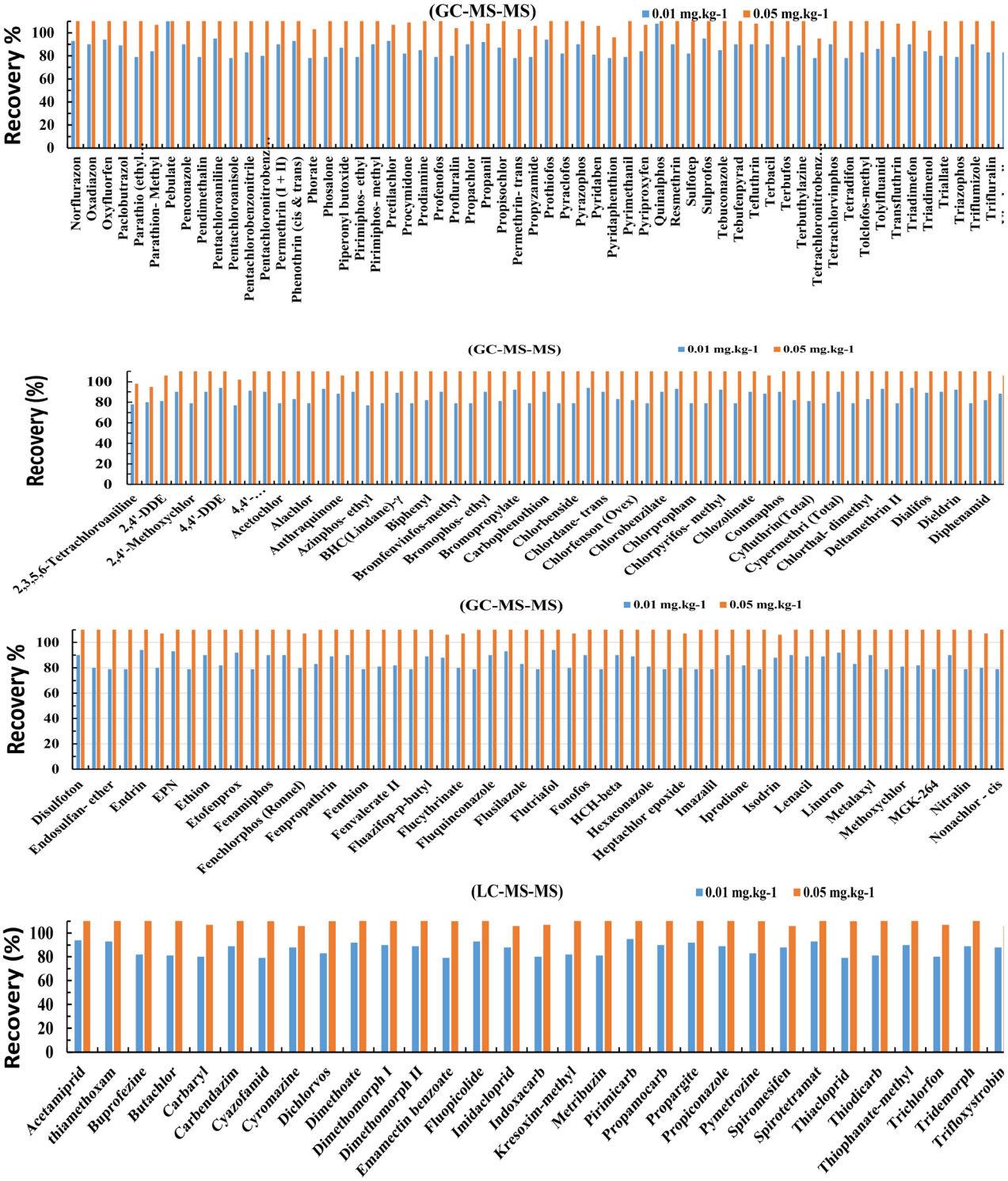

Fig. 3. Recoveries of detected pesticides in whole date fruit matrix.

MRLs and European Commission. The average of residue in date fruit belonged to Bromopropylate (0.250 mg kg^{-1}) and imazalil (0.101 mg kg^{-1}). The HI values for adult and child consumers with all pesticide residues were lower than 1. The CR was less than 1.0E-6 value. Thus, there was no carcinogenic risk to consumers of date fruits. Comparing the results of this study with some reports on pesticide residue assessments in dates shows that most of the QuEChERS measurements of pesticide residues in dates are based on a limited number of pesticides or have not been done on dates alone, so this report is different. The results of previous studies indicate an improvement in recent trends in pesticide use for crop pest and disease control in Iran. These results may indicate that pesticide management among Iranian farmers has progressed well to some extent in the past

Date fruit type	Detected pesticide	Frequency	Average of residues (mg.kg^{-1})	MRL National (mg.kg^{-1})	MRL in European Commission (mg.kg^{-1})
Piarom	Bromopropylate	3	0.250	0.05	0.01
Zahedi					
Kaloteh					
Zahedi	Cypermethrin (I + II)	1	0.042	0.05	0.05
Zahedi	Fenpropathrin	1	0.005	0.05	0.01
Piarom	Permethrine (I + II)	1	0.05	0.05	0.05
Kaloteh	Imazalil	2	0.101	0.05	0.01
Kaloteh	Endosulfan (I + II)	1	0.008	0.05	0.05

Table 1. Detected levels of pesticide residues in tested date fruit samples.

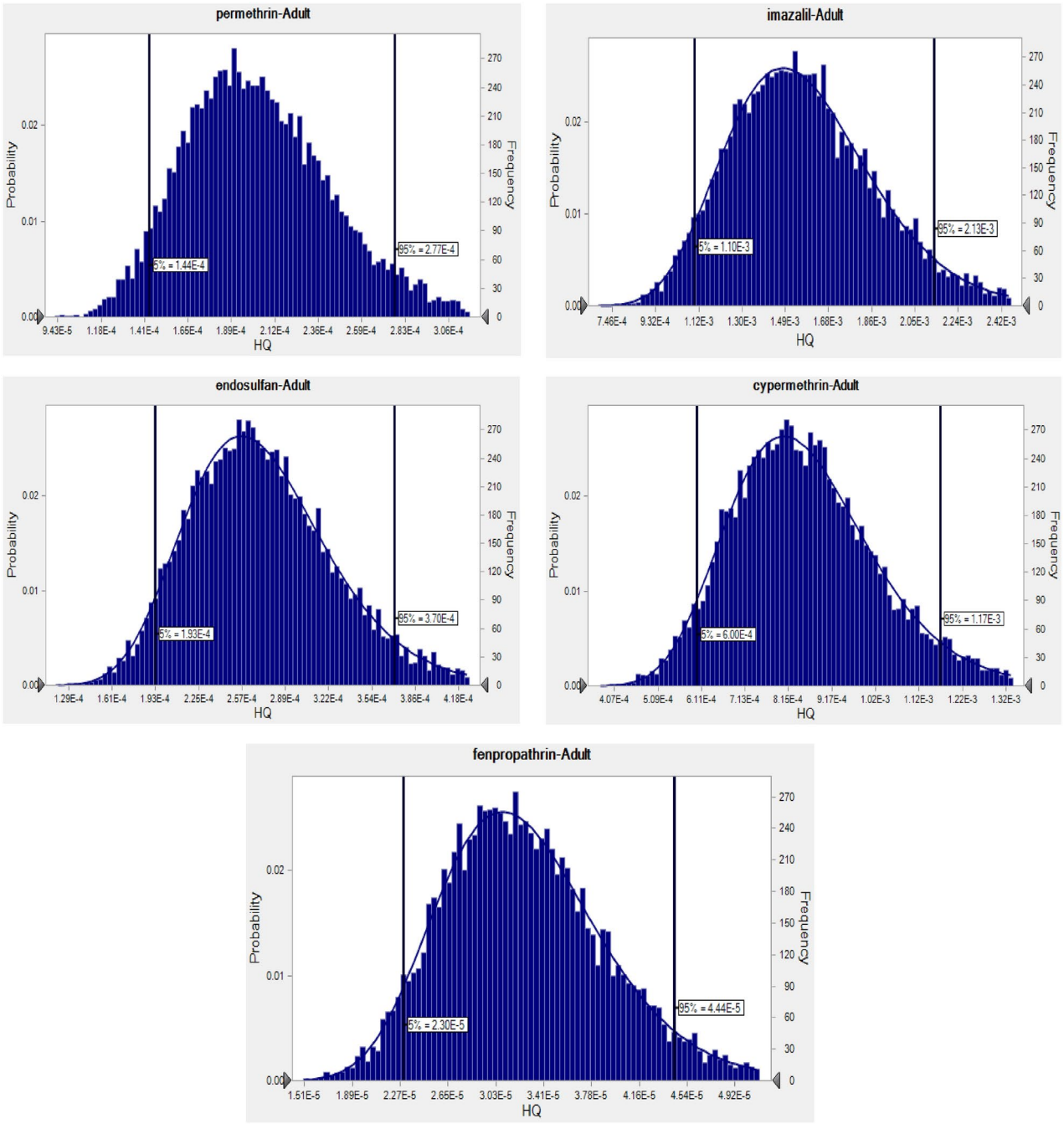

Fig. 4. HQ due to content of most pesticide residues in the fresh date fruit samples for adults.

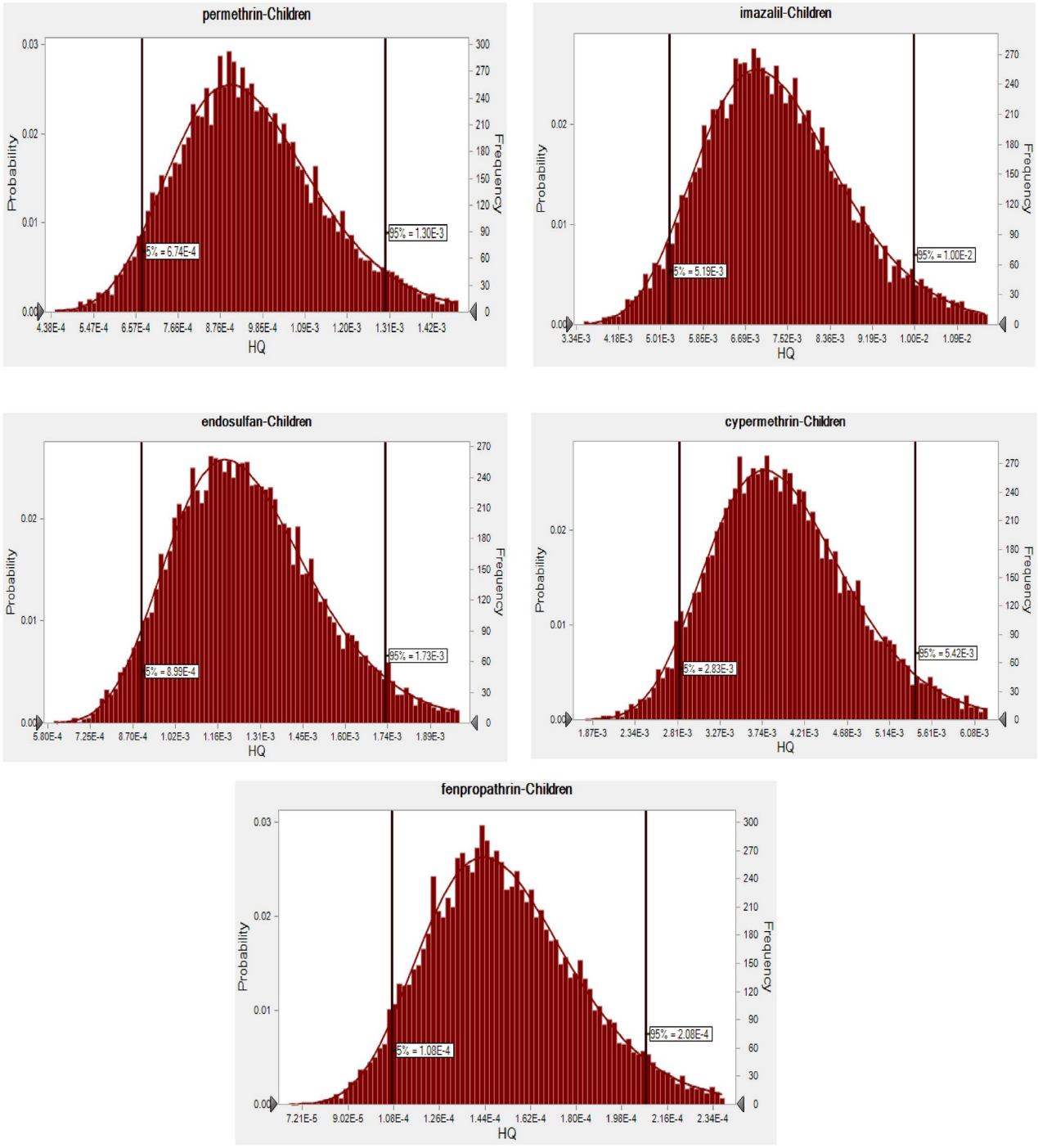

Fig. 5. HQ due to content of most pesticide residues in the fresh date fruit samples for children.

5 years. Overall, the results of this study would be useful for the regulations of the Iranian government on the safe and appropriate use of pesticides in date fruits. To control pesticide use, effective planning and management programs that follow good agricultural practice (GAP) (eg pre-harvest and safety intervals) and approved pesticide use are recommended.

Conclusions

In this study, the detection of pesticides in samples of date fruits is essential for monitoring food safety. This study has provided comprehensive information derived from the examination of 211 pesticides in 90 date fruit samples. The approach was validated for aspects such as linearity, accuracy, the matrix effect, and precision, and the limits for detection and quantification of this technique were also assessed. The utilization of a QuEChERS-UHPLC–MS/MS–GC–MS/MS allows for the detection of both the most volatile and stable pesticide residues

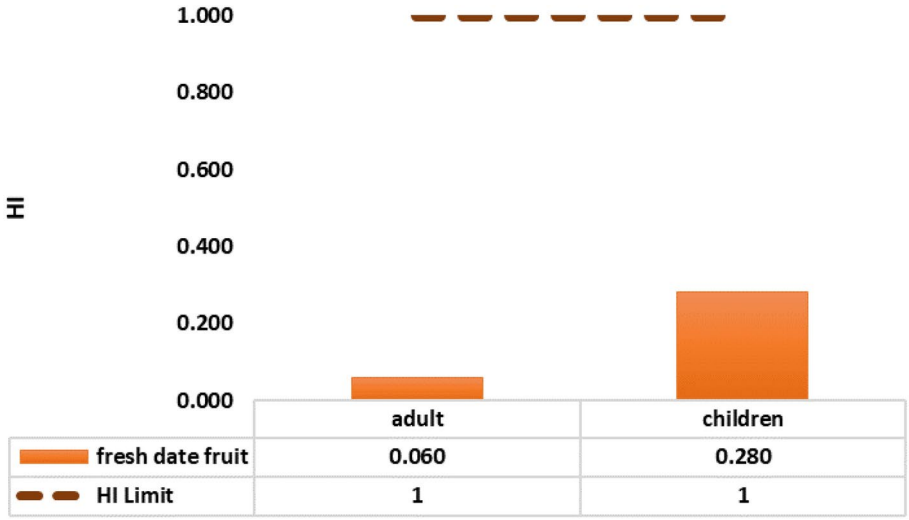

Fig. 6. HI in the adults and children consumers due to the fresh date fruit ingestion. HI < 1 means no significance non-carcinogenic effects.

Pesticide	HQ		HI	
	Adult	Children	Adult	Children
Permethrin	2.0×10^{-4}	9.3×10^{-4}	2.8×10^{-3}	1.3×10^{-2}
Imazalil	1.5×10^{-3}	7.2×10^{-3}		
Endosulfan	2.7×10^{-4}	1.2×10^{-3}		
Cypermethrin	8.4×10^{-4}	3.9×10^{-3}		
Fenpropathrin	3.2×10^{-5}	1.5×10^{-4}		

Table 2. HQ and HI of pesticide residues detected in the fresh date fruit samples. Bromopropylate not evaluated: lack of data.

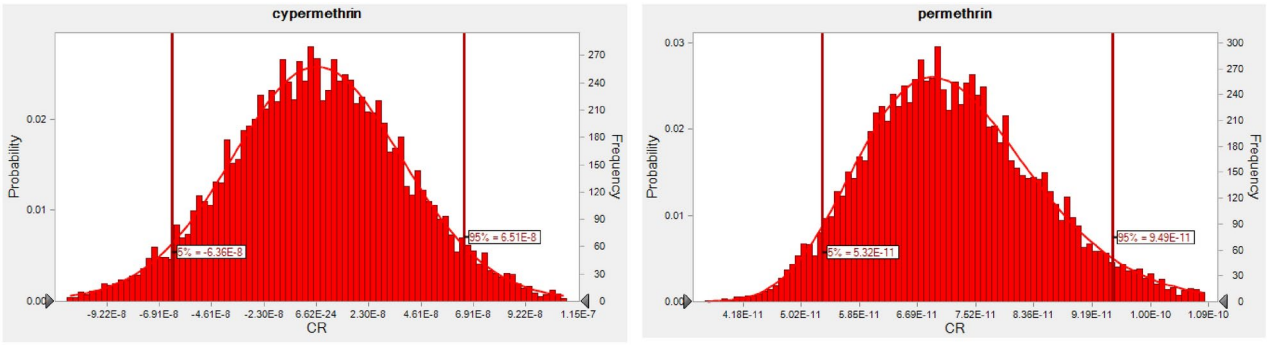

Fig. 7. Total CR due to content of cypermethrin and permethrin residue in the fresh date fruit samples for consumers.

in date fruits. The extraction technique is noted for its rapidity, simplicity, and elevated sensitivity, facilitating the identification of most compounds in a single analysis. The method described satisfies the criteria for high-throughput detection of pesticide residues in date fruits and acts as a benchmark for the assessment of pesticide residues in additional date fruit varieties. It is crucial to emphasize that the achieved percentage of recoveries for the majority of the analyzed pesticides ranges from 77 to 119%.

The results of the risk assessment were shown that the HQ values of < 1 for all pesticide residues were in date fruit samples in adult and children's consumers. The HI in a adults and children were 0.060 and 0.280 in date fruit real samples, respectively. The risk assessment results of this study indicated that pesticide residues in date fruits do not pose a potential risk to human health.

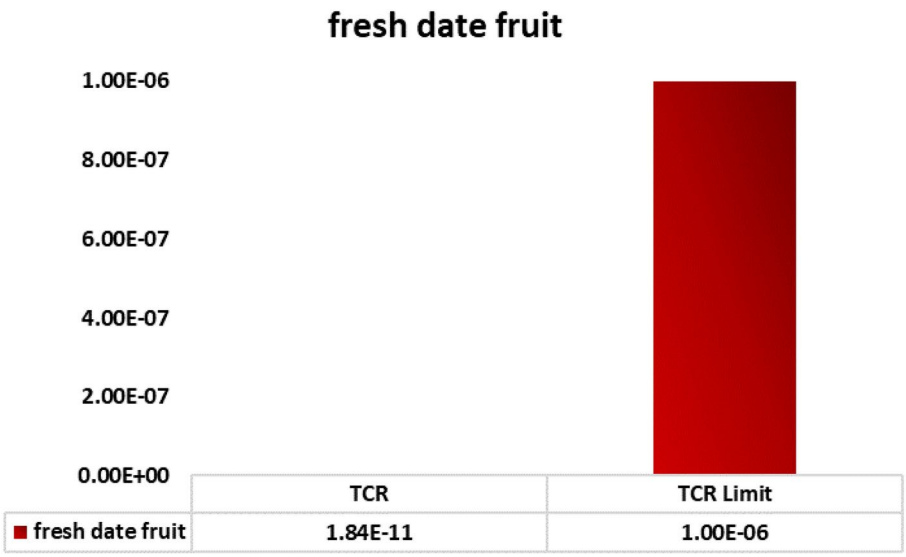

Fig. 8. Total CR in consumers due to the fresh date fruit ingestion.

Pesticide	CR	TCR	Carcinogenicity	EPA group
Permethrin		1.84×10^{-11}	Likely to be carcinogenic to humans at high doses	B
Imazalil	NE		Likely to be carcinogenic to humans at high doses	B
Endosulfan	NE		Not likely to be carcinogenic to humans	E
Cypermethrin			Possibly carcinogenic to humans	C
Fenpropathrin	NE		Not likely to be carcinogenic to humans	E
Bromopropylate	NE		Unlikely to present an acute hazard	U

Table 3. CR, TCR, carcinogenicity and EPA group of pesticide residues detected in the fresh date fruit samples. TRC, The target cancer risk (TCR) is used to assess the potential risk associated with exposure to carcinogenic agents throughout the lifetime exposure period. NE, not evaluated. Permethrin and cypermethrin: endocrine disrupting. Cypermethrin: enantiomeric.

Data availability

Data is available on request. If someone has any question can contact the corresponding authors.

Received: 27 September 2024; Accepted: 21 January 2025
Published online: 24 February 2025

References

1. Saw, G., Nagdev, P., Jeer, M. & Murali-Baskaran, R. K. Silica nanoparticles mediated insect pest management. *Pestic. Biochem. Physiol.* **194**, 105524 (2023).
2. Ren, Z. et al. Unintended consequences: Disrupting microbial communities of Nilaparvata lugens with non-target pesticides. *Pestic. Biochem. Physiol.* **194**, 105522 (2023).
3. Hassaan, M. A. & El Nemr, A. Pesticides pollution: Classifications, human health impact, extraction and treatment techniques. *The Egyptian Journal of Aquatic Research* **46**(3), 207–220 (2020).
4. Camara, M. A., Fuster, A. & Oliva, J. Determination of pesticide residues in edible snails with QuEChERS coupled to GC-MS/MS. *Food Addit. Contam. Part A* **37**(11), 1881–1887 (2020).
5. Amer, M. M., Sabry, B. A., Marrez, D. A., Hathout, A. S. & Fouzy, A. S. M. Exposure assessment of heavy metal residues in some Egyptian fruits. *Toxicol. Rep.* **6**, 538–543 (2019).
6. Zhang, H., Wang, P., Wang, J., Liu, H. & Chen, X. Assessing the impact of Chlorantraniliprole (CAP) pesticide stress on oilseed rape (*Brassia campestris* L.): Residue dynamics, enzyme activities, and metabolite profiling. *Pestic. Biochem. Physiol.* **200**, 105785 (2024).
7. Jafarian Asl, P., Niazmand, R., Razavizadeh, B. M., Shakeri, M. A. & Jahani, M. Monitoring of pesticide and some metal residues in Mazafati date fruit cultivar and risk assessment to the health. *J. Food Compos. Anal.* **115**, 104917 (2023).
8. Cámara, M. A., Cermeño, S., Martínez, G. & Oliva, J. Removal residues of pesticides in apricot, peach and orange processed and dietary exposure assessment. *Food Chem* **325**, 126936 (2020).
9. Qayyum, S. et al. Determination of pesticide residues in dates using UHPLC-QqQ-MS/MS: method development and validation. *Environ. Monit Assess.* **193**(9), 613 (2021).
10. Karizaki, V. M. Iranian dates and ethnic date-based products. *J. Ethnic Foods* **4**(3), 204–209 (2017).
11. Ben Mohamed, E. et al. The determinants of the responsible use of pesticides among date farmers in Qassim region, Saudi Arabia. *Cogent Food Agric.* **10**(1), 2314238 (2024).

12. Arbabi, M. et al. Evaluation of different treatments in control of *Oligonychus afrasiaticus* in date palm orchards of Iran. *Persian J. Acarol.* **6**(2), 20 (2017).
13. El-Saeid, M. H. & Al-Dosari, S. A. Monitoring of pesticide residues in Riyadh dates by SFE, MSE, SFC, and GC techniques. *Arab. J. Chem.* **3**(3), 179–186 (2010).
14. Taghizadeh, S. F. et al. Pesticides, metals, and polycyclic aromatic hydrocarbons in date fruits: A probabilistic assessment of risk to health of Iranian consumers. *J. Food Compos. Anal.* **98**, 103815 (2021).
15. Al-Mssallem, M. Q. Consumption of dates among saudi adults and its association with the prevalence of type 2 diabetes. *Asian J. Clin. Nutr.* **10**, 58 (2018).
16. Yue, Y. et al. Multi-omics and gut microbiome: Unveiling the pathogenic mechanisms of early-life pesticide exposure. *Pestic. Biochem. Physiol.* **199**, 105770 (2024).
17. Arab, A. & Mostafalou, S. Pesticides and insulin resistance-related metabolic diseases: Evidences and mechanisms. *Pestic. Biochem. Physiol.* **195**, 105521 (2023).
18. Kaur, R. et al. Pesticides: An alarming detrimental to health and environment. *Sci. Total Environ.* **915**, 170113 (2024).
19. Eslami, Z., Mahdavi, V. & Tajdar-oranj, B. Probabilistic health risk assessment based on Monte Carlo simulation for pesticide residues in date fruits of Iran. *Environ. Sci. Pollut. Res.* **28**(31), 42037–42050 (2021).
20. Oliva, J., Cermeño, S., Cámara, M. A., Martínez, G. & Barba, A. Disappearance of six pesticides in fresh and processed zucchini, bioavailability and health risk assessment. *Food Chem.* **229**, 172–177 (2017).
21. Shaw, I. & Vannoort, R. 10- Pesticides. In *Food Chemical Safety* (ed. Watson, D. H.) 218–237 (Woodhead Publishing, 2001).
22. MacLachlan, D. J. & Hamilton, D. Estimation methods for maximum residue limits for pesticides. *Regul. Toxicol. Pharmacol.* **58**(2), 208–218 (2010).
23. Mirshekar, A., Madjdzadeh, S. M. & Khayrandish, M. Spider wasps (Hymenoptera, Pompilidae) from the Southeastern Iran, Kerman. *J. Insect Biodivers. Syst.* **6**(1), 9–19 (2020).
24. Guide Documenton Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. EC Directorate-General for Health and Food Safety (EuropeanCommission, 2021).
25. Raposo, F. & Ibelli-Bianco, C. Performance parameters for analytical method validation: Controversies and discrepancies among numerous guidelines. *TrAC Trends Anal. Chem.* **129**, 115913 (2020).
26. Steiner, D., Krska, R., Malachová, A., Taschl, I. & Sulyok, M. Evaluation of matrix effects and extraction efficiencies of LC–MS/MS methods as the essential part for proper validation of multiclass contaminants in complex feed. *J. Agric. Food Chem.* **68**(12), 3868–3880 (2020).
27. Ain, S. N. U. et al. Assessment of arsenic in *Mangifera Indica* (Mango) contaminated by artificial ripening agent: Target hazard quotient (THQ), health risk index (HRI) and estimated daily intake (EDI). *Food Chem. Adv.* **3**, 100468 (2023).
28. Camara, M. A., Barba, A., Cermeño, S., Martinez, G. & Oliva, J. Effect of processing on the disappearance of pesticide residues in fresh-cut lettuce: Bioavailability and dietary risk. *J. Environ. Sci. Health Part B* **52**(12), 880–886 (2017).
29. Gustafsson, Å., Bergman, Å. & Weiss, J. M. Estimated daily intake of per- and polyfluoroalkyl substances related to different particle size fractions of house dust. *Chemosphere* **303**, 135061 (2022).
30. Goumenou, M. & Tsatsakis, A. Proposing new approaches for the risk characterisation of single chemicals and chemical mixtures: The source related Hazard Quotient (HQS) and Hazard Index (HIS) and the adversity specific Hazard Index (HIA). *Toxicol. Rep.* **6**, 632–636 (2019).
31. Chorol, L. & Gupta, S. K. Evaluation of groundwater heavy metal pollution index through analytical hierarchy process and its health risk assessment via Monte Carlo simulation. *Process. Saf. Environ. Prot.* **170**, 855–864 (2023).
32. Veiga-del-Baño, J. M. et al. Uncertainty and associated risks in the analysis of pesticides in homogeneous paprika samples. *Food Chem.* **429**, 136963 (2023).
33. Askari, M. et al. Bottled water safety evaluation: A comprehensive health risk assessment of oral exposure to heavy metals through deterministic and probabilistic approaches by Monte Carlo simulation. *Food Chem. Toxicol.* **185**, 114492 (2024).
34. Uwineza, L., Kim, H.-G. & Kim, C. K. Feasibility study of integrating the renewable energy system in Popova Island using the Monte Carlo model and HOMER. *Energy Strat. Rev.* **33**, 100607 (2021).
35. Ververis, E. et al. Substituting red meat with insects in burgers: Estimating the public health impact using risk-benefit assessment. *Food Chem. Toxicol.* **189**, 114764 (2024).

Acknowledgements

This research was supported by Iranian National Standards Organization of Kerman and University of Jiroft. We thank our colleagues who provided insight and expertise that greatly assisted the research.

Author contributions

Najmeh Sheibani Tezer: Data curation, Investigation, Methodology, writing the original draft, Moslem Basij: Investigation, Data curation, Supervision, Resources, Conceptualization. Mahboube Shirani: Supervision, Conducting Risk Assessment, Resources, and review and editing. Vahideh Mahdavi: Software, Conducting Risk Assessment, and Data Analysis.

Funding

This study was not supported.

Declarations

Competing interests

The authors declare no competing interests.

Consent to participate

No human subjects used at this study.

Consent to publish

No human studies were used at this study. Since, no individual 's data were used, no consent form is required.

Additional information

Supplementary Information The online version contains supplementary material available at https://doi.org/1

0.1038/s41598-025-87638-9.

Correspondence and requests for materials should be addressed to M.B. or M.S.