Contents lists available at ScienceDirect

Arabian Journal of Chemistry

journal homepage: www.ksu.edu.sa

Detection rates of pesticide residues in Saudi Arabian produce as influenced by season

Nasser M. Al-Daghri [a,*], Sherif H. Abd-Alrahman [b], Abdullah M. Alnaami [a], Syed D. Hussain [a], Osama E. Amer [a], Manal E.A. Elhalwagy [c], Majed S. Alokail [d]

[a] *Chair for Biomarkers of Chronic Diseases, Department of Biochemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*
[b] *Pesticides Residues and Environmental Pollution Department, Central Agricultural Pesticide Laboratory, Agricultural Research Center (ARC), Dokki, Giza 12618, Egypt*
[c] *Department of Mammalian Toxicology, Pesticide Central Laboratory, Agriculture Research Center, Giza 12618, Egypt*
[d] *Protein Research Chair, Department of Biochemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia*

ARTICLE INFO

Keywords:
Pesticide residue
Cypermethrin
Saudi Arabia
Maximum residue limit
Thiamethoxam

ABSTRACT

Pesticide residues and persistent organic pollutants (POPs) are known hazardous chemicals that exhibits bioaccumulation in organisms and the ecosystem in general. There is limited evidence on the levels of these contaminants among common Saudi crops grown as well as the effects of season on their levels. Hence, the present investigated the levels of pesticide residues in major fruit and vegetable crops collected during the winter and summer seasons in Saudi Arabia (SA). A total of 392 samples taken from 28 locally produced vegetables and fruits were purchased from local markets in Riyadh, SA during peak summer (N = 263) (June-August 2022) and peak winter (N = 129) (December-February 2022). Food samples were extracted and cleaned up using the modified Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) technique. Liquid chromatography with tandem mass spectrometry (LC-MS/MS) and gas chromatography–tandem mass spectrometry (GC–MS/MS) instruments were used to determine pesticide residues. Crops that had the highest percentage exceeding the maximum residue limit (MRL) include pepper (7.9 %) as well as apricot, fig and pomegranates (3.1 %). Cypermethrin was the most prevalent pesticide residue in both winter and summer samples with detection rates of 13.2 % and 14.1 % respectively ($p = 0.33$). Thiamethoxam detection rates was significantly higher in winter (7.8 %) than summer (3.0 %) ($p = 0.04$). There is a high detection rate of pesticide residues in SA independent of season, with cypermethrin being the most common. Thiamethoxam is more commonly detected in winter than summer crops. The study should be extended to include other potential sources of pesticide residues such as fishes grown in aqua farms and other poultry products.

1. Introduction

Pesticides have been a common staple in modern agriculture settings, intended to protect crops and increase yield to meet the growing food demands of the ever rising global human population. As of 2020, the world-wide use of pesticides has reached 3.5 million tons (Sharma et al., 2019), making the global pesticide market an industry estimated to be worth US$78.7 billion as of 2020 (S&P Global Commodity Insights, 2020). Pesticides are also one of the main sources of persistent organic pollutants (POPs), hazardous contaminants that affect food safety due to its bioaccumulation and persistence in the ecosystem (Guo et al., 2019). Among the more widely known detrimental health effects secondary to POPs exposure include endocrine disruption, immune and neurologic disorders, cancer and reproductive issues (Rokni et al., 2023). Hence, the widespread environmental scattering and over-all health problems directly linked to POPs gave rise to the Stockholm Convention on Persistent Organic Pollutants in May 2001, the purposes of which were enforced on May 2004 (Stockholm Convention, 2023). The Stockholm Convention is a legally binding international agreement which aims to strictly regulate POPs production, use and release. A total of twelve groups of substances under the categories of pesticides [aldrin, chlordane, DDT, dieldrin, heptachlor, hexachlorobenzene (HCB), mirex,

* Corresponding author at: Chair for Biomarkers of Chronic Diseases, Department of Biochemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia.

E-mail addresses: ndaghri@ksu.edu.sa (N.M. Al-Daghri), aalnaami@ksu.edu.sa (A.M. Alnaami), shussain@ksu.edu.sa (S.D. Hussain), omaer1@ksu.edu.sa (O.E. Amer), malokail@ksu.edu.sa (M.S. Alokail).

https://doi.org/10.1016/j.arabjc.2023.105461
Received 29 August 2023; Accepted 15 November 2023
Available online 19 November 2023

toxaphane], industrial chemicals [HCB and polychlorinated biphenyls (PCBs)] and by-products [HCB, polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans (PCDD/PCDF), and PCBs] colloquially known as the dirty dozen, were initially included to be outlawed because of its established adverse effects in the environment and more importantly on humans (Olisa et al., 2022). It is worth mentioning that risk of human exposure to POPs is not limited to food consumption as it is also present in ambient air, water and soil (Rezania et al., 2022; Aravind Kumar et al., 2022; Kumar et al., 2021).

Saudi Arabia (SA) as well as most Middle-East nations are signatories of the Stockholm Convention as well as other environmental conventions (Basel Convention, Rotterdam Convention and Montreal Protocol), yet majority of these Arab nations fail to implement existing legislation, often exacerbated by lack of treatment, perilous transport, concentration in urbanized regions and insufficient management (Hajjar, 2012). Studies on POPs and pesticide residues are also limited in SA. Among the few studies, El-Mubarak and colleagues (2015) discovered a high concentration of POPs in the ambient air of Riyadh, the capital of SA, with average concentrations of pesticides ranging from 2 to 8,216 ng/m^3, demonstrating heavy use within the capital and possibly long distance transport (El-Mubarak et al., 2015). Traces of toxic endocrine disruptors such as phthalate esters and bisphenol A were also found in treated wastewater in SA, a major concern since treated waste waters are used for agriculture (Al-Saleh et al., 2017). SA studies on humans were mostly on polycyclic aromatic hydrocarbons (PAHs), another class of POPs. These PAH studies were done in Saudi children with asthma, and found that the most prevalent circulating PAHs were naphthalene, bezanthracene and benzoacephenanthrylene, among others, ranging from 54.5 to 90.9 % of the positive samples (Al-Daghri et al., 2014). These PAHs were also found to be associated with respiratory disorders since they correlated with biomarkers of asthma in Saudi children, including IgE, interferon gamma and several interleukins (Al-Daghri et al., 2013). Finally, and in a recent review by Wei and colleagues, pesticide residues have been linked to gut dysbiosis and disruption of glucose homeostasis, leading to diabetogenic effects and other chronic disorders as observed in several epidemiologic studies (Wei et al., 2023a, 2023b). The serious clinical effects stemming from accumulated pesticide residues exposure and other contaminants therefore should be of public safety concern, given that the general population of SA already has a myriad of chronic disorders (Amer et al., 2021; Al-Othman et al., 2015; Al-Daghri et al., 2011).

To the best of our knowledge, there is scarcity of data available on the detection rates of POPs, particularly pesticide residues in SA vegetables and fruits. Furthermore, no study has been conducted as to whether seasonal variations exist in the detection rates of these contaminants in SA crops. There is evidence to suggest that pesticide residue bioaccumulation and variation are affected by season in several geographic areas (Dumanoglu et al., 2017; Nguyen et al., 2019; Wang et al., 2022), but most of these studies focused on the elements (air, water or soil) and not on actual crops. We thus hypothesize that seasonal variations exist in the detection rates of pesticide residues in fruits and vegetables locally grown in a majority non-arable land such as SA. The present study therefore aims to determine and compare the detection rates of pesticide residues in vegetables and fruits collected during the 2 main seasons in SA (summer and winter). The study also aims to identify which among the fruits and vegetables purchased in SA are more commonly contaminated by pesticide residues.

2. Methods

2.1. Materials

Pesticide standards have been purchased from Dr. Ehrenstorfer GmbH (Augsbug, Germany). Purities of the certified pesticide standards were from 99.6 to 100 %. Acetonitrile, methanol (HPLC)-grade were supplied by Sigma–Aldrich Company (St. Louis, MO, USA). Ammonium format, with 99 % of purity, was also purchased from Sigma–Aldrich Company (Stenheim, Germany). The analytical reagent grade anhydrous magnesium sulfate (anh $MgSO_4$), anhydrous sodium acetate (99.9 %, anh $C_2H_3NaO_2$), and glacial acetic acid were obtained from Merck Company (Darmstadt, Germany). Primary–secondary amine (PSA) and graphitized carbon black (GCB) sorbent were prepared from Supelco Company (Bellefonte, PA, USA). Ultrapure water of 18.2X resistivity was produced on a Milli Q purification system (Millipore, Molsheim, France). A mixture of pesticide stock standard solutions (10 mg L − 1) was prepared in acetonitrile and was stored at −18 °C. Working solutions were prepared daily to avoid degradation of pesticides by dilution of standard stock.

2.2. Study design and sampling location

In the present cross-sectional study, locally produced vegetables and fruits were purchased from leading produce markets in Riyadh, KSA during peak summer (June-August 2022) and peak winter (December-February 2022). The samples were collected according to international monitoring protocols on the global monitoring plan for POPs (UNEP, 2007; Fiedler et al., 2023).

2.3. Food (vegetables and fruits) sample preparation

Food samples were extracted and cleaned up using modified QuEChERS methodology (Quick, Easy, Cheap, Effective, Rugged, and Safe) (Abd-Alrahman, 2013; González-Curbelo et al., 2022; Alokail et al., 2023). In brief, a 1 kg worth of newly purchased vegetable or fruit samples were chopped and homogenized for 5 min at high speed in a laboratory homogenizer. Homogenized sample (15 g) was placed into 50 mL polyethylene tube, then 15 mL of acetonitrile 1 % acetic acid was added into each tube. The samples were well shaken using a vortex mixer at maximum speed. Afterwards, 4 g of anhydrous magnesium sulfate and 1.0 g of sodium chloride were added, then extract by shaking vigorously on vortex for 5 min and centrifuged for 10 min at 5,000 rpm. An aliquot of 4 mL was transferred from the supernatant to a new clean 15 mL centrifuge tube containing 100 mg PSA and 500 mg anhydrous magnesium sulfate. The samples were again shacked using a vortex for 1 min and then centrifuged for 5 min at 6,000 rpm. An aliquot of 2 mL was concentrated to dryness. All samples were prepared at the Chair for Biomarkers of Chronic Diseases (CBCD) in King Saud University (KSU), Riyadh, Saudi Arabia.

2.4. Pesticide residue analysis

Collected samples were analyzed using the modified EPA 1613 at the Pesticides and Toxicology Unit Laboratory (PTUL), Plant protection department at KSU, Riyadh, KSA. All samples were freeze dried. For the extraction step, a proper solvent (dichloromethane: Hexane 1:1 v:v) was used to extract residues and the Accelerated Solvent Extractor (ASE) was used to minimize co-extraction of any substances that may interfere the determination of POPs residues. Interfering materials was removed (clean-up) from the extract to obtain a solution suitable for quantitative examination by the selected method EPA 1613.

Mass spectrometer Agilent Ion Trap Series 240 connected with Agilent 7890 gas chromatograph was used for the determination of pesticide residues and results were confirmed with liquid chromatography with tandem mass spectrometry (LC-MS/MS). A 2 μL of each sample was injected to split-splitless injector and analytical capillary column was HB-5MS for separation. A series of selected analytical standards (1.0, 5, 10, 25, 50 and 100 ng ml^{-1}) were prepared in n-hexane. Calibration curves were generated by plotting peak area versus concentration. Excellent linearity, good separation and repeatability were observed. Acceptable limit of detection (LOD) was obtained 1.0–5.0 ng ml^{-1}. Samples in duplicates at five levels were spread equally within the analytical range. The calibration curve and recovery validation studies were repeated three times. Rate of recovery for all was ranged from 80 to 120 % for pesticide residues, respectively.

2.5. QA/QC regime

Standard quality assurance protocol were used throughout the study. For external quality control/quality assurance assessment, random sample batches were sent the Central Agricultural Pesticides Laboratory, Agricultural Research Center (ARC), Giza, Egypt. CAPL is an accredited laboratory which has an ISO-17025 accreditation certificate from the Egyptian accreditation council EGAC. The present results have been confirmed by CAPL.

2.6. Method validation

The analytical method was performed in accordance with the SANTE/12682/2019 guidelines of the EU Reference Laboratories for Residues of Pesticides (EURL) (EURL, SANTE/12862/2019). The linearity of the calibration curve was evaluated using the correlation coefficient (R2) for the peak areas against the concentrations in the range of 0.1 to 500 µg/L; R2 should greater than 0.99. The percentage maximum difference in the response factor (RF, %) should be lower than 20 %. The standard solutions were randomly injected in triplicate. The limit of detection (LOD) was determined to evaluate the sensitivity. The limit of quantitation (LOQ) of the method was established as the lowest fortification level that achieves a recovery percentage of 80–120 with a relative standard deviation (RSD) lower than 20 % (Li et al., 2017). Accuracy in terms of percentage recovery was evaluated at three fortification levels, of 10, 50 and 100 µg/kg. Precision in terms of intra-day repeatability ($n = 6$ on the same day) and inter-day repeatability ($n = 18$, on three different days at 7-day intervals) was estimated at the LOQ level.

2.7. Data analysis

Data was analyzed using SPSS version 21.0 (Chicago, IL, USA). POPs concentration was expressed as mean and standard error (SE). Detection rates were presented as frequencies and percentages (%). Mann-Whitney *U* test was used to determine differences in concentration according to season. Chi-square tests of independence was used to determine significant differences in detection rates according to season. A p-value of < 0.05 was considered statistically significant.

3. Results

Table 1 shows the lists of fruits and vegetables included in the study, the percentage of contamination and those that exceeded the maximum residue limit (MRL), the maximum legal level of concentration of pesticides or feed additives that a country will accept on the surfaces of food products (Joint FAO/WHO, 2023). Produce that had the highest percentage exceeding MRL include pepper (7.9 %) as well as apricot, fig and pomegranates (3.1 %).

Out of 392 samples obtained, N = 129 were taken in winter and N = 263 were taken in summer. Detection rates of pesticide residues was 86.8 % and 85.9 % in winter and summer, respectively (Table 2). No significant statistical differences in overall pesticide residues detection rates were found according to season ($p = 0.81$). Cypermethrin was the most commonly found pesticide residue in both winter and summer samples with detection rates of 13.2 % and 14.1 % respectively ($p = 0.33$).

Thiamethoxam detection rates was significantly higher in winter (7.8 %) than summer (3.0 %) ($p = 0.04$) as shown in Fig. 1. Nevertheless, the concentration of thiamethoxam was higher in summer samples with 0.03 ± 0.01 mg/kg versus 0.02 ± 0.01 mg/kg in winter. However, no statistically significant differences in concentration of thiamethoxam was found between summer and winter samples ($p = 0.50$).

Table 1
Percentage (%) of contamination, pesticides and > MRL found in analyzed fruits and vegetables.

Produce	Contamination		Pesticides	>MRL
	Absent	Present		
Apple	0.6	14.9	23.8	0.6
Apricot	0	13.7	42.9	3.1
Arugula	1.1	2.8	12.8	0.6
Banana	1.9	3.1	11.9	0
Cabbage	1.1	0.6	2.6	0
Cantaloupe	1.1	0.6	2.6	0
Carrot	0.6	5.6	23.1	1.1
Cucumber	0.6	10.1	30.8	0
Eggplant	1.7	2.2	10.2	0.6
Fig	0	6.2	23.8	3.1
Grapes	0.6	2.5	4.8	0
Green Bean	0.7	1.7	2.6	0.6
Kiwi	0	3.1	9.5	1.2
Lemon	1.2	11.8	21.4	0
Lettuce	1.7	1.7	5.1	0
Mandarin	0.6	5.0	14.3	0
Okra	0.6	2.2	10.2	0.6
Onion	3.9	3.9	17.9	1.7
Orange	0	12.4	14.3	0
Peach	0	5.6	21.4	0
Pear	0	8.7	23.8	0.6
Pepper	1.7	22.5	64.1	7.9
Potato	1.7	2.8	12.8	0
Pomegranate	1.2	6.8	26.2	3.1
Squash	0	9.0	30.8	0.6
Strawberry	0	3.4	15.4	0
Tomato	2.2	11.8	33.3	0.6
Water Melon	0.6	0	0	0

Note: MRL (maximum residue limit).
Absent: free sample of pesticides contamination
Present: contaminated samples.
(0): not detected.

Furthermore, the number of pesticide residues only found in summer samples include emamectin (N = 4), dinotefuran (N = 3), fenbuconazole (N = 3), pyraclostrobin (N = 3), bifenthrin (N = 2), pendimethalin (N = 2), chlorfenapyr (N = 1), cyprodinil (N = 1), diazinon (N = 1), ethoprophos (N = 1), etofenprox (N = 1), fenamiphos (N = 1), fenhexamid (N = 1), fenpyroximate (N = 1), flutriafol (N = 1), methomyl (N = 1), metribuzin (N = 1), penconazole (N = 1), propamocarb (N = 1), propiconazole (N = 1), pyridaben (N = 1), pyriproxyfen (N = 1), spirodiclofen (N = 1), tetramethrin (N = 1), and triadimenol (N = 1). In contrast, clothianidin (N = 2), fenpropimorph (N = 1), phosmet (N = 1), pirimicarb desmethyl (N = 1) and propargite (N = 1) were only detected in winter samples.

Aggregate concentration of pesticide residues according to season are shown in Table 3. The average aggregate concentration was 0.09 ± 0.02 in winter versus 0.18 ± 0.03 in summer. No statistical differences was found as indicated by insignificant p-value reported in Fig. 2 ($p = 0.38$). Furthermore, none of the pesticide residues showed any significant differences in concentration between winter and summer samples. Aggregate concentration of pesticide residues found only in one season are presented in supplementary Table S1 and no comparisons were done since they were not present in both seasons.

4. Discussion

While the detection rates of pesticide residues in Saudi vegetative crops are not influenced by season as demonstrated by the present findings, certain compounds such as thiamethoxam were observed to have a significantly higher detection rate in samples taken during the summer than winter, although concentrations were comparable. The present study also showed that irrespective of the season, detection rates in SA vegetables and fruits were high (>85 %) with cypermethrin being the most commonly detected. Finally, certain crops such as pepper,

Table 2
Detection Rates of Pesticide Residues according to season.

POPs	All	Winter	Summer	P-values
N	392	129	263	
Absent	54 (13.8)	17 (13.2)	37 (14.1)	0.81
Cypermethrin	32 (8.2)	13 (10.1)	19 (7.2)	0.33
Pyrimethanil	22 (5.6)	5 (3.9)	17 (6.5)	0.29
Indoxacarb	20 (5.1)	7 (5.4)	13 (4.9)	0.83
Imazalil	18 (4.6)	8 (6.2)	10 (3.8)	0.29
Acetamiprid	17 (4.3)	7 (5.4)	10 (3.8)	0.48
Fludioxonil	17 (4.3)	4 (3.1)	13 (4.9)	0.4
Imidacloprid	15 (3.8)	3 (2.3)	12 (4.6)	0.27
Chlorpyrifos	12 (3.1)	3 (2.3)	9 (3.4)	0.55
Thiabendazole	12 (3.1)	5 (3.9)	7 (2.7)	0.51
Azoxystrobin	10 (2.6)	4 (3.1)	6 (2.3)	0.63
Difenoconazole	10 (2.6)	3 (2.3)	7 (2.7)	0.84
Boscalid	9 (2.3)	3 (2.3)	6 (2.3)	0.98
Deltamethrin	9 (2.3)	2 (1.6)	7 (2.7)	0.49
Metalaxyl	9 (2.3)	2 (1.6)	7 (2.7)	0.49
Tebuconazole	9 (2.3)	3 (2.3)	6 (2.3)	0.98
Lambda-Cyhalothrin	8 (2.0)	2 (1.6)	6 (2.3)	0.63
Abamectin	6 (1.5)	2 (1.6)	4 (1.5)	0.98
Bifenazate	6 (1.5)	1 (0.8)	5 (1.9)	0.39
Fluopyram	5 (1.3)	1 (0.8)	4 (1.5)	0.53
2-phenylphenol	5 (1.3)	2 (1.6)	3 (1.1)	0.73
Bupirimate	4 (1.0)	3 (2.3)	1 (0.4)	0.11
Emamectin	4 (1.0)	0	4 (1.5)	0.32
Chlorantraniliprole	3 (0.8)	2 (1.6)	1 (0.4)	0.25
Dinotefuran	3 (0.8)	0 (0.0)	3 (1.1)	0.41
Fenbuconazole	3 (0.8)	0 (0.0)	3 (1.1)	0.41
Fipronil	3 (0.8)	2 (1.6)	1 (0.4)	0.25
Malathion	3 (0.8)	1 (0.8)	2 (0.8)	0.99
Myclobutanil	3 (0.8)	2 (1.6)	1 (0.4)	0.25
Pyraclostrobin	3 (0.8)	0	3 (1.1)	0.41
Trifloxystrobin	3 (0.8)	2 (1.6)	1 (0.4)	0.25
Bifenthrin	2 (0.5)	0	2 (0.8)	0.56
Carbendazim	2 (0.5)	1 (0.8)	1 (0.4)	0.61
Clothianidin	2 (0.5)	2 (1.6)	0	0.13
Pendimethalin	2 (0.5)	0	2 (0.8)	0.56
Pirimicarb	2 (0.5)	1 (0.8)	1 (0.4)	0.61
Tetraconazole	2 (0.5)	1 (0.8)	1 (0.4)	0.61
Thiophanate-methyl	2 (0.5)	1 (0.8)	1 (0.4)	0.61
Chlorfenapyr	1 (0.3)	0	1 (0.4)	0.81
Cyprodinil	1 (0.3)	0	1 (0.4)	0.81
Diazinon	1 (0.3)	0	1 (0.4)	0.81
Ethoprophos	1 (0.3)	0	1 (0.4)	0.81
Etofenprox	1 (0.3)	0	1 (0.4)	0.81
Fenamiphos	1 (0.3)	0	1 (0.4)	0.81
Fenhexamid	1 (0.3)	0	1 (0.4)	0.81
fenpropimorph	1 (0.3)	1 (0.8)	0	0.27
Fenpyroximate	1 (0.3)	0	1 (0.4)	0.81
Flutriafol	1 (0.3)	0	1 (0.4)	0.81
Methomyl	1 (0.3)	0	1 (0.4)	0.81
Metribuzin	1 (0.3)	0	1 (0.4)	0.81
Penconazole	1 (0.3)	0	1 (0.4)	0.81
Phosmet	1 (0.3)	1 (0.8)	0	0.27
Pirimicarb desmethyl	1 (0.3)	1 (0.8)	0	0.27
Propamocarb	1 (0.3)	0	1 (0.4)	0.81
Propargite	1 (0.3)	1 (0.8)	0	0.27
Propiconazole	1 (0.3)	0	1 (0.4)	0.81
Pyridaben	1 (0.3)	0	1 (0.4)	0.81
Pyriproxyfen	1 (0.3)	0	1 (0.4)	0.81
Spirodiclofen	1 (0.3)	0	1 (0.4)	0.81
Tetramethrin	1 (0.3)	0	1 (0.4)	0.81
Triadimenol	1 (0.3)	0	1 (0.4)	0.81

Note: Data presented as N (%).

apricot, fig and pomegranates have the highest amount samples that exceeded MRL. Several studies done elsewhere have also compared seasonal effects in the detection rates of pesticide residues in other samples. In Ghana, higher pesticide residues were found in water and sediment samples on rainy season than dry season, with permethrin and profenofos in particular, having higher concentrations in sediment samples during the dry season (Nyantakyi et al., 2022). In Poland, pesticide concentrations were lowest during winter in surface and ground water, and highest during spring season with 15 of the 25 pesticide residues analyzed detected (Kruć-Fijałkowska et al., 2022). Lastly, in Vietnam, where dry and wet seasons are also the norm, higher concentrations of pesticide contamination were also found during wet season, with cypermethrin, difenoconazole, and fenobucarb having the highest frequencies in vegetables (Nguyen Dang Giang et al., 2022).

Thiamethoxam is a second-generation neonicotinoid compound, a family of acetylcholine receptor inhibitors found in insecticides and is widely used as a seed dressing (Coulon et al., 2019). Despite the substantial crop protection it provides, contemporary issues from recent evidence suggest that thiamethoxam are harmful to beneficial insect species such as caged honeybees, even at sub-lethal levels (Çakıcı et al., 2023; Afza et al., 2023). The extent of potential risks in humans are less well understood, but residues of neonicotenoids including thiamethoxam have been detected in high percentages in dairy products such as cow's milk (Wei et al., 2023a, 2023b). Thiamethoxam is also the most frequently detected neonics in breast milk (Ying et al., 2023). The seasonal variation in thiamethoxam levels may be attributed to the crops itself, as the highest detection rates of pesticide residues (with the exception of pomegranate) were found in summer crops (pepper, fig and apricot). It is worthy to note that thiamethoxam is not the only neonicotinoid detected in the present study, the other 2 being acetamiprid and imidacloprid, both of which are considered as first-generation neonicotinoids (Selvam and Srinivasan, 2019). Thiamethoxam has an acceptable daily intake (ADI) of 0.02 mg/kg bodyweight/day (ADI, 2023).

Another compound of interest in the present study is cypermethrin, the most common pesticide residue detected in the vegetables and fruits analyzed. It has been previously documented as one of the most frequently detected pesticides among fresh fruits imported in the United Arab Emirates (Osaili et al., 2022). Cypermethrin is the most widely used pyrethroid as pest control (Ayad et al., 2011). Pyrethroids have relatively low toxicity and persistence as than other insecticides, but it remains highly lipophilic and therefore can penetrate the blood–brain barrier easily which can immediately affect the central nervous system (Hao et al., 2023). In South Brazil, cypermethrin and permethrin accounted for 95 % of the sum pyrethroids assessed in ambient air but showed no clear seasonal trend, making exposure not limited to oral but inhalational as well (Guida et al., 2021). However, emerging evidence suggests that cypermethrin toxicity can be mitigated by antioxidants such as glutathione (He et al., 2023), ascorbic acid and tea polyphenols (Xie et al., 2023), serving as promising antidotes to cypermethrin exposure. A study conducted in SA demonstrated that overuse of cypermethrin as insecticide has led to cypermethrin resistance in some pests, the common housefly (*Musca domestica*) in particular (Hafez and Abbas, 2023). It is worthy to note that in the present study, cypermethrin (including Z-cypermethrin and Alfa-cypermethrin) is classified as a restricted pesticide in KSA as determined by the Saudi Food and Drug Administration (SFDA), and its dangerous use is only authorized to certified individuals (SFDA, https://www.sfda.gov.sa/). Cypermethrin has a tolerable daily intake of 0.01 mg/kg/day (US EPA, 2023).

In the present study, some samples from several crops including pepper, apricot, figs and pomegranates exceeded MRL levels, suggesting that these vegetables and fruits should be monitored more closely for risk assessment. A smaller study conducted in 2019 found that some leafy vegetables purchased from Alkharj (part of central SA) also had levels of pesticides exceeding MRLs, particularly spinach, corchorus and parsley (Faraj, 2019). Residues of pesticides in fruits and vegetables vary widely across countries and cannot be compared mostly because the demand for crops are different as well as the geographic-appropriateness for certain crop varieties (Shen et al., 2013; Arshad et al., 2022). It is important to mention that MRLs are intended primarily to determine whether Good Agricultural Practice (GAP) is being implemented and to guide international trade in agricultural products treated with pesticides. MRLs are primarily assessed based on the protocols of GAP for standardization. This implies that MRLs are not necessarily safety limits, and consumption of vegetables and fruits with residues in excess of

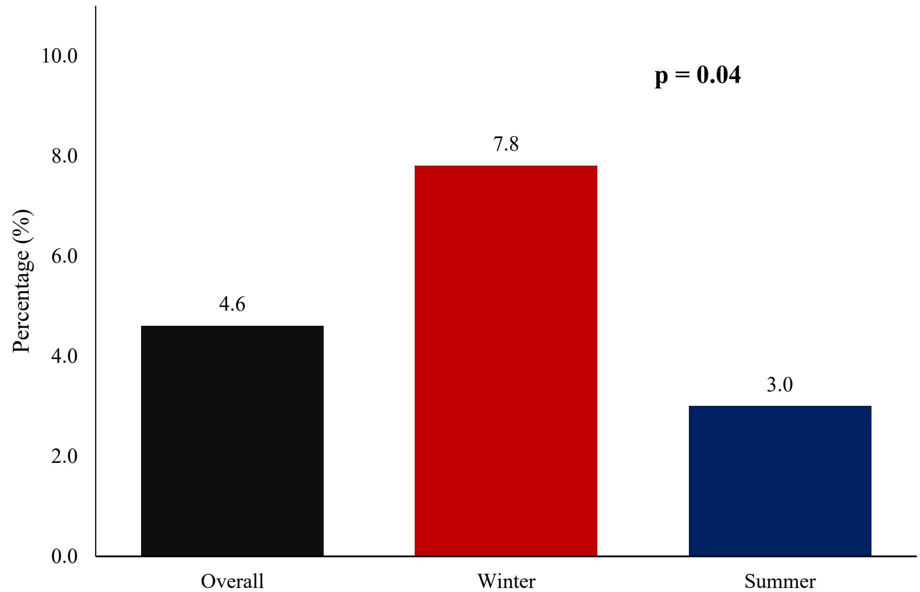

Fig. 1. Prevalence of Thiamethoxam according to Season.

Table 3
Concentration of POPs according to Season.

POPs (mg/kg)	Winter	Summer	P-value
2-phenylphenol	0.01 ± 0.00	0.01 ± 0.00	0.36
Abamectin	0.01 ± 0.01	0.02 ± 0.00	0.34
Acetamiprid	0.33 ± 0.24	0.40 ± 0.23	0.20
Azoxystrobin	0.01 ± 0.00	0.03 ± 0.02	0.75
Bifenazate	0.02	0.08 ± 0.06	0.77
Boscalid	0.03 ± 0.02	0.08 ± 0.04	0.61
Bupirimate	0.02 ± 0.02	0.02	0.64
Carbendazim	0.01	0.02	0.32
Chlorantraniliprole	0.04 ± 0.03	0.04	1.0
Chlorpyrifos	0.46 ± 0.45	0.07 ± 0.03	0.40
Cypermethrin	0.02 ± 0.01	0.30 ± 0.16	0.48
Deltamethrin	0.02 ± 0.01	0.07 ± 0.03	0.24
Difenoconazole	0.01 ± 0.00	0.06 ± 0.05	1.0
Fipronil	0.43 ± 0.41	0.02	1.0
Fludioxonil	0.11 ± 0.08	0.40 ± 0.15	0.23
Fluopyram	0.02	0.21 ± 0.06	0.16
Imazalil	0.15 ± 0.06	0.13 ± 0.06	0.56
Imidacloprid	0.02 ± 0.01	0.08 ± 0.03	0.88
Indoxacarb	0.04 ± 0.02	0.79 ± 0.31	0.06
Lambda-Cyhalothrin	0.05 ± 0.04	0.03 ± 0.01	0.74
Malathion	0.41	0.01 ± 0.00	0.22
Metalaxyl	0.03 ± 0.02	0.01 ± 0.00	0.24
Myclobutanil	0.03 ± 0.02	0.04	1.0
Pirimicarb	0.02	0.02	0.32
Pyrimethanil	0.47 ± 0.40	0.46 ± 0.26	0.22
Tebuconazole	0.03 ± 0.02	0.02 ± 0.01	0.90
Tetraconazole	0.01	0.01	0.32
Thiabendazole	0.02 ± 0.01	0.03 ± 0.01	0.87
Thiamethoxam	0.02 ± 0.01	0.03 ± 0.01	0.50
Thiophanate-methyl	0.02	0.01	0.32
Trifloxystrobin	0.01 ± 0.00	0.00	0.48

Note Data presented as Mean ± SE; P-values are obtained from Mann-Whitney U-Test; p-value < 0.05 considered significant.

MRLs does not automatically indicate a threat to health.

The authors acknowledge some limitations. The study was limited to the determination of pesticide residue detection rates in fruits and vegetables during summer and winter seasons only, and in both instances health risk assessment was not included. As such, health risk due to consumption cannot be ascertained. Nevertheless, the omnipresence of pesticide residues is not limited to agricultural products, and other food sources such as aquatic meat, poultry and dairy products should also be assessed in future investigations. The present study's strengths include the documentation of an extensive list of pesticide residues that were previously not investigated in KSA, filling the needed gap that will help policy makers in satisfying its requirements in the Stockholm convention and its responsibilities in the food safety of the Saudi community. An added strength of the study is the robustness of the methods used to determine pesticide residues that were confirmed externally by collaborating laboratories outside SA.

5. Conclusion

In conclusion, detection rates of pesticide residues in various local produce were analyzed and compared according to season using the QuEChERS technique for extraction and LC-MS/MS with GC–MS/MS for determination. There is a high detection rate of pesticide residues in SA independent of season, with cypermethrin being the most common pesticide residues detected. Thiamethoxam levels are more concentrated in summer crops, but are more frequently detected in winter. The study should be extended to include other potential sources of pesticide residues such as fishes grown in aqua farms, other poultry products and ambient air. These additional sources of will be able to provide a bigger picture of the extent of pesticide residue contamination in Saudi settings. In the meantime, closer monitoring of local agricultural products as well as its practices are needed to ultimately lessen the health risks linked to pesticide residue exposure.

Funding

This project was funded by the National Plan for Science, Technology and Innovation (MAARIFAH), King Abdulaziz City for Science and Technology, Kingdom of Saudi Arabia (Award No: 14-ENV2482-02).

CRediT authorship contribution statement

Nasser M. Al-Daghri: Writing - original draft, Resources. **Sherif H. Abd-Alrahman:** Investigation, Data curation. **Abdullah M. Alnaami:** Methodology, Validation. **Syed D. Hussain:** Formal analysis, Investigation. **Osama E. Amer:** Investigation, Data curation. **Manal E.A. Elhalwagy:** Investigation, Data curation. **Majed S. Alokail:** Supervision, Funding acquisition.

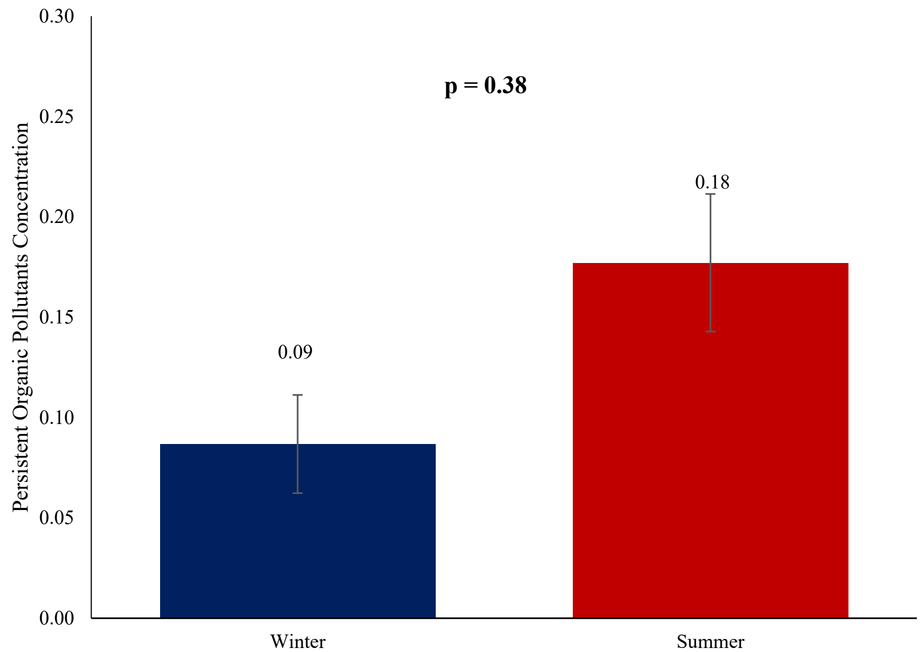

Fig. 2. Persistent Organic Pollutants according to Season.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.arabjc.2023.105461.

References

Abd-Alrahman, S.H., 2013. Dissipation of hexythiozox on beans pods by HPLC-DAD. Bull. Environ. Contam. Toxicol. 90 (4), 504–507.

Acceptable daily intakes for agricultural and veterinary chemicals. Accessed online last Nov 14, 2023 (https://apvma.gov.au/node/26596).

Afza, R., Afzal, A., Riaz, M.A., Majeed, M.Z., Idrees, A., Qadir, Z.A., Afzal, M., Hassan, B., Li, J., 2023. Sublethal and transgenerational effects of synthetic insecticides on the biological parameters and functional response of *Coccinella septempunctata* (Coleoptera: Coccinellidae) under laboratory conditions. Front. Physiol. 14, 1088712.

Al-Daghri, N.M., Al-Attas, O.S., Alokail, M.S., Alkharfy, K.M., Yousef, M., Sabico, S.L., Chrousos, G.P., 2011. Diabetes mellitus type 2 and other chronic non-communicable diseases in the central region, Saudi Arabia (Riyadh cohort 2): a decade of an epidemic. BMC Med. 9, 76.

Al-Daghri, N.M., Alokail, M.S., Abd-Alrahman, S.H., Draz, H.M., Yakout, S.M., Clerici, M., 2013. Polycyclic aromatic hydrocarbon exposure and pediatric asthma in children: a case-control study. Environ. Health 12, 1.

Al-Daghri, N.M., Alokail, M.S., Abd-Alrahman, S.H., Draz, H.M., 2014. Polycyclic aromatic hydrocarbon distribution in serum of Saudi children using HPLC-FLD: marker elevations in children with asthma. Environ. Sci. Pollut. Res. Int. 21 (20), 12085–12090.

Alokail, M.S., Abd-Alrahman, S.H., Alnaami, A.M., Hussain, S.D., Amer, O.E., Elhalwagy, M.E.A., Al-Daghri, N.M., 2023. Regional variations in pesticide residue detection rates and concentrations in Saudi Arabian crops. Toxics. 11 (9), 798.

Al-Othman, A.A., Abd-Alrahman, S.H., Al-Daghri, N.M., 2015. DDT and its metabolites are linked to increased risk of type 2 diabetes among Saudi adults: a cross-sectional study. Environ. Sci. Pollut. Res. Int. 22 (1), 379–386.

Al-Saleh, I., Elkhatib, R., Al-Rajoudi, T., Al-Qudaihi, G., 2017. Assessing the concentration of phthalate esters (PAEs) and bisphenol A (BPA) and the genotoxic potential of treated wastewater (final effluent) in Saudi Arabia. Sci. Total Environ. 578, 440–451.

Amer, O.E., Sabico, S., Khattak, M.N.K., Alnaami, A.M., Aljohani, N.J., Alfawaz, H., AlHameidi, A., Al-Daghri, N.M., 2021. Increasing Prevalence of Pediatric Metabolic Syndrome and Its Components among Arab Youth: a Time-Series Study from 2010–2019. Children (basel) 8 (12), 1129.

Aravind Kumar, J., Krithiga, T., Sathish, S., Renita, A.A., Prabu, D., Lokesh, S., Geetha, R., Namasivayam, S.K.R., Sillanpaa, M., 2022. Persistent organic pollutants in water resources: fate, occurrence, characterization and risk analysis. Sci. Total Environ. 831, 154808.

Arshad, M., Ahmed, M.S., Hussain, S.M., Hussain, N., 2022. Monitoring of level of mean concentration and toxicity equivalence (TEQ) of polychlorinated biphenyls (PCBs) in selected vegetables, beans and grains in khanewal and multan, Pakistan. Saudi J. Biol. Sci. 29 (4), 2787–2793.

Ayad, M.A., Ait Fdil, M., Mouabad, A., 2011. Effects of Cypermethrin (pyrethroid insecticide) on the valve activity behavior, byssal thread formation, and survival in air of the marine mussel Mytilus galloprovincialis. Arch. Environ. Contam. Toxicol. 60 (3), 462–470.

Çakıcı, Ö., Uysal, M., Demirözer, O., Gösterit, A., 2023. Effects of thiamethoxam on brain structure of Bombus terrestris (Hymenoptera: Apidae) workers. Chemosphere 338, 139595.

Coulon, M., Schurr, F., Martel, A.C., Cougoule, N., Bégaud, A., Mangoni, P., Di Prisco, G., Dalmon, A., Alaux, C., Ribière-Chabert, M., Le Conte, Y., Thiéry, R., Dubois, E., 2019. Influence of chronic exposure to thiamethoxam and chronic bee paralysis virus on winter honey bees. PLoS One 14 (8), e0220703.

Dumanoglu, Y., Gaga, E.O., Gungormus, E., Sofuoglu, S.C., Odabasi, M., 2017. Spatial and seasonal variations, sources, air-soil exchange, and carcinogenic risk assessment for PAHs and PCBs in air and soil of Kutahya, Turkey, the province of thermal power plants. Sci. Total Environ. 580, 920–935.

El-Mubarak, A.H., Rushdi, A.I., Al-Mutlaq, K.F., Bazeyad, A.Y., Simonich, S.L.M., Simoneit, B.R.T., 2015. Occurrence of high levels of persistent organic pollutants (POPs) in particulate matter of the ambient air of Riyadh, Saudi Arabia. Arab J. Sci. Eng. 40, 81–92.

EURL. Analytical Quality Control and Method Validation Procedures for Pesticide Residues Analysis in Food and Feed. In SANTE/12682/2019, Accessed Nov 13, 2023, https://www.eurl-pesticides.eu/userfiles/file/EurlALL/SANTE_11312_2021.pdf.

FAO/WHO, 2023 Meeting on Pesticides. https://www.who.int/publications/i/item/9789240069602 (Accessed July 31, 2023).

Faraj, T.K., 2019. Determination of pesticide residues in most commonly consumed leafy vegetables in Riyadh region (Al-Kharej Province). JKAU: Met. Environ. Arid Land Agric. Sci. 28 (2), 63–73.

Fiedler, H., Abad, E., de Boer, J., 2023. Analysis of persistent organic pollutants for the Stockholm Convention's global monitoring plan. Chemosphere 332, 138843. https://doi.org/10.1016/j.chemosphere.2023.138843.

González-Curbelo, M.Á., Varela-Martínez, D.A., Riaño-Herrera, D.A., 2022. Pesticide-residue analysis in soils by the QuEChERS method: a review. Molecules 27 (13), 4323.

Guida, Y., Pozo, K., Carvalho, G.O., Capella, R., Targino, A.C., Torres, J.P.M., Meire, R. O., 2021. Occurrence of pyrethroids in the atmosphere of urban areas of Southeastern Brazil: inhalation exposure and health risk assessment. Environ. Pollut. 290, 118020.

Guo, W., Pan, B., Sakkiah, S., Yavas, G., Ge, W., Zou, W., Tong, W., Hong, H., 2019. Persistent Organic Pollutants in Food: Contamination Sources, Health Effects and Detection Methods. Int. J. Environ. Res. Public Health 16 (22), 4361.

Hafez, A.M., Abbas, N., 2023. Biological Fitness Cost, Demographic Growth Characteristics, and Resistance Mechanism in Alpha-Cypermethrin-Resistant *Musca domestica* (Diptera: Muscidae). Biology (basel). 12 (7), 1021.

Hajjar, M.J., 2012. The persisted organic pesticides pollutant (POPs) in the in the Middle East Arab Countries. Int J Agron Plan Prod 3 (1), 11–18.
Hao, F., Bu, Y., Huang, S., Li, W., Feng, H., Wang, Y., 2023. Effects of pyrethroids on the cerebellum and related mechanisms: a narrative review. Crit. Rev. Toxicol. 53 (4), 229–243.
He, Q., Zhang, X., Yang, X., 2023. Glutathione mitigates meiotic defects in porcine oocytes exposed to beta-cypermethrin by regulating ROS levels. Toxicology 494, 153592.
Kruć-Fijałkowska, R., Dragon, K., Drożdżyński, D., Górski, J., 2022. Seasonal variation of pesticides in surface water and drinking water wells in the annual cycle in western Poland, and potential health risk assessment. Sci. Rep. 12 (1), 3317.
Kumar, B., Verma, V.K., Mishra, M., Piyush, K.V., Tiwari, A., Kumar, S., Yadav, V.P., Gargava, P., 2021. Assessment of persistent organic pollutants in soil and sediments from an urbanized flood plain area. Environ. Geochem. Health 43 (9), 3375–3392.
Li, C., Liu, R., Li, L., Li, W., He, Y., Yuan, L., 2017. Dissipation behavior and risk assessment of butralin in soybean and soil under field conditions. Environ. Monit. Assess. 189, 476.
Nguyen Dang Giang, C., Le, D.B.C., Nguyen, V.H., Hoang, T.L., Tran, T.V.T., Huynh, T.P. L., Nguyen, T.Q.T., 2022. Assessment of pesticide use and pesticide residues in vegetables from two provinces in Central Vietnam. PLoS One 17 (6), e0269789.
Nguyen, T.X., Nguyen, B.T., Tran, H.T.T., Mai, H., Duong, T.T., Bach, Q.V., 2019. Seasonal, spatial variation, and potential sources of organochlorine pesticides in water and sediment in the lower reaches of the Dong Nai river system in Vietnam. Arch. Environ. Contam. Toxicol. 77 (4), 514–526.
Nyantakyi, J.A., Wiafe, S., Akoto, O., 2022. Seasonal changes in pesticide residues in water and sediments from river Tano, Ghana. J. Environ. Public Health 2022, 8997449.
Olisah, C., Adeola, A.O., Iwuozor, K.O., Akpomie, K.G., Conradie, J., Adegoke, K.A., Oyedotun, K.O., Ighalo, J.O., Amaku, J.F., 2022. A bibliometric analysis of pre- and post-Stockholm Convention research publications on the Dirty Dozen Chemicals (DDCs) in the African environment. Chemosphere 308 (Pt 2), 136371.
Osaili, T.M., Al Sallagi, M.S., Dhanasekaran, D.K., Bani Odeh, W.A.M., Al Ali, H.J., Al Ali, A.A.S.A., Cheikh Ismail, L., Al Mehri, K.O., Pisharath, V.A., Holley, R., Obaid, R. S., 2022. Pesticide residues in fresh fruits imported into the United Arab Emirates. Heliyon 8 (12), e11946.
Rezania, A., Talaiekhozani, A., Oryani, B., Cho, J., Barghi, M., Rupani, P.F., Kamali, M., 2022. Environ. Pollut. 307, 119586.
Rokni, L., Rezaei, M., Rafieizonooz, M., Khankhajeh, E., Mohammadi, A.A., Rezania, S., 2023. Effect of persistent organic pollutants on human health in South Korea: a review of the reported diseases. Sustainability 15, 10851.
S&P Global Commodity Insights. Pesticides Market Analysis. https://www.spglobal.com/commodityinsights/en/ci/products/crop-science-pesticides.html#:~:text=Key%20facts%20about%20the%20pesticides,to%20reach%20approximately%20%2478.7%20billion. (Accessed July 30, 2023).
Selvam, V., Srinivasan, S., 2019. Neonicotinoid poisoning and management. Indian J. Crit. Care Med. 23 (Suppl 4), S260–S262.
SFDA. https://www.sfda.gov.sa/sites/default/files/2021-05/lawPestcideE.pdf. (Accessed last July 31, 2023).
Sharma, A., Kumar, V., Shahzad, B., Tanveer, M., Sidhu, G.P.S., Handa, N., Kohli, S.K., Yadav, P., Bali, A.S., Parihar, R.D., Dar, O.I., Singh, K., Jasrotia, S., Bakshi, P., Ramakrishnan, M., Kumar, S., Bhardwaj, R., Thukral, A.K., 2019. Worldwide pesticide usage and its impacts on ecosystem. SN Appl Sci 1, 1446.
Shen, L., Xia, B., Dai, X., 2013. Residues of persistent organic pollutants in frequently-consumed vegetables and assessment of human health risk based on consumption of vegetables in Huizhou, South China. Chemosphere 93 (10), 2254–2263.
Stockholm Convention. https://chm.pops.int/default.aspx. (Accessed July 30, 2023).
United Nations Environment Program (UNEP). Guidance on the global monitoring plan for persistent organic pollutants. 2007. Accessed last July 22, 2023: https://www.informea.org/en/guidance-global-monitoring-plan-persistent-organic-pollutants-preliminary-version-february-2007.
US EPA. Non-Carcinogen Tolerable Daily Intake (TDI) Values. Accessed Nov 13, 2023 (http://www.popstoolkit.com/tools/HHRA/TDI_USEPA.aspx).
Wang, C., Feng, L., Thakuri, B., Chakraborty, A., 2022. Ecological risk assessment of organochlorine pesticide mixture in South China Sea and East China Sea under the effects of seasonal changes and phase-partitioning. Mar. Pollut. Bull. 185 (Pt A), 114329.
Wei, X., Pan, Y., Tang, Z., Lin, Q., Jiang, Y., Chen, J., Xian, W., Yin, R., Li, A.J., Qiu, R., 2023a. Neonicotinoids residues in cow milk and health risks to the Chinese general population. J. Hazard. Mater. 452, 131296.
Wei, Y., Wang, L., Liu, J., 2023b. The diabetogenic effects of pesticides: evidence based on epidemiological and toxicological studies. Environ. Pollut. 331 (Pt 2), 121927.
Xie, Y., Gong, L., Liu, S., Yan, J., Zhao, S., Xia, C., Li, K., Liu, G., Mazhar, M.W., Zhao, J., 2023. Antioxidants improve β-cypermethrin degradation by alleviating oxidative damage and increasing bioavailability by Bacillus cereus GW-01. Environ. Res. 236 (Pt 1), 116680.
Ying, Z., Fu, L., Gu, S., Wang, Y., Mo, X., Tang, T., Jin, H., Zhang, Q., 2023. Development of QuEChERS coupled with UHPLC-MS/MS for simultaneous determination of eight neonicotinoid pesticides in breast milk. Environ. Monit. Assess. 195 (5), 597.