

Original Research

Quantification of Pesticide Residues and Heavy Metals in Selected Fruit and Soil Samples from the Aseer Region, Saudi Arabia

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Abstract

Pesticides play a crucial role in improving agricultural productivity by protecting crops from pests and diseases. However, improper application of these chemical agents poses significant risks to human health and the environment. Soil, a fundamental resource in agriculture, can adsorb and retain pesticides. Once bound to soil particles, these compounds may undergo rapid degradation or be released gradually into the environment and groundwater systems. Persistent pesticides are particularly concerning due to their prolonged environmental presence, which can lead to detrimental effects on living organisms through bioaccumulation and ecological disruption. Similarly, the presence of heavy metals in soil presents substantial ecological and health risks. The main challenge in analyzing pesticide residues or heavy metals lies in the complexity of developing methods that ensure high sensitivity, accuracy, and precision while overcoming interference from diverse sample components.

Once a suitable analytical method is established and its accuracy and precision are verified, it is applied to real samples to evaluate their contamination by pesticides or heavy metals. The literature shows limited data on soil and fruit contamination by pesticides and heavy metals in the Aseer region, especially in Wadi Bin Hashbal. This demonstrates the necessity of research to evaluate soil and fruit quality in this important agricultural area. This study validates the QuEChERS method for detecting pesticide residues in four fruit samples obtained from local supermarkets in the Aseer region, Saudi Arabia, and two soil samples collected from Wadi Bin Hashbal and the Suda area in the same region, using gas chromatography-mass spectrometry (GC-MS). Calibration of pesticide standards yielded

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correlation coefficients ranging from 0.9997 to 0.9916, ensuring reliable quantitative analysis. Recovery rates for the studied pesticides in lemon samples ranged from 76.4% to 100.5%, while soil samples from Wadi Bin Hashbal exhibited recoveries between 70.5% and 90.3%. The relative standard deviation (RSD%) for lemon samples ranged from 2.19% to 10.69%, whereas for soil samples from Wadi Bin Hashbal, the RSD% ranged from 3.63% to 11.32%. The analysis revealed that all tested samples were free of pesticide residues, except for diazinon in the soil sample from Suda, piperophos in both the soil-Suda and apple samples, and permethrin-2 in the tangerine sample. The concentrations of these detected pesticides fell within the range of the limit of quantification (LOQ) and the limit of detection (LOD). Specifically, the LOD values for the analyzed pesticides were $\leq 0.112 \mu\text{g/g}$ (propryzamide), while LOQ values were $\leq 0.204 \mu\text{g/g}$ (propryzamide). Additionally, the concentrations of heavy metals in soil samples from Wadi Bin Hashbal, irrigated with treated and untreated water, were measured across different seasons using inductively coupled plasma mass spectrometry (ICP-MS). The results indicated that some heavy metal concentrations exceeded permissible limits set by the Kingdom of Saudi Arabia, with the lowest concentrations observed during the spring season.

Keywords: pesticides, QuEChERS, GC-MS/MS, fruit, soil, heavy metal, ICP-MS

Introduction

Fruits are a vital component of the human diet, supplying essential nutrients necessary for various physiological functions. However, like all crops, fruits are highly susceptible to pests and diseases during growth and storage, which can compromise their quality and yield. To address these challenges and enhance agricultural productivity, pesticides are extensively employed worldwide [1, 2]. While the use of pesticides is critical for ensuring crop protection, their improper application poses serious health risks, including migraines, nausea, endocrine disruption, fetal harm, chronic diseases, and even cancer. Additionally, the misuse of pesticides can lead to environmental repercussions such as pest resistance, harm to non-target organisms, and broader ecological disturbances [3, 4].

Soil, being fundamental to agricultural practices, plays a major role in storing and retaining pesticides. Pesticides bound to soil particles can either degrade rapidly or be released slowly into the environment and groundwater systems, posing risks to ecosystems and human health. This is particularly concerning in the case of persistent pesticides, which degrade slowly and accumulate in biological systems, leading to long-term environmental and health risks [5, 6]. As a result, stringent control programs and regulations have been implemented globally to ensure the safety and quality of agricultural products. These initiatives focus on monitoring and regulating pesticide residue contamination in water, soil, and food, aiming to safeguard public health and preserve the environment. Over time, maximum residue limit (MRL) regulations have become increasingly rigorous, particularly for highly toxic pesticides [7]. This trend presents notable challenges for analysts, requiring the development of advanced methods to comply with these strict standards. The complexity arises from the need to develop and apply methods that can achieve high sensitivity, accuracy, and precision while dealing with diverse and

often interfering sample components. Furthermore, these methods must be efficient, cost-effective, and compliant with stringent regulatory standards. Striking a balance between these factors is crucial to ensuring food safety, protecting consumers, and mitigating environmental risks [8]. Numerous studies have been conducted in this field with the aim of achieving accurate and efficient analysis of pesticide residues. These efforts have led to the development of various analytical procedures, which typically involve sequential steps such as extraction, clean-up, separation, and detection. Each step plays a critical role in ensuring the reliability and precision of the analysis, particularly when dealing with complex matrices such as fruits and soil [9]. Numerous extraction techniques have been suggested for extracting pesticides from fruit and soil, including microextraction in the solid phase [10], matrix solid-phase microdispersion [11], dispersive liquid-liquid microextraction [12, 13], microwave-assisted extraction [14], ultrasonic and Soxhlet extraction [15], and solid-liquid extraction [16]. The QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) method has recently become one of the most effective methods to extract pesticides from food and soil samples. This method, first presented by Anastassiades et al. in 2003 [17], has proven to be highly effective, with minimal interference from the sample matrix and high target compound recovery rates. This method is versatile and can be customized to meet specific analytical requirements [18]. It involves using an acetonitrile-based solvent for the salting-out extraction, followed by dispersive solid-phase extraction [19].

The flexibility of the QuEChERS approach is a powerful feature that is no less important than the other confirmed advantages, such as simplicity and efficiency. Most of the analytical procedures used in the determination of pesticides are based on the use of chromatographic techniques, mainly gas chromatography (GC) with a selective detector such as a mass spectrometry (MS) detector [20]. One of the greatest advantages of GC-MS analysis is the possible

use of electron ionization–mass spectrum (EI-MS) spectral library searching for the identification of unknown components extracted from complex food matrices [3].

In parallel to pesticide contamination, heavy metal pollution has become a critical environmental issue due to its adverse effects on ecosystems and human health. Heavy metals, defined by their high density (specific gravity > 5.0) and atomic weight (63.5-200.6), include essential elements such as zinc (Zn), iron (Fe), copper (Cu), molybdenum (Mo), and manganese (Mn), which are required in trace amounts for plant and animal nutrition. However, these metals can become toxic at higher concentrations [21, 22]. The primary sources of heavy metal pollution include anthropogenic activities such as industrial operations, mining, metal plating, and pesticide production [23]. Due to their non-biodegradable nature, heavy metals persist in the environment, causing bioaccumulation and long-term ecological damage [24, 25]. In soil, the mobility and bioavailability of heavy metals are influenced by various factors, including the chemical composition of the soil [26] and its interactions with organic matter and metal oxides, for example, oxides and hydroxides of iron, aluminum, and manganese can form complexes with organic matter, affecting the retention and mobility of heavy metals [27]. Organic matter in soil, through its functional groups, interacts with heavy metals and facilitates the formation of metal-organic complexes, influencing their bioavailability [28, 29]. The complex nature of heavy metal contamination demands advanced analytical methods capable of detecting trace and ultra-trace levels of these elements with high precision and accuracy. Inductively Coupled Plasma Mass Spectrometry (ICP-MS) has emerged as the gold standard in heavy metal analysis due to its exceptional sensitivity, high selectivity, and ability to achieve detection limits far lower than those offered by other multi-element techniques. This makes ICP-MS particularly effective for analyzing heavy metals in complex environmental matrices, providing reliable data for monitoring and mitigation efforts [30-33].

Upon reviewing the available literature, it appears that there is limited information available regarding the contamination of soil and fruits with pesticide residues and heavy metals in the Aseer region, Saudi Arabia [34-36]. It is worth mentioning that no study has been conducted on the soil of Wadi Bin Hashbal to assess pesticides and heavy metals contained within it. This gap underscores the need for dedicated research to evaluate soil health and potential pesticide and heavy metal contamination in this agriculturally significant region. This study aims to validate the QuEChERS method for the detection and quantification of ten standard pesticides: Dimethoate, Diazinon, Propyzamide, Pirimicarb, Chlorpyrifos, Fipronil, Profenofos, Ethion, Piperophos, and Permethrin-2. These pesticides were analyzed in selected fruit samples obtained from local supermarkets and soil samples collected from Wadi Bin

Hashbal and the Suda area in the Aseer region using gas chromatography-mass spectrometry (GC-MS). Furthermore, the study investigates the concentrations of some metals and heavy metals in soil from Wadi Bin Hashbal, comparing areas irrigated with treated water and those not irrigated with treated water. These samples were collected during three seasons (winter, spring, and summer) and analyzed using inductively coupled plasma mass spectrometry (ICP-MS).

Materials and Methods

The respective pesticide standards were acquired from Aldrich in Steinheim, Germany, and Fisher Scientific. These standards included Dimethoate, Diazinon, Propyzamide, Pirimicarb, Chlorpyrifos, Fipronil, Profenofos, Ethion, Piperophos, and Permethrin-2, which were obtained from Leicestershire, the United Kingdom. Pure sodium chloride and anhydrous magnesium sulfate of reagent grade were supplied by BDH in Lutterworth, the United Kingdom. For internal standard purposes, tributyl phosphate (TBP) was acquired from Steinheim, Germany's Sigma-Aldrich. To facilitate the sample preparation process, QuEChERS kits from CHROMAtific were utilized. These kits included packets of salt from Heidenrod, Germany, that contained 300 mg of primary-secondary amine, 900 mg of $MgSO_4$, and 150 mg of C18. During the sample preparation phase, Jiangsu Zhenji Instruments, Ltd. centrifuge model 800 and 50 mL centrifuge tubes from Corning, Inc. in New York, America, were employed.

The pesticide standards, fruit samples, and soil extract samples underwent GC-MS chromatographic analysis using the Shimadzu GC/MS-Q2010 Ultra instrument from Kyoto, Japan. The instrument was outfitted with a 250°C split/splitless injector and the Shimadzu AOC-20i autosampler. A Restek RXISIL 5MS fused silica column measuring 30 m in length, 0.25 mm in diameter, and 0.25 μ m in film thickness was used to separate the standards of the pesticide and the extracts of the study. The column temperature was initially set at 100°C for 1 minute. Subsequently, it gradually rose at a rate of 10°C per minute until reaching a final temperature of 300°C, where it remained constant for 5 minutes. The total runtime of the method was 26 minutes. The injection volume for splitless mode was 1 L, while in split mode, it was 1.0 L, and the split vent was opened after 1 minute. The mass spectrometer's operational conditions were as follows: the analyzer temperature was fixed at 230°C, while the MS ion source temperature was maintained at 230°C. The MS quadrupole temperature was adjusted to 150°C. The electron multiplier voltage was adjusted to 1200 V at a temperature of 250°C. Additionally, the transfer line temperature was maintained at 200°C. Lastly, the electron multiplier temperature was set at 230°C. An electron impact with 70 eV of energy was observed.

Using a scan range of 200 to 500 m/z, the MS device was operational.

Preparation of Standard Pesticide Mixtures

A concentrated pesticide mixture (250 µg/ml) was prepared, and this solution was diluted with acetonitrile to establish working standards of 0.5, 1, 1.5, 2, 2.5, and 3 µg/ml. These working standards were applied to validate the method and optimize the QuEChERS methods' influencing factors. The internal standards, primary solutions, and working dilutions were all kept below 4°C.

QuEChERS Extraction Procedure

Different types of fruits (Apple, Lemon, Pomegranate, and Tangerine) were obtained from local supermarkets in the Aseer region, and two samples of soil (soil-Wadi Bin Hashbal and soil-Suda) were collected from the surface layer (0-30 cm depth) in the Aseer region in 2023. The best way to prepare the samples for QuEChERS involved measuring 10 g of every sample and transferring it into a centrifuge tube. Subsequently, 10 mL of acetonitrile and 15 µL of TBP (100 µg/ml) were added to the tube. The sample was shaken by hand for a short period to homogenize it. After allowing the mixture to stand at 4°C for 30 minutes, it was supplemented with 1.0 g of NaCl and 4.0 g of MgSO₄. The mixture was gently handled for approximately one minute to ensure that crystalline agglomerates did not form when hydrating MgSO₄. Next, the mixture was placed in a centrifuge and spun at a speed of 4000 rpm for 5 minutes. Then, the liquid above the sediment was carefully moved to another centrifuge tube with 150 mg of C18, 300 mg of PSA, and 900 mg of MgSO₄. After vortexing for a minute and spinning it at a speed of 4000 rpm for five minutes, we took one mL of the liquid above the sediment and put it directly into vials for the GC-MS analyses.

Method Validation

The QuEChERS method, in conjunction with GC-MS, was utilized to analyze 10 different pesticides in both fruit and soil matrices. Various parameters, including precision, accuracy, limit of detection (LOD), linearity, and limit of quantification (LOQ), were determined.

Calibration curves were generated by performing triple injections of each standard mixture containing the examined pesticides, along with the internal standard (TBP), at a range from 0.5 to 3 µg/ml. The method's accuracy and precision were assessed by recovery percentages and relative standard deviation (RSD%). Lemon and soil-Wadi Bin Hashbal samples were chosen for this evaluation.

Under the optimum conditions, recovery studies of the pesticide mixture were conducted at a medium

concentration of 1.5 µg/ml using 10 g of the test samples. The recovery percentage for each pesticide was determined by contrasting the apex areas of the standard pesticides in the sample to those in the calibration standard, after subtracting the peak area from the examined samples. The detection and quantification limits were calculated by analyzing the signal-to-noise ratio of the specific ions used for each identified pesticide.

Sample Extraction for Heavy Metals Analysis

A soil sample was collected from the surface layer (0-30 cm depth). A gram of soil was weighed and dissolved in 8 ml of concentrated nitric acid with one ml of 30% hydrogen peroxide the total volume was 10 mL. The samples were digested by microwave digester Milestone Ethos(SK-10 • High-pressure digestion rotor, 10 TFM vessels), Sorisole (BG) – Italy. The extracted samples were diluted by Di-H₂O to 40 mL, including blank, standards and samples.

Results and Discussion

Chromatographic Analysis Optimization

To find the optimal compromise between separation and resolution for the analyzed pesticides in the shortest possible time, a series of tests were conducted. GC-MS running in full-scan mode was employed to identify the individual pesticides in the pesticide standard mixture by detecting their mass fragments (m/z). The complete separation of all pesticides was achieved within a time frame of less than 25 minutes. In addition to identifying the pesticides based on their retention duration, the full scan MS mode enabled confirmation of each pesticide standard by comparing its electron ionization (EI) spectrum to the reference spectrum obtained from well-known MS spectral libraries such as NIST and Wiley. For quantification purposes, the ion with the highest signal-to-noise ratio and no signs of chromatographic interference was selected as the most abundant ion. A chromatogram of the standard pesticide solution separated under ideal conditions and at a concentration of one µg/mL is shown in Fig. 1. The retention time (RT) and primary characteristic (m/z) values for each of the ten pesticides are shown in Table 1.

The Single Ion Monitoring (SIM) mode can be employed in GC-MS using a single quadrupole mass spectrometer to enhance sensitivity and selectivity. By reducing noise and focusing on the target analytes, this mode allows for higher precision. For each pesticide, three specific ions were selected in SIM mode. The remaining ions were utilized as qualifier ions for confirmation, while the most abundant ion (base peak) was used as the quantifier ion. This method involves identifying pesticides based on their ions, targets, and retention times. The quantification and qualification

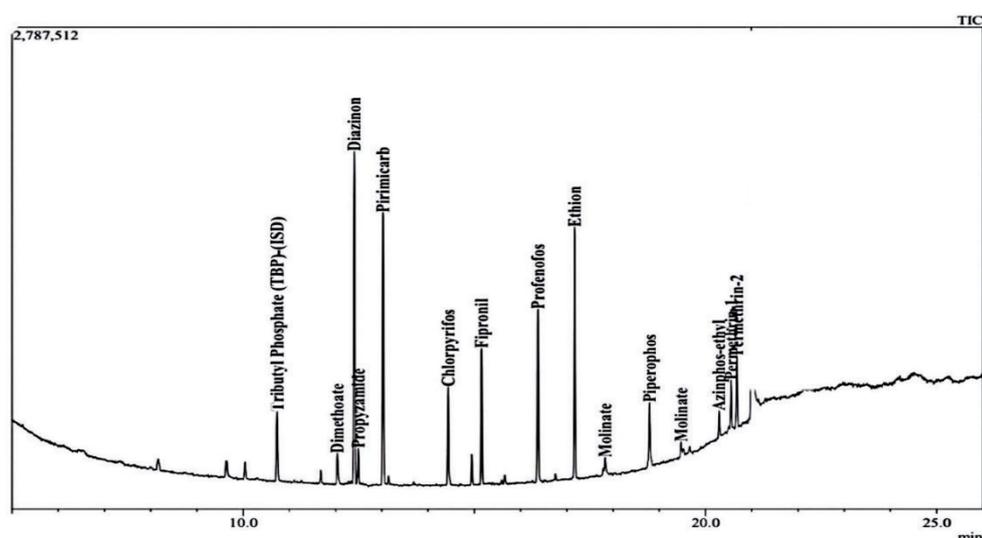


Fig. 1. Chromatogram of the pesticide standard mixture at a concentration of 1 $\mu\text{g}/\text{mL}$.

ions used in SIM mode for each investigated pesticide at their respective retention times are shown in Table 1.

Method Validation

The studied pesticides showed acceptable linearity, as evidenced by the coefficient of correlation values varying from 0.9997 to 0.9916, which guarantees accurate quantification. Table 2 presents the calibration information for each pesticide, including the regression equations and coefficients.

To assess the method's sensitivity, the LOD and LOQ were determined. The LOD represents the minimum concentration of the analyte that can be detected with a signal-to-noise ratio of 3/1, while the LOQ represents the lowest concentration that can be accurately quantified with a signal-to-noise ratio of 10/1. Table 3 provides an overview of the quality measures for the pesticides, including their respective LOD and LOQ values. For propyzamide, we found that the LOD was $\leq 0.112 \mu\text{g}/\text{g}$, and the LOQ was $\leq 0.204 \mu\text{g}/\text{g}$.

To assess the effectiveness of the methodology, we examined recovery and repeatability. Table 4 displays the studied pesticides in the lemon and soil-Wadi Bin Hashbal samples, along with the corresponding recovery and repeatability data. The percentage of pesticide recoveries in the lemon sample varied from 76.4% to 100.5%, whereas in the soil-Wadi Bin Hashbal sample, the range was from 70.5% to 90.3%. The relative standard deviations varied from 2.19% to 10.69% in the lemon sample and from 3.63% to 11.32% in the soil-Wadi Bin Hashbal sample. Overall, the validation results for the tested pesticides demonstrated the method's efficiency.

Fruit and Soil Samples Analysis

A total of four fruit types (Apple, Lemon, Pomegranate, and Tangerine) were subjected to analysis.

These fruit samples were obtained from a local market in the Aseer region in 2023. In addition, two soil samples (soil-Wadi Bin Hashbal and soil-Suda) were collected from the Aseer region, Saudi Arabia. The findings of the analyzed samples are summarized in Table 5. Fig. 2a) and 2b) displays representative GC-MS chromatograms for two selected samples. As can be seen in Table 5, all extracts were found to be free of pesticides, except for diazinon in the soil-Suda sample, piperophos in the soil-Suda and apple samples, and permethrin-2 in the tangerine sample. The concentrations of these three detected pesticides were between the LOD and the LOQ. Therefore, the specific concentration values are not provided, but their presence is indicated as "Trace" (TR) in Table 5.

Referring to previous studies, the most recent research on estimating pesticide residues from fruits in the Aseer region was conducted in 2020 [35]. The study included several types of fruits from the region, among which were lemons and pomegranates, which were also included in this study. However, the study conducted in 2020 did not employ the QuEChERS method for extraction. Additionally, it investigated a different set of pesticides compared to those analyzed in our research. The recovery rates reported in their study were lower than those achieved in our study, not exceeding 91.78%. Furthermore, the study detected the presence of several pesticides in apples and pomegranates, with some concentrations falling below the limit of detection (LOD). It is noteworthy that no prior studies have assessed pesticide residues in the soils of Suda or Wadi Bin Hashbal. However, in 2011 [36], a study monitored multiple pesticide residues in soil samples from various regions across Saudi Arabia, including Abha in the Aseer region. The results revealed that Abha and Wadi Al-Dawasir had the highest pesticide residue levels, with dimethoate concentrations reaching 0.7 mg/kg. This concentration exceeds the levels observed in the present study, reflecting a notable advancement

Table 1. Chemical structures, retention duration, and primary characteristic m/z values of the pesticides under investigation.

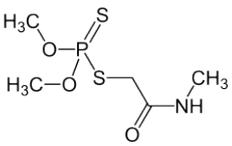
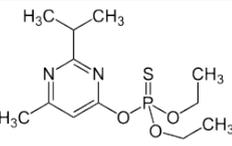
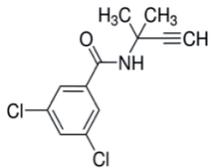
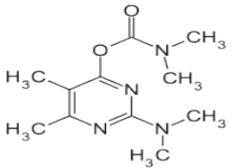
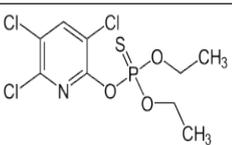
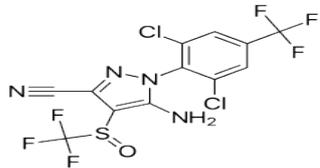
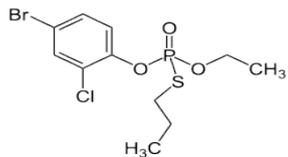
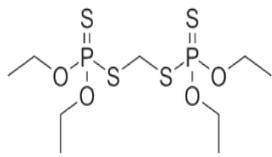
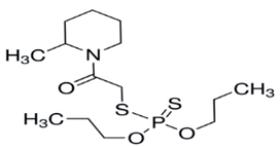
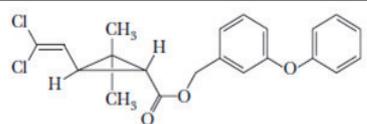
Pesticides	Chemical structure	Retention Time (min)	m/z
Dimethoate		12.055	87, 93, 125
Diazinon		12.406	179, 137, 152
Propyzamide		12.494	173, 175, 254
Pirimicarb		13.027	166, 72, 238
Chlorpyrifos		14.436	97, 199, 197
Fipronil		15.159	367, 369, 213
Profenofos		16.378	97, 139, 43
Ethion		17.170	231, 97, 153
Piperophos		17.839	55, 69, 41
Permethrin-2		20.681	183, 163, 165

Table 2. The calibration data (equation and regression coefficient) of the studied pesticides.

Pesticides	Equation	Regression coefficient (R ²)	Linear Range (µg/ml)
Dimethoate	$y = 0.0001x - 0.108$	0.9959	1-3
Diazinon	$y = 0.0002x + 0.0433$	0.9947	0.5-3
Propyzamide	$y = 5E-05x + 0.008$	0.9802	0.5-3
Pirimicarb	$y = 0.0006x + 0.018$	0.9972	0.5-3
Chlorpyrifos	$y = 7E-05x + 0.0014$	0.9942	0.5-3
Fipronil	$y = 0.0003x - 0.0362$	0.9999	0.5-3
Profenofos	$y = 0.0001x - 0.068$	0.9992	1-3
Ethion	$y = 0.0005x - 0.0746$	0.9992	0.5-3
Piperophos	$y = 4E-05x + 0.0365$	0.9928	0.5-3
Permethrin-2	$y = 0.0002x - 0.02$	0.9972	0.5-3

Table 3. Limit of detection (LOD) and Limit of quantitation (LOQ) for the specific pesticides employed in the present study.

Pesticides	LOD (µg/g)	LOQ (µg/g)
Dimethoate	0.058	0.088
Diazinon	0.058	0.105
Propyzamide	0.112	0.204
Pirimicarb	0.042	0.076
Chlorpyrifos	0.059	0.081
Fipronil	0.009	0.014
Profenofos	0.025	0.038
Ethion	0.023	0.034
Piperophos	0.068	0.082
Permethrin-2	0.042	0.077

in public awareness regarding the detrimental impacts of pesticides. Such awareness appears to have contributed to a reduction in pesticide usage over the past decade, indicating a positive shift towards more sustainable agricultural practices.

Heavy Metals Determination

Samples were measured three times during the year 2023: in winter, spring, and summer (Table 6-8). The results showed that the lowest concentrations were in the spring. Increased precipitation during spring can enhance the leaching of heavy metals from upper soil layers into deeper strata or groundwater. From the data obtained for the soil (Wadi Bin Hashbal) irrigated with treated water and not irrigated with treated water, a slight difference was found in the concentration levels for all measured elements (Fig. 3). On the other hand, higher concentration levels than those permissible under

Table 4. Recovery and repeatability data for the studied pesticides in lemon and soil-Wadi Bin Hashbal samples.

Pesticides	Recovery %		Relative Standard Deviation% (RSD%)	
	Lemon	Soil-Wadi Bin Hashbal	Lemon	Soil-Wadi Bin Hashbal
Dimethoate	79.52	81.66	6.34	3.63
Diazinon	100.57	72.43	3.66	9.43
Propyzamide	76.49	87.33	8.13	5.21
Pirimicarb	96.43	90.30	5.11	8.23
Chlorpyrifos	91.82	85.41	9.56	10.44
Fipronil	99.10	80.22	2.19	4.29
Profenofos	95.34	86.12	9.20	11.32
Ethion	98.65	74.82	10.15	7.12
Piperophos	88.74	88.33	6.78	10.26
Permethrin-2	85.92	77.21	10.69	11.14

Table 5. The pesticides identified in the examined samples.

Pesticides	Soil-Suda	Soil-Wadi Bin Hashbal	Apple	Lemon	Pomegranate	Tangerine
Dimethoate	ND	ND	ND	ND	ND	ND
Diazinon	TR	ND	ND	ND	ND	ND
Propyzamide	ND	ND	ND	ND	ND	ND
Pirimicarb	ND	ND	ND	ND	ND	ND
Chlorpyrifos	ND	ND	ND	ND	ND	ND
Fipronil	ND	ND	ND	ND	ND	ND
Profenofos	ND	ND	ND	ND	ND	ND
Ethion	ND	ND	ND	ND	ND	ND
Piperophos	TR	ND	TR	ND	ND	ND
Permethrin-2	ND	ND	ND	ND	ND	TR

TR: Trace, located between LOD and LOQ. ND: Not detected.

Table 6. Measurements of Some Elements and Heavy metals in soil and Treated water in the spring.

Sample Name	Atomic mass	Soil-Wadi Bin Hashbal with treated water	Soil-Wadi Bin Hashbal without treated water	Treated Water	MRL (mg/kg) in soil	MRL (mg/dm ³) in water
Ag	106, 109	0.0424	0.0323	0.0000	3	0.5
Al	27	2420	2367	0.0124	2000	5.0
As	75	1.03	0.966	0.0015	20	0.1
Ba	138	13.9	13.4	0.0104	50	1.0
Be	9	0.326	0.313	0.0011	3	0.1
Bi	209	0.528	0.5266	0.0026	2	0.002
Ca	44	1080	1035	34.0	300	0.1
Cd	112, 114	0.00083	0.00063	0.0003	3	0.01
Co	59	1.92	1.84	0.0052	50	0.05
Cr	52	4.18	3.78	0.0011	100	0.05
Cs	133	0.649	0.614	0.0025	-	-
Cu	63	2.85	2.35	0.0060	100	0.017
Fe	56	4320	4113	0.236	5000	2.0
Ga	69	2.41	2.334	0.0039	-	-
In	115	0.558	0.555	0.0028	-	-
K	39	560	544	19.9	-	-
Li	7	3.38	3.332	0.0072	-	0.07
Mg	24	1060	1045	10.9	500	0.1
Mn	55	83.7	82.5	0.0070	2000	0.2
Na	23	32.1	31.78	0.120	20	0.2
Ni	58	30.6	30.33	0.0030	50	1.2
Pb	206, 207 and 208	1.69	1.678	0.00018	100	0.065
Rb	85	3.93	3.85	0.0144	-	-
Se	78	2.34	2.325	0.0014	-	0.05



Zn	66	18.6	18.533	0.0132	300	0.20
Se	80	15.3	15.24	0.126	10	0.02
Sr	88	8.55	8.298	0.248	10	0.1
Tl	203	0.0061	0.0057	0.0000	0.1	0.01
U	238	0.469	0.467	0.0010	2	0.001
V	51	6.32	6.313	0.0054	-	0.1

MRL: Maximum Residue Level.

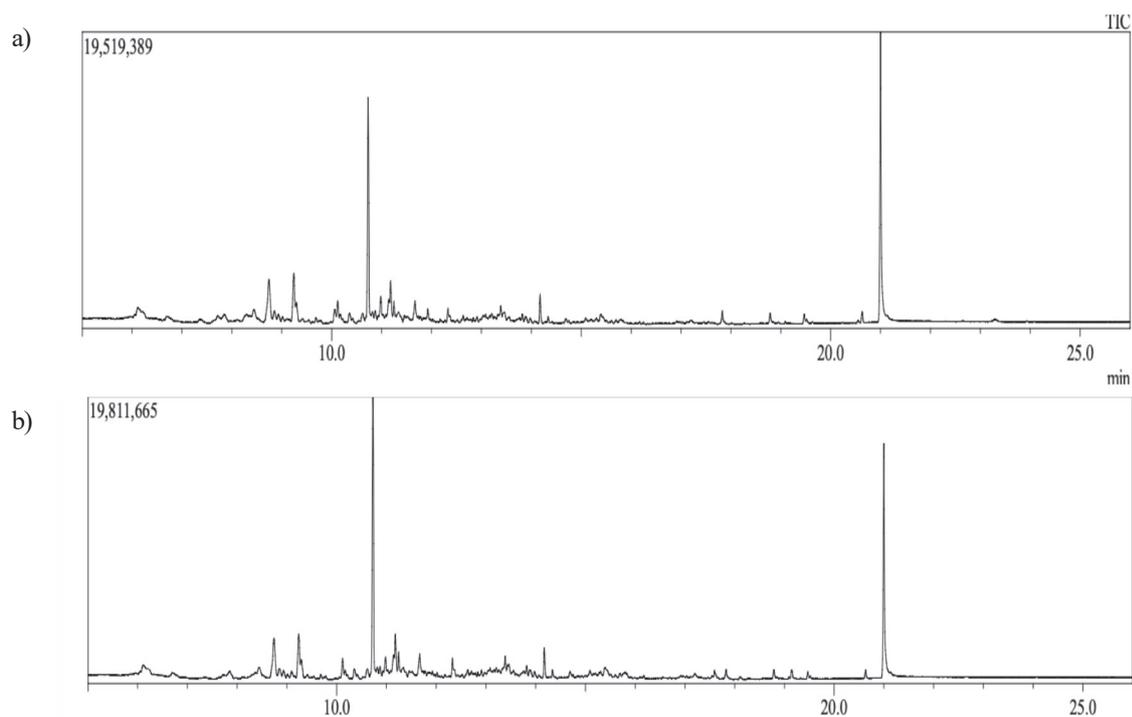


Fig. 2. Chromatograms for some of the examined samples from the GC-MS: a) apple sample and b) soil-suda sample.

Table 7. Measurements of some elements and heavy metals in soil and treated water in the winter.

Sample Name	Atomic mass	Soil-Wadi Bin Hashbal with treated water	Soil-Wadi Bin Hashbal without treated water	Treated Water	MRL (mg/kg) in soil	MRL (mg/dm ³) in water
Ag	106, 109	0.053	0.0404	0.0000	3	0.5
Al	27	3025	2959	0.0155	2000	5.0
As	75	1.29	1.2075	0.0018	20	0.1
Ba	138	17.3	16.75	0.013	50	1.0
Be	9	0.408	0.391	0.0013	3	0.1
Bi	209	0.66	0.6582	0.0032	2	0.002
Ca	44	1350	1294	42.5	300	0.1
Cd	112, 114	0.001	0.00079	0.00038	3	0.01
Co	59	2.4	2.3	0.0065	50	0.05
Cr	52	5.225	4.72	0.0014	100	0.05
Cs	133	0.811	0.768	0.0031	-	-
Cu	63	3.56	2.94	0.0075	100	0.017

Fe	56	5287.5	5141.25	0.3295	5000	2.0
Ga	69	3.01	2.918	0.0049	-	-
In	115	0.698	0.694	0.0035	-	-
K	39	700	680	24.9	-	-
Li	7	4.22	4.165	0.009	-	0.07
Mg	24	1325	1306.25	13.6	500	0.1
Mn	55	104.6	103	0.0088	2000	0.2
Na	23	40.1	39.72	0.15	20	0.2
Ni	58	38.25	37.91	0.0038	50	1.2
Pb	206, 207 and 208	2.1	2.1	0.0002	100	0.065
Rb	85	4.91	4.81	0.018	-	-
Se	78	2.9	2.9	0.0018	-	0.05
Zn	66	23.25	23.16	0.0165	300	0.20
Se	80	19.1	19.1	0.158	10	0.02
Sr	88	10.69	10.37	0.31	10	0.1
Tl	203	0.0076	0.0071	0.0000	0.1	0.01
U	238	0.586	0.584	0.00125	2	0.001
V	51	7.6	7.89	0.0068	-	0.1

MRL: Maximum Residue Level.

Table 8. Measurements of some elements and heavy metals in soil and treated water in the summer.

Sample Name	Atomic mass	Soil-Wadi Bin Hashbal with treated water	Soil-Wadi Bin Hashbal without treated water	Treated Water	MRL mg/kg in soil	MRL mg/dm ³ in water
Ag	106, 109	0.05	0.0388	0.0000	3	0.5
Al	27	2904	2840.4	0.0148	2000	5.0
As	75	1.24	1.1592	0.0018	20	0.1
Ba	138	16.68	16.1	0.0125	50	1.0
Be	9	0.39	0.376	0.0031	3	0.1
Bi	209	0.761	0.758	0.0031	2	0.002
Ca	44	1296	1242	40.8	300	0.1
Cd	112, 114	0.001	0.00076	0.00036	3	0.01
Co	59	2.3	2.21	0.0062	50	0.05
Cr	52	5.02	4.54	0.0013	100	0.05
Cs	133	0.779	0.737	0.003	-	-
Cu	63	3.42	2.82	0.0072	100	0.017
Fe	56	5184	4935.6	0.2832	5000	2.0
Ga	69	2.9	2.8	0.0047	-	-
In	115	0.67	0.666	0.0034	-	-
K	39	672	652.8	23.9	-	-
Li	7	4.1	4.0	0.0086	-	0.07
Mg	24	1272	1254	13.1	500	0.1



Mn	55	100.44	99	0.0084	2000	0.2
Na	23	38.5	38.14	0.14	20	0.2
Ni	58	36.72	36.4	0.0036	50	1.2
Pb	206, 207 and 208	2.03	2.01	0.00022	100	0.065
Rb	85	4.72	4.62	0.0173	-	-
Se	78	2.81	2.79	0.0017	-	0.05
Zn	66	22.32	22.24	0.016	300	0.20
Se	80	18.4	18.3	0.151	10	0.02
Sr	88	10.26	10.0	0.3	10	0.1
Tl	203	0.0073	0.0068	0.0000	0.1	0.01
U	238	0.563	0.56	0.0012	2	0.001
V	51	7.6	7.58	0.0065	-	0.1

MRL: Maximum Residue Level.

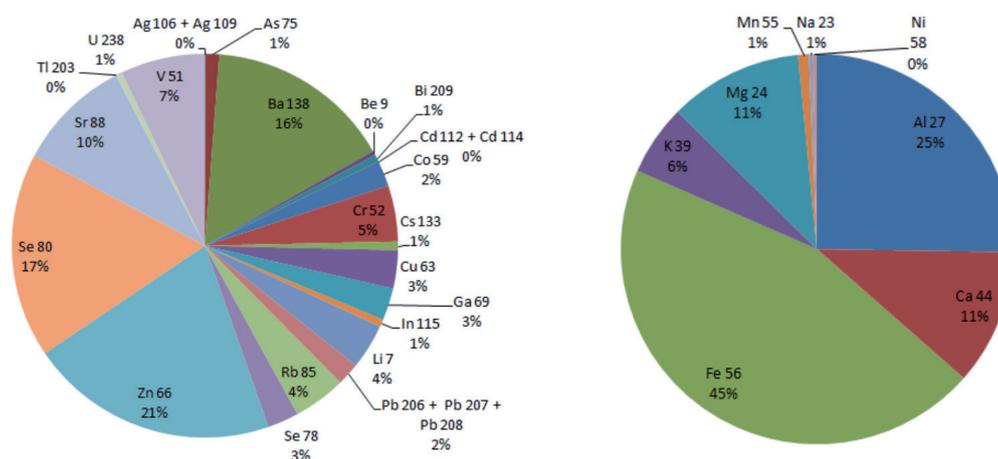


Fig. 3. Circle graph for elements with low concentrations on the left and also elements with high concentrations on the right for Soil-Wadi Bin Hashbal with treated water.

Saudi Arabian standards were found for the following elements: aluminum, calcium, iron, potassium, magnesium, manganese, sodium, and nickel in both soil irrigated with treated water and not irrigated with treated water. For the measurement of heavy metal concentrations in treated water used for irrigation, it was found that the concentrations of aluminum, calcium, iron, potassium, magnesium, manganese, sodium, and nickel, in addition to selenium and strontium, exceeded the MRL accredited by Saudi Arabia [37, 38]. Increasing aluminum in the soil is considered to affect plant growth, but low concentrations are beneficial, as is the case for nickel and selenium [39, 40]. Calcium, iron, and potassium, as well as magnesium, are known to play an important role in plant growth [41-44]. In contrast, manganese contributes to soil acidity and plant toxicity [45]. Sodium salts in soil are considered to negatively

affect plant growth [46]. As previously noted, no prior study has been conducted to assess heavy metal concentrations in the soil of Wadi Bin Hashbal across different seasons of the year. Consequently, the results obtained in this study represent the first comprehensive analysis of this significant agricultural area.

In the future, the study will be expanded to include a larger number of pesticides, heavy metals, and additional samples. Various analytical methods will be optimized and evaluated to enhance accuracy and precision. The results obtained will be compared with data from other regions of the Kingdom. Additionally, the findings will be presented to the Saudi Ministry of Environment, Water, and Agriculture to facilitate appropriate actions based on the conclusions drawn.

Conclusions

This study validated the QuEChERS method for the detection and quantification of pesticides in selected fruit samples obtained from local supermarkets and soil samples collected from Wadi Bin Hashbal and the Suda area in the Aseer region, Saudi Arabia. Calibration demonstrated strong correlation coefficients (0.9916-0.9997), with recovery rates of 76.4-100.5% in lemon samples and 70.5-90.3% in soil, along with RSD% values of 2.19-10.69% and 3.63-11.32%, respectively. These results indicate the high accuracy and precision of the QuEChERS method as an extraction method for pesticides in fruits and soil, followed by analysis using the GC-MS instrument. The analysis revealed that all extracts, except for the soil-Suda sample containing diazinon, the soil-Suda and apple samples containing piperophos, and the tangerine sample containing permethrin-2, were free of detectable levels of pesticides. The concentrations of these three detected pesticides were found to be between the LOD and LOQ. The heavy metal analysis showed elevated concentrations of certain elements, such as manganese, which is considered harmful to the environment, while most elements were within permissible limits. The findings also indicated that some heavy metal concentrations exceeded the allowable limits set by the Kingdom of Saudi Arabia, with the lowest concentrations observed during the spring season. We recommend consistently monitoring pesticide residues and heavy metals in both soil and a broader range of crops over extended periods to enhance safety and environmental health.

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Conflict of Interest

The authors declare no conflict of interest.

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