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The Impact of Pesticide Residues on Soil Health for Sustainable Vegetable Production in Arid Areas

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Abstract: The assessment of pesticide residues in agricultural soils is an essential prerogative in maintaining environmental health standards. Intensive vegetable cultivation is practiced in the Al-Kharj area of the eastern Najd region of Saudi Arabia, where excessive applications of agrochemicals are reported to pollute vegetable-growing soils, challenging the sustainable management of soils and groundwater resources. This study aimed to monitor the levels of thirty-two types of pesticide residues in the soils of vegetable fields and the estimated potential health risk for humans due to non-dietary exposure to pesticides in soils in the Al-Kharj region. Pesticide residues were evaluated at 0–10 cm and 10–20 cm depths at 20 sampling sites from Al-Kharj. Gas chromatograph-mass spectrometry, coupled with a quadrupole mass spectrometer with a GC column, was used in the analysis. The results indicated that agrochemical residues show prolonged soil pollution that may cause adverse impacts on human and environment. Herbicides Atrazine, Isoproturpon, and Linuron have been detected in the soils, and these pose many problematic environmental threats. Bromoxynil, Pendimetholin, and Diclofop-methyl could be used as per the recommendations to sustainably manage soil and water resources in the Al-Kharj area. Resmethrin, Methidathion, Ethoprophos, Tetramethrin, Bromophis-methyl, Bifenthion, Permethrin, Fenoxycarb, Cyfluthrin, Phosmet, and Azinophos-methyl can be used safely in the Al-Kharj agricultural area, maintaining sustainable soils and water resources. Applications of Carbaryl require sufficient care, while Endosulfan, Deltamethrin, Lindane, Chlorpyrifos, Chlorpyrifos-methly, Dimethoate, Heptachlor, and Mevinphos, which are detected in soils, require policy guidelines to limit the use to ensure sustainability. Policy interventions need to be formulated to increase the sustainability of soil management and groundwater resources in the Al-Kharj region to ensure the safety of people who are in direct contact with the agrochemicals used and to ensure the safety of agricultural products generated in this region.

Keywords: pesticides; residues; soil; contamination; arid environments; vegetable; Saudi Arabia

1. Introduction

The global population is expected to reach 9.4–10 billion by 2050 [1]. With the increase in world population, the demand for agricultural products, especially grains, fruits, and vegetables, has been increasing in many areas. Supplies to cater to the needs of these agricultural commodities have been met with the excessive use of agrochemicals to reduce crop loss. Almost one-third of agricultural commodities are produced using chemical pesticides [2]. In 2012, on average, around 3.8 million tons of chemical pesticides were applied to agricultural land [3]. The Food and Agriculture Organization (FAO) has computed the average pesticide application rates per hectare of arable lands, and interestingly the

highest average value roughly 6.5–60 kg/ha was reported in Asia, and some were in South American countries [4,5]. Further, it is reported that while the use of herbicides in Asia remained low, the use of insecticides was very high [4].

Agrochemical usage has positively influenced crop yields by preventing crop damage and losses [5]. However, the adverse environmental issues of the intoxication of farmers and their families, and even ecological pollution, are being reported. The intensive and widespread use of agrochemicals can increase soil pollution, thereby increasing environmental and health risks [6]. Soil is the sink of applied agrochemicals, where its physical and chemical properties play a crucial role in the fate, behavior, and dispersion of chemical pesticides [6]. Soils also act as the repository of agrochemicals used in agriculture. Intentional poisonings by agrochemicals kill an estimated 355,000 people annually due to excessive exposure and the inappropriate use of toxic chemicals [7–10].

Minimizing exposure to environmental toxicants like pesticides, especially in consumables, remains one of the primary concerns in Saudi Arabia [11]. Pesticides such as organophosphates, organochlorines, pyrethroids, carbamates and herbicides, acaricides, and insecticides are used either singly or in combinations of variable concentrations to cater to a wide variety of pests [12]. The extensive use of pesticides in Saudi Arabia at present not only leads to the extensive pollution of the environment, but also constitutes a potential risk to human and environmental health [13–17]. However, a portion of pesticides and other agrochemicals applied to crop fields contaminate the soil. The high soil persistence of such pesticides and their toxicity to humans will pose further concerns that need to be addressed reasonably to minimize adverse impacts.

Around 60% of the soil samples evaluated in Nepali agricultural soils contained pesticides (25% of the soil samples had a single residue, and 35% had mixtures of two or more residues) in 39 different pesticide combinations among 147 tested samples [18]. Further, they reported that the pesticide residues were found more frequently in topsoil. At the same time, at least some pesticides are not easily bio-degradable and/or remain in the ecological system, causing different environmental issues. Pesticide residues in soils get washed away with running water and floods and leach into deeper soil layers with irrigation water, thus finding their way into ground- and surface-water sources. Pesticides can also be emitted from soil pools into the atmosphere through volatilization [19], which may adversely affect air quality [20] and surface water quality [21]. The concentration of pesticides tends to increase with soil depth [22]. Pesticide concentrations found in the bottom soil layers may increase the risk of groundwater pollution [23]. Hence, farmers are exposed to pesticide-contaminated soils via different pathways such as dermal contact, direct ingestion, non-dietary ingestion, and inhalation [24].

The measurement of pesticide residues in agricultural soils is an essential prerogative in maintaining environmental health standards and thus minimizing the harmful impacts of pesticides. Therefore, the current study evaluates the pesticide residues in two depths of vegetable root zones (i.e., 0–10 cm and 10–20 cm) in the Riyadh region of Saudi Arabia, where vegetable cultivation is practiced intensively. The current study aimed to monitor the levels of various pesticide residues in the soil of vegetable fields and estimate the potential health risk for humans caused by non-dietary exposure to pesticides in soils from various vegetable-growing regions of Riyadh, in the Kingdom of Saudi Arabia, and to evaluate the sustainable management of soil and water resources.

2. Materials and Methods

2.1. Study Area

The Al-Kharj area is located in the eastern Najd region, and lies between 23°35′–24°5′ N latitude and 46°55′–48°10′ E longitude. The mean annual rainfall received in this region is 94.6 mm. The temperature of the study area varies from 6 °C to 46 °C, with an average minimum temperature of 10 °C and average maximum temperature of 44 °C. The relative humidity differed between 6% to 65%. Due to warm temperatures and low humidity, the evaporation rate is higher, and the mean annual measure of evaporation is 3070 mm.

Al-Kharj has two series of escarpments: Najd plateau and Tuwayq Mountains. Al-Kharj's plains' soils are composed of alluvium deposits (sand and gravel) and hydraulically connected to Wasia-Bayiadh sandstone or Sulaiy-Arab limestone aquifers. The thickness of alluvium deposits varies from 30 to 65 m, and the water table depth varies between 30 and 120 m.

The land use of northern and western parts of the study area are mainly agricultural practices, and excessive fertilizers and agrochemicals (herbicides, insecticides, fungicides, etc.) are used extensively. Due to excessive usage of agrochemicals, the soils are being polluted, and groundwater faces the threat of pollution [25].

2.2. The Collection of Soil Samples

Soil samples were taken within one cultivation season from the Al-Kharj agricultural practice areas into sterile polythene bags. Soil samples were collected from 20 locations (Figure 1) and at 0–10 cm and 10–20 cm depths. For each site, three sub-sampling areas were identified to collect the soil samples. Three soil samples (or triplicates) were collected from each site at each depth. The samples of three sites were thoroughly mixed to obtain a composite sample. Collected soil samples were air-dried and sieved through a 2.0 mm sieve. Three subsamples were selected from each composite sample for the analysis.
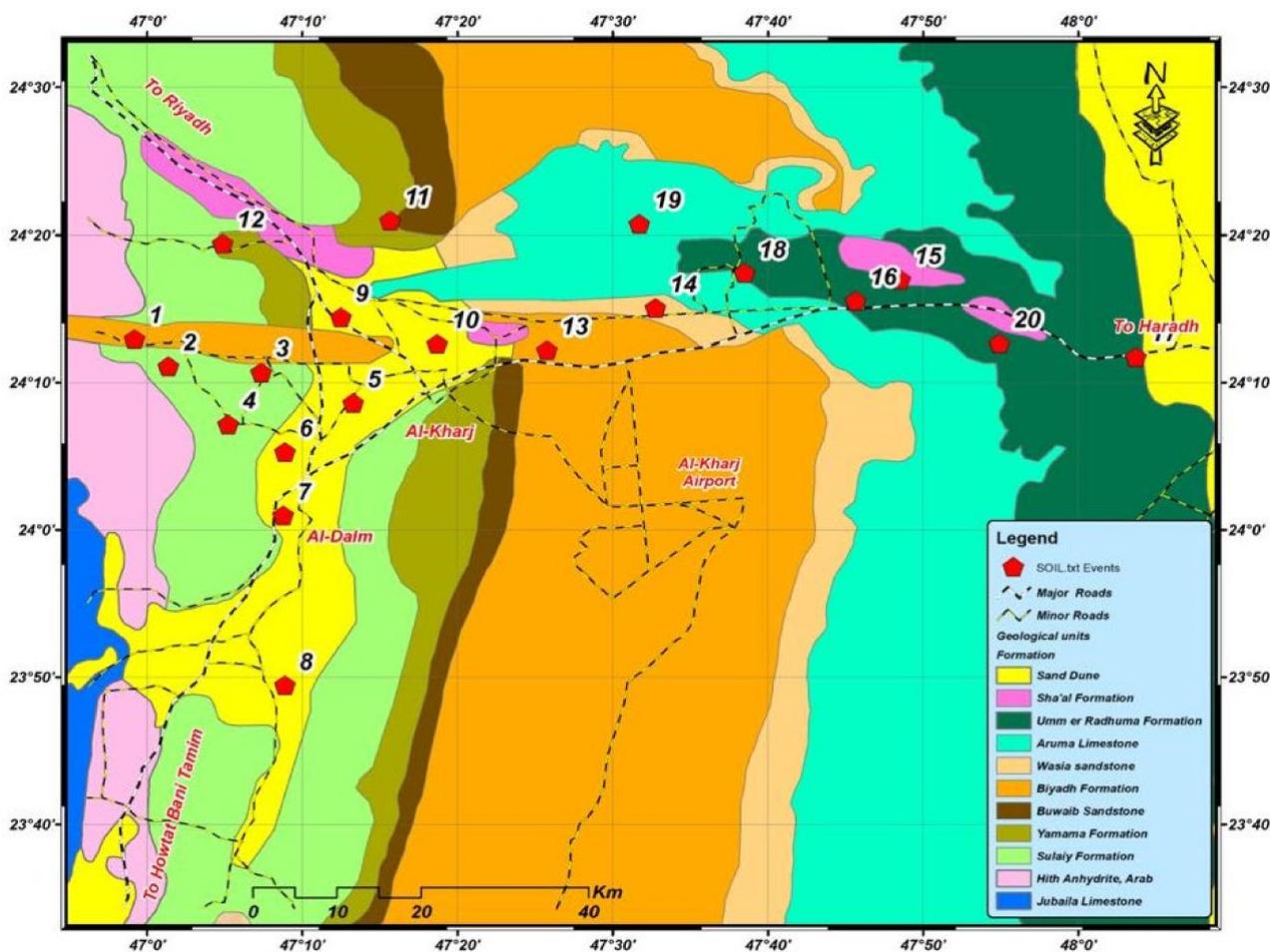

Figure 1. Sampling sites and rock and soil types.

2.3. Pesticide Standards

The samples of 32 pesticides (Spinosad, chlorpyrifos-methyl, dimethoate, chlorpyrifos, lindane (γ–HCH), methidathion, heptachlor, α-B-endosulfan, o,p-DDT, p, p-DDT, bifenthrin, permethrin, β-cyfluthrin, and methomyl) with 98–99% purity were obtained for

analysis. A 1 mg/mL stock solution was prepared, dissolving 20 mg in pure analytical-standard acetone (purity of about 99.9%). The single composite standard solution was prepared according to the Limit of Detection (LOD) by diluting with acetone. All standards were stored at standard temperature (4 °C). Residue analysis-grade solvents (acetone, acetonitrile, petroleum ether, and other reagents such as sodium chloride and anhydrous sodium sulfate) were used in this study.

The spiking solution was prepared as mixed compound calibration solutions in acetone. Florisil 60–100 mesh (Fluka) was used for residue analysis. Florisil and anhydrous sodium sulfate were activated at 100 °C overnight, and were stored in 500 mL glass flasks. These solutions were stored in an oven at 100 °C. Deionization water was used to rinse all the glassware, which were then washed with acetone and dried at 100 °C–130 °C in an oven for 24 h.

2.4. Extraction and Partitioning

A soil sample (25 g) was placed in a stainless steel 1 L jar, and 100 mL of acetonitrile was added for extraction. The mixtures were filtered into 500 mL suction flasks through Buchner funnels fitted with shark-skin filter papers. Aliquots from the filtrate were then transferred to 1 L separator funnels, and then 100 mL of petroleum ether was added. These mixtures were vigorously shaken for 1–2 min, and then 100 mL of saturated NaCl solution and 600 mL of water were added. The mixtures were vigorously mixed again, and the separator funnel was held in a horizontal position for a few minutes. The aqueous layers were discarded, and the solvent layers were washed twice with distilled water. The washed layers were then transferred into 100 mL beakers and washed again with 1 of 5 g anhydrous sodium sulfate. Finally, the extracts were concentrated to 1 mL using a rotary evaporator, and those were transferred directly into GC vials [16].

2.5. Recovery Experiment

A 25 g homogenized soil sample was spiked with a mixture of standard pesticide solution with a concentration of 0.10 μg/mL of each compound. The spiked soil samples were analyzed after waiting about 30 min to allow the solvent to evaporate and to allow the pesticide to absorb into the sample. Extraction from the soil sample was performed using QuEChERS and analyzed with GC-MS/MSTQD [26]. The recovery % and LOD for the 32 tested pesticides are given in Table 1.

Table 1. Recovery percentage and limit of detection (LOD) for tested pesticides in soil samples.

Pesticide	Type	Spiking Level (μg/g)	LOD (μg/g)	Recovery %
Iprobenfos	fungicide	0.10	0.004	98.6 ± 2.12
Bromoxynil	herbicide	0.10	0.001	91.4 ± 1.58
Isoproturon	herbicide	0.10	0.001	93.2 ± 1.92
Atrazine	herbicide	0.10	0.002	90.2 ± 2.68
Pendimethalin	herbicide	0.10	0.002	93.9 ± 2.10
Diclofop methyl	herbicide	0.10	0.001	91.6 ± 2.35
Linuron	herbicide	0.10	0.004	92.2 ± 2.11
Chlorpyrifos methyl	insecticide	0.10	0.001	94.9 ± 1.20
Dimethoate	insecticide and acaricide	0.10	0.001	98.6 ± 1.08
Chlorpyrifos	pesticide	0.10	0.001	95.9 ± 2.40
Lindane (γ–HCH)	insecticide	0.10	0.001	96.3 ± 1.10

Table 1. *Cont.*

| Pesticide	Type	Spiking Level (µg/g)	LOD (µg/g)	Recovery %
Bromophos methyl	insecticide	0.10	0.001	93.6 ± 2.12
Abamectin	insecticide, nematicide, and miticide	0.10	0.001	92.4 ± 2.40
Methidathion	insecticide	0.10	0.001	92.2 ± 2.32
Heptachlor	insecticide	0.10	0.001	96.6 ± 1.18
Endosulfan	insecticide and acaricide	0.10	0.001	95.9 ± 2.31
Bifenthion	insecticide	0.10	0.001	91.4 ± 2.58
Ametraz	acaricide and insecticide	0.10	0.002	89.9 ± 3.00
Permethrin	insecticide	0.10	0.002	91.2 ± 1.35
Cyfluthrin	insecticide	0.10	0.004	91.5 ± 2.56
Resmethrin	insecticide	0.10	0.003	97.2 ± 3.16
Mevinphos	insecticide	0.10	0.009	94.2 ± 2.66
Deltamethrin	insecticide	0.10	0.005	96.8 ± 2.19
Tetramethrin	insecticide	0.10	0.002	96.2 ± 2.44
Azinophos-ethyl	insecticide	0.10	0.003	96.7 ± 3.16
Cypermethrin	insecticide	0.10	0.01	97.1 ± 2.73
Ethoprophos	insecticide	0.10	0.005	93.5 ± 3.50
Carbaryl	insecticide	0.10	0.003	99.2 ± 3.46
Phosmet	insecticide	0.10	0.003	91.8 ± 2.88
Fenoxycarb	insect growth regulator	0.10	0.007	95.5 ± 3.28
p, p-DDE	metabolite of DDT	0.10	0.001	96.3 ± 1.16
p, p-DDD	metabolite of DDT	0.10	0.001	94.2 ± 2.64

2.6. The Measurement of Pesticide Residues

A gas chromatograph-mass spectrometer (Agilent model 6890N), coupled with a quadrupole mass spectrometer (model 5975B) with a GC column (HP-5MS 5% phenyl—95% methyl siloxane, 30 m × 0.25 mm id × 0.25 µm film thickness) was used in the analysis. The samples were injected in splitless mode. The GS operation conditions used in this analysis were splitless injections at an injector temperature of 250 °C. The carrier gas used was helium (99.9 purity) at a flow rate of 0.9 mL/min with column head pressure of 7.4 psi, oven temperature at 70 °C (for 2 min), then raised to 130 °C at a rate of 25 °C/min and then increased to 220 °C at a rate of 2 °C/min, and then again raised to 280 °C at a rate of 10 °C/min and held for 4.6 min. The selective ion monitoring (SIM) mode was routinely set in the MS system used. Based on the peak area, one target and one or two qualifier ions based on standard procedures were used to quantify each compound. Parameters of the mass spectrometer were set as electron impact ionization mode with 70 eV electron energy, scan mass range 100–400 at 0.62 s/cycle, ion source temperature at 230 °C, MS quad temperature at 150 °C, EM voltage at 1450, and the solvent delay of 4 min. An aliquot of 2 µL of the samples was injected into the gas chromatography-mass spectrometer under the standard conditions. Then, the pesticide residues were identified by the comparison of retention time values with reference standards. Confirmation of results was performed using selected ion monitoring (SIM) mode, the quantifier, and the qualifying ion [16,27].

3. Results

3.1. The Residues of Herbicides

The residues of six herbicides, namely, Bromoxynil, Isoproturon, Atrazine, Pendimethalin, Diclofop methyl, and Linuron, were found in the soil samples acquired from 20 study sites at both depths. Based on all herbicides in the topsoil, the sampling sites were grouped into four main clusters, as depicted in Figure 2. The above clustering status was further confirmed by the Global R (0.94) value of the analysis of similarities (ANOSIM). It was evident that sites 13 and 15 were clustering together due to moderate levels of Atrazine and Bromoxynil. Meanwhile, sites 10 and 16 formed another subset due to moderate Isoproturon and Diclofop methyl levels in topsoil. The presence of Atrazine, Diclofop methyl, and Isoproturon at exceptional levels could be identified as the reason behind the clustering of sites 6, 8, and 17 (Figure 2).
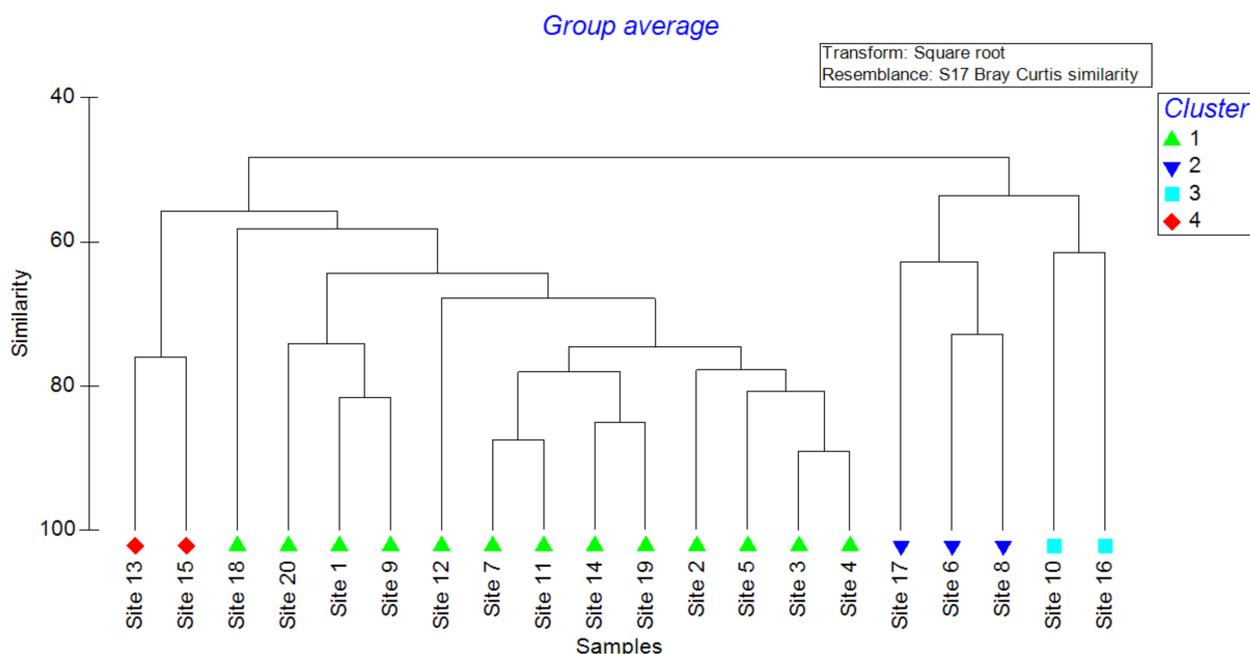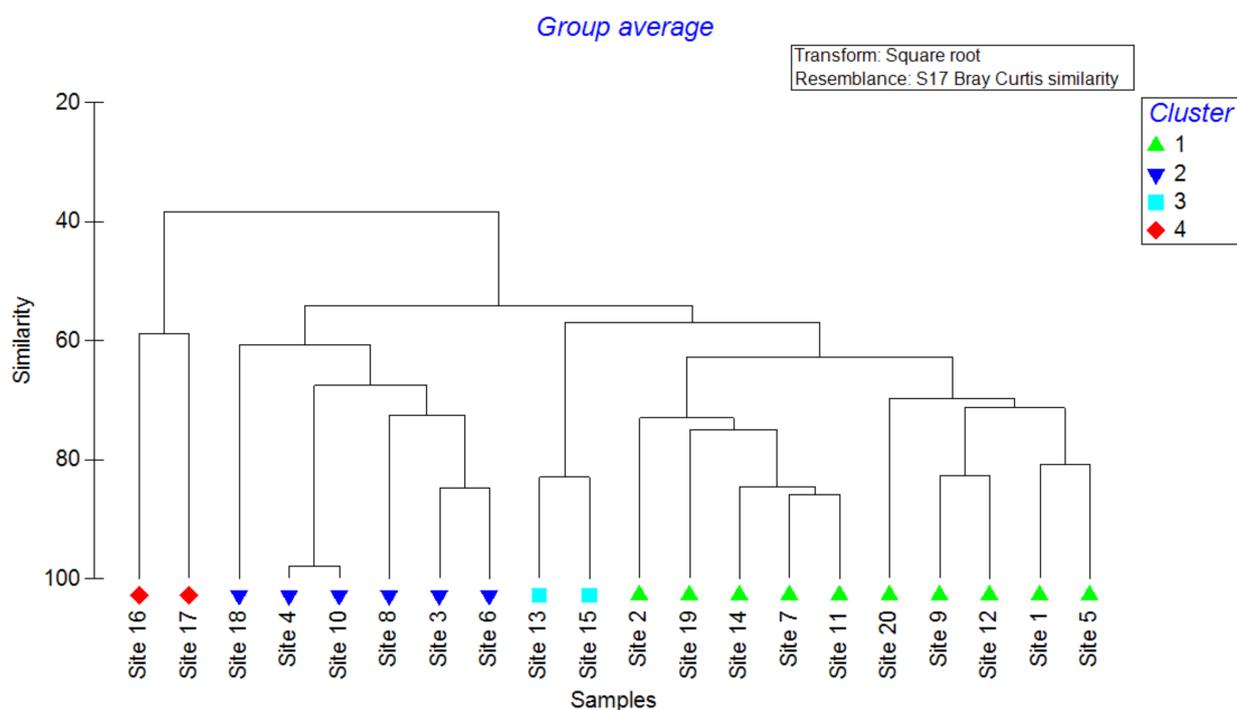

Figure 2. Dendrogram of the cluster analysis of sites based on the residual level of herbicides in topsoil.

Atrazine was seen as the most common herbicide residue at most sites, reporting the highest mean contamination level of 2.73 ± 0.27 ppm and 3.84 ± 0.41 ppm at depths 0–10 cm and 10–20 cm, respectively (Table 2). Among the topsoil samples, the highest level of Atrazine was reported from Site 9 at both the depths. Meanwhile, sites 5, 16, 20, and 11 reported the highest residue levels of Isoproturon (0.60 ± 0.21 ppm), Diclofop methyl (1.41 ± 0.25 ppm), Bromoxynil (1.25 ± 0.12 ppm), and Pendimethalin (0.37 ± 0.07 ppm) in topsoil (0–10 cm), as shown in Table 2. Bromoxynil was reported at 18 sites at both the depths and Atrazine was reported at 18 sites at the depth of 0–10 cm and 17 sites at the depth of 10–20 cm. Diclofop methyl was reported at 17 sites at both depths.

The soil samples of the 10–20 cm depth also reported residues of previous herbicides. Atrazine reported the highest mean residual level (1.48 ± 0.28 ppm) in 17 sites, while Linuron reported the lowest mean residual level (0.18 ± 0.03 ppm). On the other hand, Bromoxynil was most abundant, being reported in 18 locations, while Linuron was only reported from 4 sites (Table 2). Based on the presence of all herbicides, the sampling sites were clustered into four main clusters, as in the case of topsoil (Figure 3), which was further confirmed by the Global R (0.89) value of the ANOSIM. It was evident that both sites 13 and 15 clustered together, while sites 16 and 17 formed another subset. Meanwhile, sites 3, 4, 6, 8, 10, and 18 formed the third cluster (Figure 3).

Table 2. Mean residual levels of herbicides at 0–10 cm and 10–20 cm depths at study sites.

Herbicide	0–10 cm				10–20 cm			
	Concentration		Highest Site	Number of Sites	Concentration		Highest Site	Number of Sites
	Highest	Lowest			Highest	Lowest		
Bromoxynil	1.25 ± 0.12	0.04 ± 0.02	20	18	1.66 ± 0.26	0.07 ± 0.06	1	18
Isoproturon	0.60 ± 0.21	0.08 ± 0.03	5	13	0.73 ± 0.18	0.11 ± 0.04	5	13
Atrazine	2.73 ± 0.27	0.19 ± 0.02	9	18	3.84 ± 0.41	0.14 ± 0.03	9	17
Pendimethalin	0.37 ± 0.07	0.03 ± 0.02	14	10	0.47 ± 0.14	0.03 ± 0.02	14	11
Diclofop methyl	1.41 ± 0.25	0.03 ± 0.02	16	17	1.84 ± 0.31	0.03 ± 0.02	16	17
Linuron	0.37 ± 0.07	0.06 ± 0.03	15	4	0.24 ± 0.02	0.11 ± 0.04	19	4

Figure 3. Dendrogram of the cluster analysis of sites based on the residual level of herbicides in inner soil.

3.2. The Residues of Insecticides

Interestingly, a total of 21 pesticide residues (Chlorpyrifos methyl, Dimethoate, Chlorpyrifos, Lindane (γ–HCH), Bromophos methyl, Methidathion, Heptachlor, Endosulfan, Bifenthion, Permethrin, Cyfluthrin, Resmethrin, Mevinphos, Deltamethrin, Tetramethrin, Azinophos-ethyl, Cypermethrin, Ethoprophos, Carbaryl, Phosmet, and Fenoxycarb) (Table 1) were found in the topsoil samples collected at the 0–10 cm depth. The pesticide Cypermethrin remained the most abundant pesticide residue, reported at nineteen sites, while Mevinphos was reported only at two sites (Table 3). Fenoxycarb reported the highest residual level (0.53 ± 0.11 ppm), while Mevinphos reported the lowest (0.14 ± 0.08 ppm). Four main clusters were observed based on the dendrogram of the cluster analysis (Figure 4), where sites 6, 15, and 20 formed three clusters, while the rest formed the fourth cluster. This clustering status was further verified based on the Global R (0.93) value of the ANOSIM. Site 6 reported relatively higher levels of Heptachlor (0.58 ± 0.17 ppm), Resmethrin (0.88 ± 0.04 ppm), and Phosmet (0.43 ± 0.09 ppm). On the contrary, higher levels of Dimethoate (0.62 ± 0.29 ppm), Endosulfan (0.97 ± 0.11 ppm), and Fenoxycarb (1.18 ± 0.19 ppm) were reported at Site 15. Meanwhile, the presence of Bromophos methyl (1.09 ± 0.24 ppm), Cyfluthrin (022 ± 0.02 ppm), Cypermethrin (1.08 ± 0.36 ppm), Fenoxycarb (1.39 ± 0.23 ppm), and Permethrin

(0.60 ± 0.21 ppm) at higher levels could be the reason for Site 20 to remain as a separate cluster (Table 3). It was evident that both sites 13 and 15 clustered together, while sites 16 and 17 formed another subset. Meanwhile, sites 3, 4, 6, 8, 10, and 18 formed the third cluster (Figure 4).

Table 3. Highest and lowest residual levels of pesticides in 0–10 cm and 10–20 cm depths at study sites.

Pesticide	0–10 cm				10–20 cm			
	Concentration		Highest Site	Number of Sites	Concentration		Highest Site	Number of Sites
	Highest	Lowest			Highest	Lowest		
Chlorpyrifos methyl	1.11 ± 0.24	0.06 ± 0.03	9	12	1.27 ± 0.15	0.13 ± 0.04	9	12
Dimethoate	0.77 ± 0.18	0.06 ± 0.02	14, 17	14	0.87 ± 0.12	0.07 ± 0.04	14, 17	14
Chlorpyrifos	0.66 ± 0.21	0.09 ± 0.02	11	15	0.78 ± 0.18	0.04 ± 0.01	11	16
Lindane (γ–HCH)	1.22 ± 0.21	0.08 ± 0.02	18	16	1.24 ± 0.22	0.11 ± 0.04	18	15
Bromophos methyl	1.09 ± 0.24	0.06 ± 0.03	20	15	1.17 ± 0.22	0.13 ± 0.04	20	16
Methidathion	1.09 ± 0.24	0.03 ± 0.02	8	18	1.14 ± 0.22	0.08 ± 0.02	8	18
Heptachlor	0.73 ± 0.21	0.03 ± 0.01	19	14	0.93 ± 0.19	0.02 ± 0.01	1	14
Endosulfan	0.97 ± 0.11	0.09 ± 0.02	15	18	0.89 ± 0.04	0.14 ± 0.07	15	18
Bifenthion	0.51 ± 0.05	0.05 ± 0.02	14	15	0.60 ± 0.11	0.10 ± 0.03	14	15
Permethrin	0.68 ± 0.21	0.04 ± 0.02	18	14	0.84 ± 0.22	0.11 ± 0.05	5	13
Cyfluthrin	0.66 ± 0.08	0.06 ± 0.03	5	13	0.78 ± 0.03	0.11 ± 0.04	5	13
Resmethrin	0.88 ± 0.04	0.03 ± 0.02	6	19	0.91 ± 0.04	0.08 ± 0.03	6	19
Mevinphos	0.22 ± 0.09	0.06 ± 0.03	6	2	0.18 ± 0.09	0.08 ± 0.05	6	2
Deltamethrin	1.07 ± 0.32	0.08 ± 0.03	18	18	1.22 ± 0.19	0.04 ± 0.01	18	18
Tetramethrin	1.26 ± 0.03	0.04 ± 0.02	18	16	1.78 ± 0.14	0.07 ± 0.06	18	16
Azinophos-ethyl	0.60 ± 0.12	0.06 ± 0.04	4, 10	7	0.83 ± 0.27	0.08 ± 0.01	4, 10	7
Cypermethrin	1.41 ± 0.25	0.08 ± 0.02	3	19	1.84 ± 0.31	0.08 ± 0.02	3, 15	19
Ethoprophos	1.29 ± 0.21	0.06 ± 0.03	2	16	1.54 ± 0.29	0.13 ± 0.04	2	15
Carbaryl	1.42 ± 0.26	0.08 ± 0.02	11	17	1.82 ± 0.22	0.11 ± 0.02	11	17
Phosmet	0.63 ± 0.21	0.03 ± 0.02	19	7	0.66 ± 0.18	0.29 ± 0.10	19	6
Fenoxycarb	1.39 ± 0.23	0.08 ± 0.02	20	14	1.37 ± 0.25	0.08 ± 0.06	20	13

In the soil samples collected at the 10–20 cm depth, both Cypermethrin and Resmethrin remained the most abundant, and were reported in 19 sites. On the contrary, Mevinphos was only reported at two sites, namely Sites 3 and 6 (Table 3). Fenoxycarb reported the highest mean residual level among the 20 sites at 0.64 ± 0.13 ppm, followed by Cypermethrin (0.56 ± 0.07 ppm) and Carbaryl (0.53 ± 0.079 ppm). Meanwhile, Mevinphos reported the lowest average residual level (0.13 ± 0.01 ppm), as shown in Table 3. Based on the overall residual effect of all 21 pesticides, the study sites denoted five significant clusters, which remained substantial according to the ANOSIM (Global R of 0.87). Sites 3, 4, 10, 13, and 17 that reported relatively higher levels of Cypermethrin and Lindane (γ–HCH) made one cluster (Figure 5). The second cluster was made with sites 2, 6, 12, and 19, which were characterized by notable Ethoprophos, Heptachlor, and Resmethrin levels. The highest Fenoxycarb (1.26 ± 0.22 ppm) and Endosulfan (0.89 ± 0.04 ppm) levels in Site 15 remained as the third cluster. Site 18 reported the highest residual levels of Deltamethrin (1.22 ± 0.19 ppm), Lindane (1.24 ± 0.22 ppm), and Tetramethrin (1.78 ± 0.14 ppm) and formed the fourth cluster, while the remaining sites formed the fifth (Figure 5).
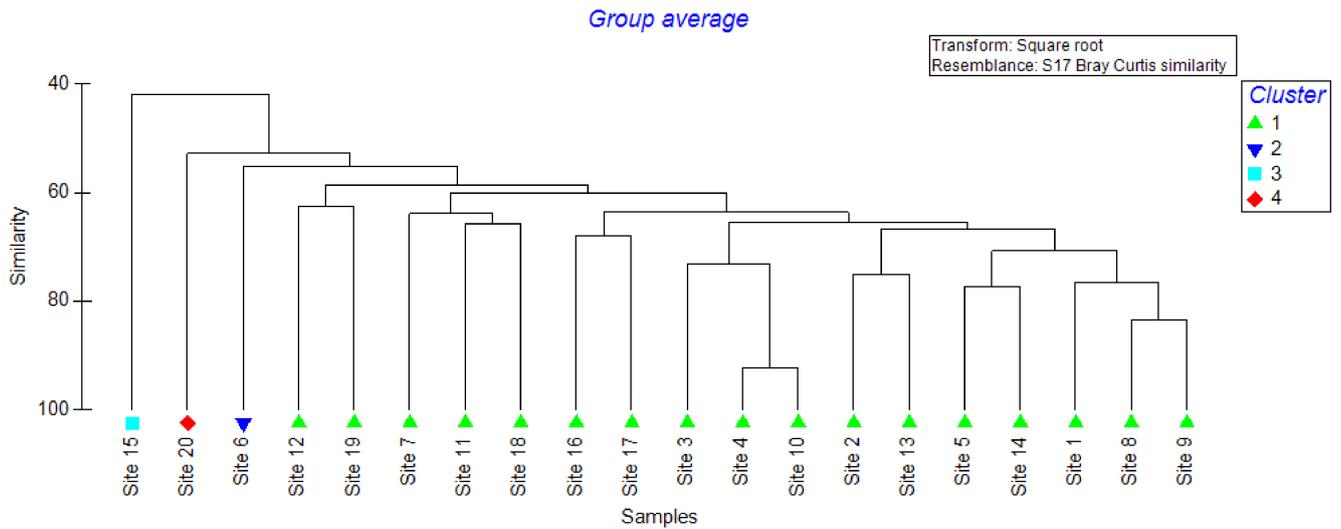
Figure 4. Dendrogram of the cluster analysis of sites based on the residual level of pesticides in topsoil.
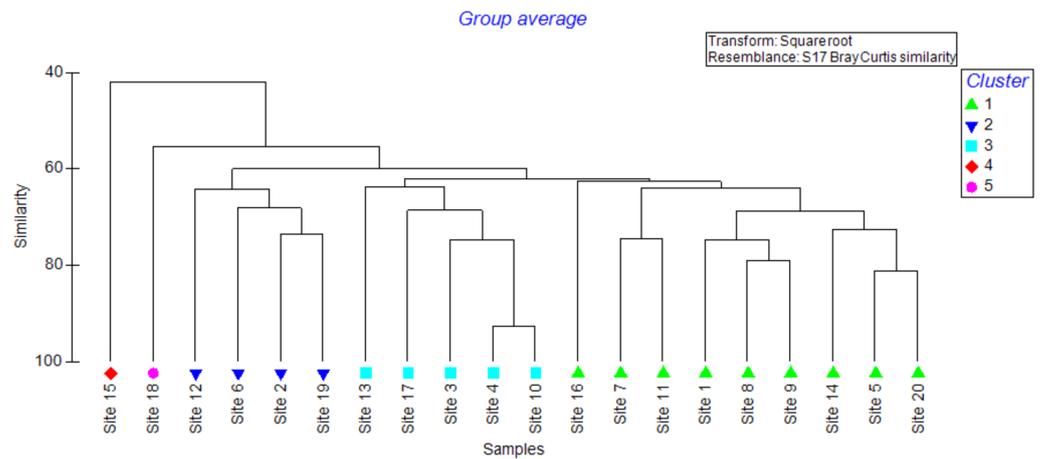
Figure 5. Dendrogram of the cluster analysis of sites based on the residual level of pesticides in inner soil.

3.3. The Residues of Other Agrochemicals

The topsoil samples collected from the study sites detected the residues of five other agrochemicals, namely, Abamectin, Amitraz, Iprobenfos, and two derivatives of DDT. Abamectin denoted the highest mean residual level (0.71 ± 0.18 ppm). In the case of abundance, Abamectin was reported in the topsoil samples of 16 sites, while p, p-DDE, and p, p-DDD accounted for the lowest (Table 2). The sampling sites were clustered into four main clusters based on all agrochemicals in 10–20 cm soil depth, as depicted in Figure 6. The above clustering status was further confirmed by the Global R (0.90) value of the ANOSIM. The presence of relatively higher Iprobenfos had caused Sites 6, 7, and 9 to form one cluster (Figure 6), while Site 8 formed another, since only Amitraz was present in the soil (Table 4). With notably higher levels of Abamectin and Amitraz, Sites 4, 10, 11, 14, 16, 17, and 19 formed the third cluster, while the remaining formed the fourth (Figure 6).
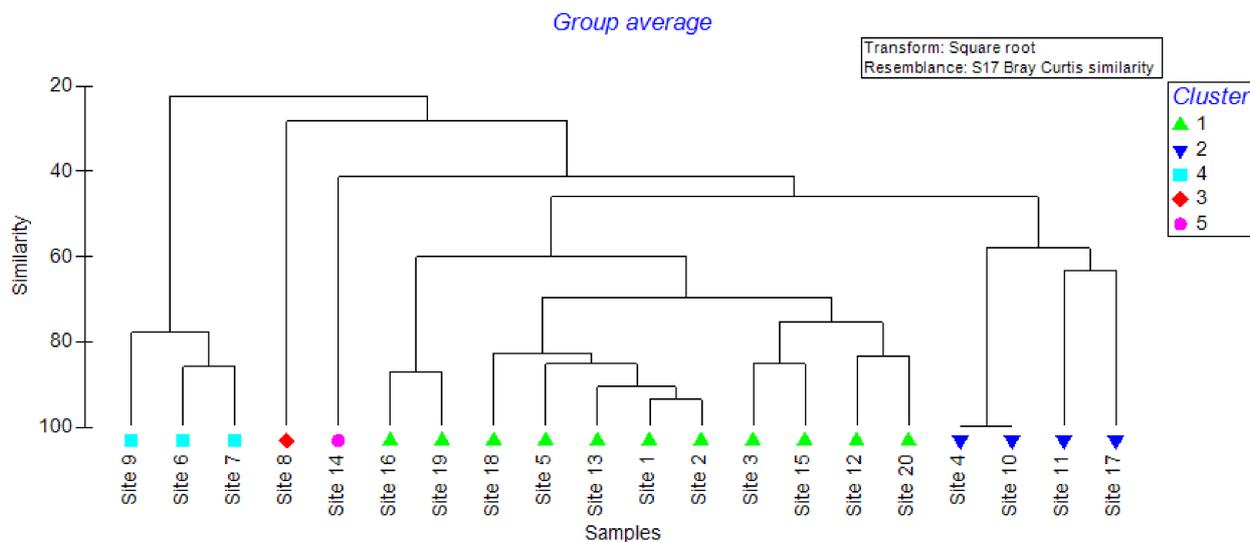
Figure 6. Dendrogram of the cluster analysis of sites based on the residual level of other agrochemicals in topsoil.

Table 4. Detection of agrochemical residues in soil layers 0–10 cm and 10–20 cm at Al-Kharj study sites.

Name of Agro-Chemical	Sites																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Bromoxynil																				
Isoproturon																				
Atrazine																				
Pendimethalin																				
Diclofop methyl																				
Linuron																				
Chlorpyrifos methyl																				
Dimethoate																				
Chlorpyrifos																				
Lindane (γ–HCH)																				
Bromophos methyl																				
Methidathion																				
Heptachlor																				
Endosulfan																				
Bifenthion																				
Permethrin																				
Cyfluthrin																				
Resmethrin																				

Table 4. *Cont.*

Name of Agro-Chemical	Sites																			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
Mevinphos																				
Deltamethrin																				
Tetramethrin																				
Azinophos-ethyl																				
Cypermethrin																				
Ethoprophos																				
Carbaryl																				
Phosmet																				
Fenoxycarb																				
Iprobenfos																				
Abamectin																				
Ametraz																				
p, p-DDE																				
p, p-DDD																				
Total Chemicals (0–10 cm)	23	28	20	23	26	19	23	21	19	20	22	21	21	20	18	21	16	20	23	23
Total Chemicals (10–20 cm)	23	27	20	22	27	20	21	20	19	20	23	20	20	20	18	22	16	20	23	25

Detected in both layers   Detected only in 0–10 cm   Detected only in 10–20 cm

In the case of the 10–20 cm soil depth, Abamectin remained the most abundant in the soil samples, being reported at 16 sites, while both p, p-DDE and p, p-DDD were reported only at six sites as the least highest (Table 4). Abamectin reported the highest mean residual level of the inner soil samples as 0.81 ± 0.19 ppm, followed by Iprobenfos (0.59 ± 0.14 ppm). On the other hand, p, p-DDE, and p, p-DDD accounted for the lowest mean residual level of 0.01 ± 0.001 ppm (Table 4). Five clusters of study sites emerged based on the overall residuals of other agrochemicals in deep soil (Figure 7). Sites 4, 10, 11, and 17 reported the highest Abamectin levels, forming one cluster, followed by Sites 6, 7, and 9, which formed the second cluster. However, Iprobenfos was found in the soil samples of the second cluster (Figure 7). Meanwhile, Site 8 and Site 14 reported only Ametraz and Abamectin residues, respectively, forming the third and fourth clusters. The remaining sites formed the fifth cluster.

Figure 7. Dendrogram of the cluster analysis of sites based on the residual level of other agrochemicals in inner soil.

4. Discussion

4.1. The Availability of Agrochemical Residues in Soil Layers

Out of the twenty localities where soil samples were analyzed, all the sites reported the availability of at least several pesticide residues. Mevinphos was reported from two sites, while Linuron was reported from four sites. In the case of p, p-DDE and p, p-DDD, around six sites denoted notable levels of these residues, while azinophos-ethyl was found at seven sites. All the other pesticides were reported in more than fifty percent of the soil sampling sites. Cypermethrin and Resmethrin were the most commonly detected pesticide residues, at 19 sites, followed by Deltamethrin, Endosulfan, Methidathion, Atrazine, and Bromoxynil, at 18 locations. Almost all the sites showed a mixture of several pesticide residues at both the depth levels studied. Out of the 32 pesticides that were studied, Site 17 reported 17 types of pesticide residue, while Site 2 reported a combination of 27 pesticide residues. Overall, the mean concentration of pesticides ranged from 0.004 ± 0.002 µg/g (p, p-DDD) to 3.84 ± 0.41 µg/g (Atrazine). The highest pesticide residue concentrations are primarily reported from the inner soil layer (10–20 cm) compared to the outer layer.

4.2. Herbicide Residues

Based on the results reported in Tables 2 and 4, the most commonly used herbicides in the vegetable cultivation sites were Bromoxynil, Atrazine and Diclofop methyl. The herbicide residue reported least is Linuron. Isoproturon and Pendimethalin were reported moderately. Isoproturon, Pendimethalin, and Diclofop methyl were reported at 13, 10 (11 sites in the 10–20 cm layer), and 17 sites, respectively. However, these three herbicides were not detected in the groundwater samples analyzed by El Alfy and Faraj [25]. Sites 13 and 15 reported moderate levels of Atrazine and Bromoxynil, Sites 10 and 16 reported moderate levels of Isoproturon and Diclofop methyl levels in topsoil, and Sites 6, 8, and 17 reported Atrazine, Diclofop methyl, and Isoproturon at exceptional levels (Figures 2 and 3).

Atrazine is a systemic herbicide used for broadleaf weeds both before and after emergence. It is also used to control some grass weeds [28,29]. Under anaerobic conditions, Atrazine has a half-life of around 578 days in water [28], and its half-life in water exposed to sunlight is 168 days [30]. Atrazine has a low to moderate solubility in water [28]. Atrazine does not bind well to the soil and can easily move [30], contaminating water resources.

Bromoxynil is a selective foliage-applied contact herbicide used to control a variety of grasses and broadleaf weeds. The hydrolysis half-life for the degradation of Bromoxynil ranges from 1 day to 34 days. Exposure to sunlight and aerobic and anaerobic degradative processes increases the degradation rate of Bromoxynil. The US Environmental Protec-

tion Agency (USEPA) reported that the potential for groundwater contamination from Bromoxynil is low, as it does not exhibit mobility or persistence characteristics. Therefore, Bromoxynil is normally not found in groundwater [31]. Environmental fate studies indicated that Bromoxynil (phenol and octanoate) does not persist in surface waters [31]. An aerobic aquatic metabolism study has shown the rapid degradation of Bromoxynil, with a half-life of <12 h [31].

Linuron is used to control germinating and newly emerging broad-leafed weeds and grasses. The use of Linuron is prohibited directly to water or to areas where water is available. Linuron entails relatively low acute toxic and dietary risks (acute and chronic) in humans, which appear to be minimal (Add Ref). Information on persistence, mobility and dissipation pathways, the persistence and mobility of several degradates of Linuron is not available, hence the environmental fate assessment of Linuron is incomplete [32]. Parent Linuron is moderately persistent and relatively immobile, but increased mobility is reported when applied to coarse-textured soils and soils with low levels of organic matter. Linuron can be washed into surface-water bodies through runoff. Linuron is moderately persistent in aerobic soil with a metabolism half-life ranging from 57 to 100 days [32]. As Linuron is sufficiently persistent, it may be mobile under certain environmental conditions and has the potential to impact groundwater quality [32]. However, Linuron residues were reported in fresh leafy vegetable, coriander, and mint harvests from the study sites as 0.064 µg/L and 0.0053 µg/L, respectively [11].

El Alfy and Faraj [25] investigated the availability of 32 different agrochemical residues in groundwater in the same study sites, and detected 22 agrochemicals in the groundwater. Atrazine is widely used to control weeds in agricultural areas and is used excessively in the study sites. This herbicide is moderately persistent and degrades in three months in water. El Alfy and Faraj [25] also reported that Atrazine was detected in 72.5% samples of groundwater they analyzed (ND—1.3 µg/L). The soils analyzed from the same area in this study show a range of 2.73 ± 0.27 ppm to 0.19 ± 0.02 ppm at the 0–10 cm layer in 18 out of 20 sites and of 3.84 ± 0.14 ppm to 0.14 ± 0.03 ppm at the 10–20 cm layer at 17 out of 20 sites. The higher hydraulic conductivity of the soils (alluvium sediments) and frequent irrigation have accelerated the recharge of groundwater leaching Atrazine into the groundwater. Further, Sites 6, 8, 13, 15, and 17 recorded higher concentrations of Atrazine, which needs special attention when intensive agriculture is practiced. Soil contamination with higher concentrations of Atrazine has contaminated the groundwater in these sites. El Alfy and Faraj [25] reported that 37.5% of the groundwater samples analyzed showed Atrazine concentrations above the legal limit of >0.1 µg/L [33,34]. Agrochemicals in drinking water are regulated by [33,34] and pesticides at 0.1 µg/L, and a total amount of pesticides at 0.5 µg/L is established as the rule of maximum concentrations.

Diclofop-methyl is used to control various grass weed species. Diclofop-methyl is not persistent in soil under aerobic conditions and has very low persistence in anaerobic soil or water [35]. It is reported that Diclofop-methyl or its acid degradate does not migrate to groundwater even under worst-case scenario applications [35]. Hence, USEPA has concluded that Diclofop-methyl is unlikely to reach surface and groundwater [35]. With appropriate engineering controls, the application of Diclofop-methyl is safer and can minimize the health risks of direct contaminations while applying the herbicide. Therefore, Diclofop-methyl is a herbicide which can be used sustainably to control grass weeds in the study sites with appropriate engineering controls during application.

Pendimethalin, a selective herbicide, is used to control broadleaf and grass weed species. Pendimethalin dissipates in the environment by binding to soil, microbially mediated metabolism and volatilization [36], and it is essentially immobile in soil. The persistence of Pendimethalin decreases with increased temperature, increased moisture, and decreased soil organic carbon [36]. The potential for groundwater contamination from Pendimethalin residues is low [36]. El Alfy and Faraj [25] reported that Pendimethalin is not reported from groundwater sources even though Pendimethalin is detected in soils

in this study. Hence, Pendimethalin is a herbicide that can be safely used in the study environment to maintain sustainable soils and water resources.

Isoproturon is used as a pre-and post-emergence control weedicide to control annual grasses and many broadleaf weeds. It is slightly water-soluble and, depending on rainfall and irrigation conditions and soil properties, it can reach the groundwater [37]. Due to the absence of microbial activity, accumulated intolerable concentrations in drinking water are reported [38]. Isoproturon inflicts higher environmental hazards and health risks, hence it is classified as a WHO Class III hazardous material [39,40]. El Alfy and Faraj [25] reported that Isoproturon is not reported at groundwater sources, even though Isoproturon is detected in soils in this study at 13 sites. However, due to the toxicity of Isoproturon and the high potential of contaminating the groundwater sources and related persistence; it is recommended to avoid this herbicide from applications in the Al-Kharj area.

Therefore, good agricultural practices need to be implemented to make sure the soils and groundwater in the area are sustainably used in the future. Bromoxynil could be a safer and environmentally friendly herbicide compared to Atrazine. The replacement of Atrazine with Bromoxynil could enhance the sustainability of the soil and water resources in the region. As the fate of the metabolites of Linuron are unknown, and as it has relative mobility in certain problematic soils, it can be avoided to maintain the sustainability of soils and water resources. Based on the above, in order to manage soils and the water resources of the vegetable-growing Al Kharj area, the use of Atrazine, Isoproturon, and Linuron could be minimized. Bromoxynil, Pendimethalin, and Diclofop methyl could be used to control weeds. These findings could lead to policy recommendations to increase the sustainability of vegetable and other crop productions in the Al Kharj area.

4.3. Pesticide Residues

The residues of twenty-one pesticides were detected at the soil sampling sites where Resmethrin and Cypermethrin were reported from 19 sites out of the 20 sites sampled. Methidathion, Endosulfan, and Deltamethrin were reported at 18 sites; Carbaryl was reported at 17 sites; Ethoprophos, Tetramethrin, and Lindane were reported at 16 sites; Chlorpyrifos, Bromophos methyl, and Bifenthion were reported at 15 sites; Dimethoate, Heptachlor, Permethrin, and Fenoxycarb were detected at 14 sites; Cyfluthrin was detected at 13 sites; Chlorpyrifos methyl was detected at 12 sites; Phosmet and Azinophos ethyl was recorded at 7 sites; and Mevinphos was detected at only 2 sites (Tables 3 and 4). El Alfy and Faraj [25] reported that Chlorpyrifos methyl, Dimethoate, Chlorpyrifos, Lindane, Heptachlor, Endosulfan, Bifenthion, Cyfluthrin, Resmethrin, Deltamethrin, Tetramethrin, Azinophos ethyl, Cypermethrin, Carbaryl, and Fenoxycarb residues were detected from groundwater from the study sites. Further, Methidathion, Ethoprophos, Bromophos methyl, Permethrin, Phosmet, and Mevinphos were not detected in the groundwater samples [25] even though those were detected in soils. Sites 3, 4, 10, 13, and 17 recorded higher levels of Cypermethrin and Lindane (γ–HCH), and Sites 2, 6, 12, and 19 recorded higher concentrations of Ethoprophos, Heptachlor, and Resmethrin (Figures 4 and 5).

Cypermethrin is an insecticide used to control a wide range of pests. Cypermethrin adsorbed strongly to organic carbon and has little mobility in soil [41]. Therefore, Cypermethrin is not likely to leach into groundwater. Cypermethrin reaches surface water bodies through runoff events accompanied by soil erosion [41]. Cypermethrin is moderately persistent in the environment and in soil, under both aerobic and anaerobic conditions. Cypermethrin biodegrades relatively slowly [41]. Cypermethrin was detected in both the soil layers in 19 sites out of the 20 sites. Further, El Alfy and Faraj [25] reported that Cypermethrin was detected in 45% of the groundwater samples analyzed with concentrations varying between 0.02 and 0.82 µg/L, and 10% of the samples were above the legal limit of 0.1 µg/L. Though Cypermethrin is not likely to leach into groundwater, in Al-Kharj, an intensive agricultural area, a considerable amount of the chemical has reached the groundwater table, which needs further investigation. Good agricultural practices need

to be introduced to minimize the leaching of Cypermethrin to groundwater and also to minimize residue concentrations in soils.

Resmethrin is a broad-spectrum, non-systemic, synthetic pyrethroid insecticide used widely in mosquito abatement. When exposed to light, Resmethrin degrades rapidly due to photolysis [42]. However, resmethrin is more persistent when not subjected to photolysis. Resmethrin has low mobility and a high affinity to bind to soils/sediments and organic carbon; therefore, it is not expected to leach to groundwater [42]. In the soil layers analyzed, residues of Resmethrin were recorded at 19 sites, as it binds to soils/sediment and, according to El Alfy and Faraj [25], residues of Resmethrin were found only in 4 groundwater sampling sites out of the 40 evaluated.

Endosulfan is a restricted-use pesticide applied against aphids, fruit worms, beetles, leafhoppers, moth larvae, and white flies on a wide variety of crops [43]. The use of endosulfan is being restricted to certain crops, and the use is banned in many countries. Endosulfan can be released into air, water, and soil. Endosulfan is not often detected in groundwater, as endosulfan attaches to soil particles and is not expected to move from the soil. However, when added to water, Endosulfan is more difficult to break down [43]. In soil layers analyzed from Al-Kharj, Endosulfan residues were recorded at 18 sites, indicating its wide use as it binds to soils/sediments. El Alfy and Faraj [25] recorded the availability of Endosulfan residues in 70% of the groundwater samples analyzed from Al-Kharj even though Endosulfan is not often detected in groundwater [43]. Endosulfan applied during irrigation events has moved it into groundwater. Twenty percent of the groundwater samples that were detected with residues of Endosulfan were above the legal limit of 0.1 µg/L [25]. As Endosulfan has a longer half-life, and as it poses serious health risks to human beings and other organisms, the use of Endosulfan needs to be strictly regulated and banned. Therefore, urgent policy decisions are required to limit the usage of Endosulfan in the Al-Kharj and other agricultural areas in Saudi Arabia to safeguard the people from adverse health effects and to ensure the sustainability of soil and water resources.

Deltamethrin is a contact insecticide. Deltamethrin is used to control a wide range of pests including Coleoptera, Heteroptera, and Homoptera [25]. Due to soil adsorption properties, Deltamethrin has a low potential to leach into groundwater [25]. Deltamethrin is a neurotoxin that is highly toxic to humans and mammals. Deltamethrin residues were recorded from 18 sites, indicating its wide use as it binds to soils/sediments. El Alfy and Faraj [25] recorded that out of the 40 groundwater sampling sites analyzed, 27.5% detected Deltamethrin, and 12.5% of the groundwater samples exceeded the legal limit of 0.1 µg/L. As Deltamethrin is highly toxic to humans, urgent actions need to be taken to minimize the excessive usage of Deltamethrin to ensure the safety of people and also to make sure the soils and groundwater are used sustainably.

Methidathion is a broad-spectrum organophosphate insecticide/acaricide used to control agricultural insects and mite pests on various crops. Methidathion is relatively nonpersistent in soils with aerobic and anaerobic soil half-lives of 11 and 10 days, respectively [44]. Methidathion is unlikely to persist in water due to rapid degradation and shorter half-lives; hence, it is not a serious groundwater or drinking water problem. It is further unlikely to persist in soil long enough to result in a significant contamination of groundwater. However, Methidathion may enter surface water via spray drift, in runoff water, and as residue adsorbed to eroding soil particles. None of the known degradates of Methidathion are of toxicological concern [44]. Methidathion residues were recorded at 18 sites in both the soil layers out of the 20 sites. However, Methidathion was not detected in groundwater samples sampled at 40 sites by El Alfy and Faraj [25]. As Methidathion is not leached to the groundwater in the Al-Kharj area, even though it was detected in the soils of 18 sites, in terms of sustainable groundwater management, it is a safer insecticide. With appropriate dosing and safer application practices, it can be used to manage soils sustainably.

Carbaryl is used in agriculture to control pests on terrestrial food crops. Depending upon conditions, carbaryl has a half-life ranging from 4 to 72 days in soil. Carbaryl breaks

down faster in sandy, flooded, or well-aerated soils. Carbaryl does not dissolve well in water and sticks to soil [45]. Mineral and organic matter in soils have been found to contribute to carbaryl adsorption. However, carbaryl is widely used and can last a long time under the right conditions. Carbaryl is commonly found in groundwater [45]. Carbaryl is moderately soluble in water. The solubility of Carbaryl increases with an increase in temperature and amounts of organic solvents [46]. Carbaryl was recorded at 17 sites in soil layers from the Al-Kharj area (Tables 4 and 5), and El Alfy and Faraj [25] reported that 82.5% of the groundwater samples analyzed were contaminated with Carbaryl, and 25% of the samples analyzed were above the legal limit of 0.1 µg/L. The higher temperature of groundwater in the Al-Kharj area [25] could be a reason for the higher residual contents shown in groundwater. Carbaryl has low persistence in outdoor environments; hence, by taking sufficient care in application with appropriate technology, protective measures, and proper dosages, damages to soil, water, and humans can be minimized. Further, Carbaryl could be replaced with a much safer insecticide to minimize soil and water contamination.

Table 5. Mean residual levels of other agrochemicals at 0–10 cm and 10–20 cm depths at study sites.

Other Agro-Chemical	0–10 cm				10–20 cm			
	Concentration		Highest Site	Number of Sites	Concentration		Highest Site	Number of Sites
	Highest	Lowest			Highest	Lowest		
Iprobenfos	1.47 ± 0.17	0.06 ± 0.03	20	13	1.80 ± 0.21	0.13 ± 0.04	20	13
Abamectin	3.03 ± 0.21	0.21 ± 0.09	11	14	3.33 ± 0.39	0.18 ± 0.03	11	14
Ametraz	2.30 ± 0.32	0.08 ± 0.04	18	13	2.28 ± 0.25	0.11 ± 0.04	17	13
p, p-DDE	0.013 ± 0.008	0.006 ± 0.003	5	4	0.022 ± 0.009	0.008 ± 0.002	12	6
p, p-DDD	0.013 ± 0.004	0.011 ± 0.003	19	4	0.019 ± 0.008	0.004 ± 0.002	12	6

Ethoprophos is a broad-spectrum organophosphate insecticide and nematicide used to control soil-dwelling insects and nematodes. Most of the risks of Ethoprophos are contributed to dermal exposure through occupational risks, which can be minimized through the handler's personal protective equipment and engineering controls [47]. Soil incorporation (Ethoprophos remaining on the soil surface can runoff or be ingested), canceling certain uses, reducing maximum application rates, preventing broadcasting, and limiting the number of applications are ways of minimizing occupational risks [47]. Ethoprophos is moderately mobile in soils, and with increasing organic matter contents, its mobility decreases in soils [47]. Ethoprophos's movement was limited to the top 25 cm layer, and the concentrations of Ethoprophos were below the detection limit (0.2–2 µg dm^{-3}) in all soil layers between 25 and 120 cm depths [48]. Ethoprophos was detected in top soil layers at 16 sites out of the 20 sites, and it was detected only in 15 inner layers. Ethoprophos residues were not detected in the groundwater samples analyzed [25] as Ethoprophos is not leached into deeper soil layers [48]. With appropriate personal protective equipment and engineering controls for the handler, the occupational risks of using Ethoprophos can be minimized, and with appropriate dosages and recommendations, the soils and water resources can be managed sustainably.

Tetramethrin is a broad-spectrum, non-systemic, synthetic pyrethroid pesticide used to control flying and crawling insects in several commercial, horticultural and residential applications. Tetramethrin decomposes rapidly by photolysis and hydrolysis in shallow, non-turbid water. Tetramethrin is not expected to reach water bodies in sufficient concentrations to induce phytotoxic effects [49]. Runoff exposure is not expected due to very short photolysis, hydrolysis, and field dissipation half-lives [49]. Tetramethrin is slightly mobile in soil and is not expected to adversely impact groundwater or surface water; therefore, drinking water contamination is not an issue [49]. Tetramethrin was dissipated from the upper 15 cm of soil with a DT50 (time to 50% degradation) of 3 h [49]. Hence, Tetramethrin

does not pose the threat of groundwater contamination. Tetramethrin was detected at 16 soil sampling sites in the Al-Kharj area, but it was detected in groundwater from only one site [25]. As Tetramethrin does not pose the risk of groundwater pollution, and as it decomposes very quickly in soil layers, it can be used to maintain soil and groundwater resources sustainably.

Lindane is an organochloride pesticide used with a wide range of applications. Lindane is extremely persistent and tends to bio-concentrate and bio-accumulate due to continuing exposure. Lindane can migrate over long distances through air, water, and sediment [50]. Once accumulated in fatty tissues, Lindane residues will remain there for an undetermined amount of time. Registration for all uses of Lindane were canceled by the USEPA [50]. Over 50 countries have either applied a ban or levied strict regulations on the usage of Lindane [51]. However, it is still being used in developing countries. Lindane was detected in 16 soil sampling sites in the Al-Kharj area with considerable concentrations, even though it is a banned pesticide in many countries. Further, El Alfy and Faraj [25] detected Lindane residues in 75% of the groundwater sampling sites of the 40 sites sampled. Further, they reported that 22.5% of the sampling sites showed Lindane concentrations above the legal limit of 0.1 µg/L. As safer alternatives are available to replace Lindane, it is recommended to strictly ban the use of Lindane in order to sustain the soil and water resources and to minimize its health impacts on living beings.

Chlorpyrifos, Chlorpyrifos methyl, an organophosphate insecticide, acaricide, and miticide are used to control foliage and soil-borne insect pests. The acute and chronic exposure of chlorpyrifos causes genotoxicity as well as mutagenic effects [52]. One of the metabolic products of Chlorpyrifos and Chlorpyrifos methyl shows potential health hazards due to its high affinity to the DNA molecule [53], and it is highly mobile in soil and is leachable [54]. The half-life of Chlorpyrifos in soils is typically between 60 and 120 days; further, it can deviate from 2 weeks to over 1 year, depending on the soil type, climate, and other conditions [55]. In August 2021, EPA released a final rule revoking all tolerances for Chlorpyrifos and Chlorpyrifos methyl and banned the registered food uses of Chlorpyrifos and Chlorpyrifos methyl [56]. Several countries are gradually banning the use of Chlorpyrifos and Chlorpyrifos methyl due to their adverse health risks. The European Commission withdrew all authorizations for plant protection products containing the active substances Chlorpyrifos and Chlorpyrifos methyl from 2020. Chlorpyrifos residues were detected at 15 and 16 sites in the 0–10 cm and 10–20 cm layers, respectively. Chlorpyrifos methyl residues were detected at 12 soil sampling sites. Further, 57.5% and 40% of the groundwater sampling sites out of the 40 sites evaluated by El Alfy and Faraj [25] contained Chlorpyrifos and Chlorpyrifos-methyl residues, respectively, and 10% and 5% of the samples were above the legal limit of 0.1 µg/L, respectively. The present study and the study on groundwater did not analyze for metabolic products of Chlorpyrifos and Chlorpyrifos-methyl. The above results show that Chlorpyrifos and Chlorpyrifos-methyl are intensively used, which was confirmed by El Alfy and Faraj [25]. Therefore, a policy recommendation is vital to limit or ban the use of Chlorpyrifos and Chlorpyrifos-methyl in Al-Kharj and other agricultural areas in Saudi Arabia to protect the soils and water from contamination and to minimize the health hazards to workers and consumers.

Bromophos-methyl is an obsolete organophosphate insecticide with a low aqueous solubility and is quite volatile. It is not generally persistent in soil systems but has the potential to leach into groundwater. Bromophos-methyl is moderately toxic to mammals if ingested [57]. Bromophos-methyl residues were detected at 15 and 16 sites in the 0–10 cm and 10–20 cm layers, respectively. However, Bromophos-methyl residues were not recorded in the groundwater, as reported by El Alfy and Faraj [25]. Hence, Bromophos-methyl can be used to manage soils and water resources sustainably in the Al-Kharj area.

Bifenthion (Bifenthrin) is an insecticide from the pyrethroid family. Bifenthrin is used against a wide range of insects and mites. The aerobic half-life of bifenthrin in soil ranges from 97 to 250 days, depending on the soil type. It is immobile in soil containing high amounts of silt, clay, and organic matter and has low mobility in sandy soil containing small

amounts of organic matter. Hence, Bifenthrin has a low potential to contaminate groundwater, as it binds to soil and has a low water solubility [58]. El Alfy and Faraj [25], from their study in the Al-Kharj area, reported that Bifenthrin was only detected in groundwater from two sampling sites, even though this study detected Bifenthrin residues at 15 sites out of the 20 sites sampled. However, bifenthrin which is soil-bound has the potential to contaminate surface waters through runoff. The risks of using Bifenthrin can be minimized by applying it in appropriate dosages and recommendations so that soil and groundwater resources in the Al-Kharj area can be managed sustainably.

Dimethoate is a systemic organophosphate insecticide used on a large variety of field-grown agricultural crops, tree crops, and ornamental crops for a wide range of insect pests. All non-agricultural uses, including residential uses and usage for several vegetable and fruit crops, were canceled. Dimethoate is a highly mobile, relatively non-persistent organophosphate insecticide [59]. Dimethoate is highly soluble in water, has very weak adsorption characteristics to soil [25], and leaches through soil into groundwater under certain conditions [59]. The use of this chemical in areas where soils are permeable, particularly where the water table is shallow, may result in groundwater contamination [59]. Dimethoate was detected at 14 sampling sites out of the 20 sites studied, and residues were detected in 72.5% of the groundwater samples of the 40 sampling sites studied by El Alfy and Faraj [25]. However, all the residues were below the legal limit. As Dimethoate is banned for several crops by the USEPA, it is prudent to ban the application of Dimethoate to such crops and similar crops grown in the Al-Kharj area. Further, the leaching of Dimethoate needs to be controlled to make water resources safer for different applications.

Heptachlor, an organochlorine, was used as an insecticide, as a soil and seed treatment, and to control ants, cutworms, maggots, termites, and other pests in agriculture and in the home. Heptachlor has a low water solubility and it is subject to long-range transport and wet deposition. The sale of heptachlor was voluntarily canceled in 1987, and nearly all registered uses of heptachlor have been canceled by the USEPA [60]. Hepachlor residues were detected in 14 soil-sampling sites in the Al-Kharj area. El Alfy and Faraj [25] reported that 52.5% of the groundwater samples they analyzed contained residues of Heptachlor and 12.5% of the samples had exceeded the legal limit of 0.1 µg/L. These results show that even though Heptachlor is banned for use in many countries, it is used intensively in Al-Kharj's agricultural areas. Due to heavy toxicity, the persistence of degradants of Heptachlor, and due to many other adverse impacts, a policy decision needs to be taken to ban the use of Heptachlor to ensure sustainable agriculture in the Al-Kharj area and in Saudi Arabia.

Permethrin, a pyrethroid class of pesticides, is used in/on food/feed crops, livestock and livestock housing, modes of transportation, structures, buildings (including food handling establishments), and Public Health Mosquito abatement programs [61]. The average half-life of permethrin in aerobic soils is 39.5 days, with a range from 11.6 to 113 days. When permethrin enters an aquatic system, some is degraded by sunlight while in the water column, but the majority binds tightly to the sediment. Permethrin is not likely to contaminate groundwater due to its low water solubility and strong adsorption to soil. Permethrin residues were recorded from 14 soil sampling sites, but residues were not detected in the groundwater samples analyzed from the same area by El Alfy and Faraj [25]. As Permethrin is bound by soil particles and degrades quickly, it is a safer pesticide to control pests and mosquitos, replacing other questionable pesticides. The proper and recommended usage of Permethrin will ensure the sustainable management of soil and groundwater resources in the Al-Kharj region.

Fenoxycarb is a carbamate insect-specific growth regulator used to control moths, scale insects, fire ants, fleas, mosquitoes, and other insects. Fenoxycarb degrades in soils by hydrolysis, and residues are not detected three days after application [62]. Fenoxycarb has moderate to strong soil adsorption characteristics; hence, it has a low potential for leaching [62]. However, 14 and 13 soil sampling sites, at 0–10 cm and 10–20 cm, respectively, showed traces of fenoxycarb. Further, El Alfy and Faraj [25] detected Fenoxycarb residues

in 22.5% of the groundwater samples they analyzed from 40 sites in the Al-Kharj area with 5% of the samples recording above the legal limit of 0.1 µg/L. Sandy soils with higher permeability in the study area combined with the heavy use of Fenoxycarb, coupled with excessive irrigation, could have leached the residues into groundwater. The application of Fenoxycarb according to the recommended doses could ensure the sustainable use of soil and water resources in the area.

Cyfluthrin, a pyrethroid insecticide, is used to control insects on several crops and pests like ants, silverfish, cockroaches, termites, weevils, fleas, mosquitoes, and flies. It is less toxic to people and mammals because they break Cyfluthrin down faster than insects. Cyfluthrin is broken down by water or sunlight; hence, it is moderately persistent in soils. Cyfluthrin is less dissolved in water and is immobile in soil. Therefore, it is unlikely to leach. Cyfluthrin breaks down faster in soils with high organic contents, in soils without oxygen, and those with high clay contents. If used on the soil surface, the half-life of Cyfluthrin is about 2 to 16 days; in water, with sunlight, it is around 12 days, and it is about 193 days without sunlight [63]. Cyfluthrin breaks down faster in people and mammals than in insects; hence, Cyfluthrin is less toxic to people and mammals [63]. Cyfluthrin residues were detected at 13 soil sampling sites in the Al-Kharj area. Only 5 groundwater sampling sites out of the 40 sites contained Cyfluthrin residues [25]. Therefore, Cyfluthrin could be used safely in the management of crops in the Al-Kharj area, following recommended doses to sustain the management of soil and groundwater resources.

Phosmet, an organophosphate insecticide, is used on a variety of insects on many crops and to control fleas, lice, hornflies, sarcoptic mange, and ticks on cattle, swine, and dogs. Phosmet rapidly hydrolyses under alkaline and neutral conditions and, to a much lesser extent, under acidic conditions. Microbial degradation is a major route of dissipation. In soils where microbial activity is minimal, leaching may be significant. Phosmet degrades rapidly under aerobic conditions in soil (3 days) and more slowly under anaerobic conditions (15 days). Phosmet oxon, the only known degradation of toxicological concern, is less mobile than phosmet. Hence, Phosmet or Phosmet oxon is limited to the upper soil layers and was not detected in lower soil layers and groundwater [64]. Acute and chronic dietary risk assessments for food and drinking water are reported to be of the least concern [64]. Seven soil sampling sites out of the twenty sites studied showed traces of Phosmet. El Alfy and Faraj [25] reported that Phosmet was not detected in groundwater samples from the study site. Based on the above, Phosmet could be used with the recommended dosages to manage the soil and groundwater resources' sustainably in the Al-Kharj region.

Azinphos-methyl is a highly persistent, broad-spectrum insecticide. The persistence of Azinphos-methyl in soil is low under field conditions. Azinphos-methyl has low water solubility and is fairly immobile in soil because it is adsorbed strongly to soil particles. Therefore, groundwater contamination is unlikely to happen. Azinphos-methyl dissipates more rapidly from soils in surface layers in water [65]. Seven soil sampling sites out of the twenty sites studied showed traces of Azinphos-methyl. El Alfy and Faraj [25] reported that Azinphos-methyl was detected only from one groundwater sampling site out of the forty study sites. Azinphos-methyl, therefore, could be used with the recommended dosages to manage the soil and groundwater resources sustainably in the Al-Kharj region.

Mevinphos, an Organophosphate, is a contact/systemic insecticide–acaricide. Due to high toxicity, the use of Mevinphos was discontinued in the United States following the recommendation of the United States Environmental Protection Agency in 1994 [66]. Mevinphos is registered outside the U.S. for use in vegetables and fruit crops to control insect pests. Exposure to Mevinphos can cause rapid fatal organophosphate poisoning [67]. Mevinphos is readily soluble in water and hydrolyzes at pH 7, with a half-life of 15 to 39 days. Mevinphos is a volatile compound; thus, it is unlikely to persist where it has been applied. Because mevinphos is rapidly hydrolyzed in water, and rapidly metabolized in soil, it is unlikely to become a groundwater contaminant [68]. Mevinphos residues were detected at two soil sampling sites out of the twenty sites evaluated. El Alfy and Faraj [25]

reported that Mevinphos residues were not detected from any of the groundwater sampling sites. However, considering the toxicity of Mevinphos and considering the discontinuation of use by USEPA and in many other countries, a policy decision needs to be made to ban the use of Mevinphos in Al-Kharj and other agricultural areas in the Kingdom.

4.4. The Residues of Other Agrochemicals

Based on the results reported in Tables 4 and 5, the other agrochemicals most commonly used in vegetable cultivation sites are Iprobenfos, Abamectin, and Amitraz. The metabolites of DDT, p, p-DDE and p, p-DDD are reported the least. Abamectin is reported at 14 sites (both layers), and Iprobenfos and Amitraz are reported at 13 sites (both layers). p, p-DDE and p, p-DDD residues are reported at four sites in the top soil layer (0–10 cm) while those were detected from six sites in 10–20 cm layer. Iprobenfos, Ametraz, p, p-DDE and p, p-DDD residues were detected in the groundwater samples analyzed by El Alfy and Faraj [25]. However, Abamectin residues were not detected from the groundwater samples collected from the study area. Abamectin denoted the highest mean residual level (3.03 ± 0.21 ppm) and was reported in topsoil samples of 14 sites (Tables 4 and 5). In the inner soil layers also, Abamectin was reported to have the highest mean residual level (3.33 ± 0.39 ppm). Sites 6, 7, and 9 showed higher Iprobenfos residues (Figures 6 and 7) in both layers. Sites 4, 10, 11, 14, 16, 17, and 19 show higher Abamectin and Amitraz residues in the 0–10 cm layer (Figure 6). In the inner soil layer, Sites 4, 10, 11, and 17 showed the highest Abamectin levels while Sites 8 and 14 reported only Ametraz and Abamectin residues (Figure 7, Table 4). Site 14 did not record residues of any of these chemicals while Sites 6 and 9 recorded residues of only Iprobenfos. Sites 4 and 10 recorded only the residues of Abamectin.

Iprobenfos is a systemic fungicide that is mainly applied in rice cultivations. Iprobenfos is mainly degraded by microorganisms and its half-life is 5.7 days at 28 °C in aqueous systems. The hydrolysis of Iprobenfos is accelerated by the higher temperature, and photodegradation is accelerated by lower pH [69]. Iprobenfos has a moderately mobile and moderately leaching potential [70]. Higher concentrations of Iprobenfos were detected in river water, which could be due to the higher solubility of Iprobenfos in water with a lower affinity to be adsorbed in soil; hence, Iprobenfos is washed down with runoff [71]. El Alfy and Faraj [25] detected Iprobenfos residues from two sites out of the forty sites in which groundwater was analyzed for agrochemical residues. The present study detected Iprobenfos in soils in 13 sites out of the 20 sites analyzed. As rice is not cultivated in the Al-Kharj area, the application of Iprobenfos can be prevented with an appropriate fungicide to control fungal diseases in the vegetables cultivated in the area. Policy decisions need to be taken on recommended fungicides to be used, and the use of non-recommended pesticides needs to be prevented through regulations to sustain soil and water resources in the region.

Amitraz is an insecticide and acaricide sprayed on crops and livestock. Parent Amitraz rapidly degrades in the environment to form two primary transformation products and a secondary transformation product. As Amitraz rapidly degrades in the environment, Amitraz does not pose a pollution risk on ground or surface waters [72]. However, 2 out of 40 water sampling sites analyzed by El Alfy and Faraj [25] detected Amitraz. In this study, the residues of parent Amitraz (Table 5) was detected from 13 out of 20 sites in both the soil layers. Transformation products have shown moderate persistence in aquatic and terrestrial environments [72], but those are relatively immobile in soil [72]. Some of the Amitraz degradates show chronic toxicity with more persistence in aquatic environments [72]; hence, the availability of Amitraz degradants needs to be evaluated in these environments. Therefore, Amitraz needs to be applied with caution to minimize harmful impacts due to Amitraz degradants to ensure the sustainability of soil and water resources in the Al-Kharj area.

Abamectin is a miticide/nematicide. Abamectin is not dissolved in water; rather, the particles are suspended in water [73]. Abamectin on soil surfaces or in clear, shallow

surface water undergoes rapid photodegradation (half-life < 1 day). However, suspended sediments and a lack of mixing decrease the rate of photodegradation, and Abamectin residues are adsorbed to sediments, reducing aqueous concentrations. Abamectin slowly biodegrades in soils (half-life is 80.6 days), and its impact on groundwater is minimal [73]. Abamectin was not detected by El Alfy and Faraj [25] in groundwater samples analyzed from 40 sites, even though considerable Abamectin residues (Table 5) were detected at 14 soil sampling sites out of the 20 sites sampled (Table 4). When applied according to prescribed doses, Abamectin can be used to maintain the sustainable use of soil and water resources in the Al-Kharj area.

DDT, DDE, and DDD are persistent in the soil for a very long time, potentially for centuries. DDT is mainly broken down slowly by microbial action into p, p-DDE, and p, p-DDD [74]. These chemicals also evaporate, air drifted and deposited in remote places. They are strongly adsorbed to soil and therefore generally remain in the surface layers of soils. Some soil particles with runoff enter into surface water bodies, polluting them. Only a very small amount leach and enter into groundwater [74]. The length of time these derivatives remain in the soil depends on many factors including the temperature and type of soil [74]. The levels of p, p-DDE in foods have been decreasing and are expected to continue to decrease further. El Alfy and Faraj [25] detected p, p-DDE and p, p-DDD in 4 water sampling sites out of 40 sampling sites. p, p-DDE, and p, p-DDD were detected in four sites in the soil layer of 0–10 cm and in an inner layer in six sites. These sites need to be continuously monitored to minimize the adverse health impacts on humans.

Farmers usually tend to apply most pesticides with higher application rates, with more applications, and with shorter application intervals. This leads to higher concentrations of pesticide residues in the soil environment. The fate of pesticides in soils is determined by their various factors: mobility, persistence, and volatility [18]. Furthermore, pesticide properties such as phosphorus and nitrogen levels, organic carbon content, and soil pH affect distribution and occurrence [75,76], and based on these factors, the leaching potential of the pesticide residues is determined to suggest the risk of groundwater pollution. Therefore, the pesticide application in the Al-Kharj region needs to be monitored continuously with measures to control contaminations to protect the water resources from decay by pesticide residues which can create an unhealthy environment. In addition, integrated pest and disease management approaches and good agricultural practices can be introduced to minimize toxic pesticides. Thin permeable soils, permeable aquifers, and shallow water tables are especially vulnerable to pesticides and prolonged exposure to pesticides [25]. They can cause adverse effects to human health and the ecosystem, putting the sustainability of agricultural production at stake.

The pesticide soil regulatory guidance values (PSRGVs) proposed by different agencies worldwide have given widely varying values for an individual pesticide [77]. Fifty-four nations have regulated more than 19,400 pesticide soil regulatory guidance values (RGVs), and a total of 22 pesticides have been regulated with more than 100 soil RGVs. RGVs for an individual pesticide could vary over eight (Lindane soil RGVs) or even nine (Dieldrin soil RGVs) orders of magnitude [77]. The worldwide standard values are not readily applicable to avoid human health risks by pesticides, as they have not been computed considering major human exposure pathways [77]. Therefore, there is a need to derive RGVs to commonly used pesticides in intensive agriculture in the Kingdom of Saudi Arabia. RGVs derived from agricultural soils in Saudi Arabia are important to maintain sustainable agricultural production, minimizing health and other environmental risks to humans, biota, and the environment.

5. Conclusions

Pesticides applied to vegetables in Al-Kharj's agricultural areas polluted the agricultural soils. This study showed many pesticides with residues in the soil samples collected from the 20 sites at two different depths. Pesticide concentrations were sufficiently low in some soil samples (<LOD). Out of the 32 pesticides sampled from all the 20 sites, all the

pesticides were recorded at least in several locations. Herbicides Atrazine, Isoproturpon and Linuron have many problematic environmental effects, and Atrazine pollutes groundwater sources. Hence, the use of these herbicides needs to be minimized, while herbicides Bromoxynil, Pendimetholin, and Diclofop-methyl could be used as per the recommendations to control weeds and sustainably manage soil and water and groundwater resources in addition to the contamination of agricultural products in the Al-Kharj area.

Cypermethrin is usually not likely to leach into groundwater, but in the Al-Kharj area it was reported at 19 sites and was found in 45% of the groundwater sampling sites. This needs further investigation, and, also, good agricultural practices could be introduced to minimize leaching Cypemethrin into groundwater.

With proper and recommended usages and with protective equipment and engineering controls, the insecticides Resmethrin, Methidathion, Ethoprophos, Tetramethrin, Bromophis-methyl, Bifenthion, Permethrin, Fenoxycarb, Cyfluthrin, Phosmet, and Azinophosmethyl can be used safely in the Al-Kharj agricultural area, maintaining sustainable soils and water resources. Carbaryl could be applied with sufficient care with appropriate technology and proper dosages, as Carbaryl poses adverse impacts. It could be replaced with safer alternatives to ensure the sustainable management of soil and water resources.

Endosulfan, Deltamethrin, Lindane, Chlorpyrifos, Chlorpyrifos-methyl, Dimethoate, Heptachlor, and Mevinphos are banned by USEPA and in many countries due to toxicity, persistence, and other problematic environmental effects. These pesticides are still in use in the Al-Kharj area, which needs strict restriction. Policy decisions are required to limit the use or ban the use of these pesticides and to replace them with safer ones in order to manage soils and water resources sustainably and to ensure the safety of people who use these chemicals and who consume agricultural products.

Iprobenfos, which is mainly used for paddy, is reported to be used in the Al-Kharj area to control fungal diseases. Policy decisions need to be taken to restrict non-recommended agrochemicals and recommend safer agrochemicals through regulations to sustain soil and water resources in the region. Abamectin could be applied according to the recommendations to maintain the sustainable use of the soil and water resources of the regions. However, the use of Amitraz requires a caution to minimize the harmful impacts due to Amitraz degradants.

Based on these findings, policy interventions could be formulated to increase the sustainable management of soil and groundwater resources in the Al-Kharj region, to ensure the safety of people in direct contact with these used agrochemicals, and also to ensure the safety of agricultural products generated from this region. Further, concentrations of the metabolites of these agrochemicals need to be evaluated to make sure such metabolites do not pose any environmental and health risks.

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