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Determination of Pesticide Residues in Agricultural Soil Samples Collected from Sinai and Ismailia Governorates, Egypt

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Abstract

Soil contamination by pesticide residues is a major concern due to their high soil persistence and dangerous effect on humans. Therefore, the aim of this study was to detect and determine the concentration of pesticide residues in agricultural soil samples. Agricultural soil samples were collected from three Egyptian governorates and were extracted using the QuEChERS method and analyzed by gas chromatography-mass spectrometry. A total of twenty different pesticide residues (approximately 43% of the tested pesticides) were detected in agricultural soil samples obtained from the three governorates. South Sinai was heavily contaminated by pesticides, with a total concentration of 0.505 mg/kg, followed by Ismailia (0.207 mg/kg) and North Sinai (0.075 mg/kg). According to its use in agriculture, the percentage of pesticide residues detected revealed that 60% of the pesticides were fungicides and 35% were insecticides. In Ismailia governorate, carbendazim was detected in 40% of agricultural soil samples. In North Sinai governorate, boscalid and chlorpyrifos were detected in 66.66% of the soil samples. In South Sinai governorate, thiophanate-methyl, metalaxyl, and carbendazim were detected in 50% of the soil samples. This study revealed the presence of different pesticide residues in Egyptian agricultural soil samples, which can affect agricultural products grown on contaminated agricultural soil. The accumulation of mixtures of pesticide residues in soil constitutes mostly toxic chemicals that are a worldwide environmental issue that must be considered in the agricultural production sustainability assessment. These results could be used as a base for designing environmental maps to cover the pesticide residue contamination that affects agricultural crops in Egypt.

Keywords: Agriculture soils; pesticide residues; fungicides; insecticides; Acaricide; GC/MS/MS.

1. Introduction

Pesticides are extensively used by agricultural producers, due to the growing demand for high-quality food, which resulted in their increased accumulation on the surface layers of soil and persistence in the environment [1]. However, these pesticides could directly pollute the agro-environment and cause health risks even at trace levels, since a huge majority of applied pesticides enter the environment, agricultural products, and even the food chain [2, 3].

Pesticides usages in Egypt showed a progressive increase during the last years, whereas in 2019 pesticides used were at a level of 13,178 tonnes, and in 2018 the level of pesticides recorded 11,352 tonnes with an increase of 16.09%. It was reported that excess pesticides affect almost all crops, whereas these pesticides could directly be deposited into the

soil and surface or subjected to off-site transport, as less than 0.1% of the applied pesticides protect crops [4, 5, 6]. The excessive accumulation of pesticides in the soil may lead to their transfer and infiltration into groundwater, thus contaminating them, causing a serious risk [7, 8]. On the other hand, Berrada et al. [9] stated that chemical pesticides are possibly carcinogenic, mutagenic, and endocrine-disrupting. They added that these chemical pesticides could cause paralysis among other mild and acute disorders.

Soil is a natural environment for the growth and development of plants, containing a combination of organic and mineral components occurring in gaseous, aqueous, and solid states [1]. In soil, the fate of pesticides is influenced by many factors related to chemical, physical, and photochemical processes, as well as biological transformation [10, 11]. Though

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there are several efforts to reduce the mobility of pesticides within the environment, their application has led to unavoidable transfer by spray drift, infiltration, leaching and runoff, sorption, and volatilization from treated areas [12, 13, 14].

Due to the chemical structure of the pesticides, and the complex nature of the soil, several extraction methods for studying pesticide residues in soil have been used, including microwave-assisted solvent extraction (MASE), ultrasonic solvent extraction (USE), supercritical fluid extraction (SFE), matrix solid-phase dispersion (MSPD), and Soxhlet extraction [15, 16]. In 2003, Anastassiades et al. [17] introduced the QuEChERS method, which was developed as an attractive alternative technique for the pesticide multi-residue analysis in solid matrices [18, 19].

Previously, several analytical methods were used to analyze pesticides such as capillary electrophoresis, high performance liquid chromatography (HPLC) coupled with UV detection, and gas chromatography (GC) with flame ionization detector (FID), or with electron capture detection (ECD) or nitrogen phosphorus detection (NPD) [18]. Lately, liquid chromatography (LC) and gas chromatography (GC) coupled with tandem mass spectrometry (MS/MS) are regularly used as basic, complementary techniques for large-scale multi-class pesticides analyses [20].

Pesticides are the most common xenobiotic pollutants in soil and are considered dangerous to humans and wildlife. Therefore, it is necessary to spread public awareness about the hazards of pesticide residues among farmers, distributors, and retailers to realize the safe use of pesticides and minimize the health risks to human consumers. Also, knowing the level of soil contamination is very important because plants can absorb several pollutants and increase the risk to human health [21]. As a result, monitoring their residue levels in agricultural soils is critical since it gives extremely significant information on the real amount of soil pollution and environmental risk associated with their use. Therefore, the aim of this study was to detect and determine the concentration of pesticide residues in agricultural soil samples.

2. Materials and Methods

2.1. Chemicals and Reagents

Toluene, n-hexane, acetone, acetonitrile, ethyl acetate, and formic acid HPLC grade were purchased from Merck (Darmstadt, Germany). All studied pesticide standards were purchased from Santa Cruz Biotechnology Inc., (Santa Cruz, CA 95060, USA). QuEChERS extraction kits (4 g anhydrous magnesium sulfate (MgSO4), 1 g sodium chloride (NaCl), 1 g trisodium citrate dihydrate (Na3C6H5O7•2H2O), and 0.5 g disodium hydrogen citrate sesquihydrate (Na2HC6H5O7•1.5H2O)) were purchased from Agilent (USA). Centrifuge tubes (15 mL) containing a cleaning-up mixture for d-SPE of 150 mg anhydrous magnesium sulfate and 25 mg primary secondary amines (PSA) were purchased from Agilent (USA). Pure water was obtained from a Milli-Q system (Millipore, Billerica, MA 01821, USA), and was cooled to about 4 °C.

2.2. Sample collection

During the period from April to June 2020, agricultural soil samples were collected randomly from three Egyptian governorates (Ismailia, North Sinai, and South Sinai). Ismailia governorate is located at 30°35′ North latitude and 32°16′ East longitude. North Sinai governorate is located at 30°5' North latitude and 33°6'East longitude, whereas South Sinai governorate is located 29°05'North latitude and 33°83'East longitude. Different types of agricultural soil samples, and agricultural products grown, are shown in Table (1). Sample collection, preservation, and storage were based on the method of USEPA [22]. In the laboratory, agricultural soil samples were air-dried and sieved by passing through a 2 mm sieve.

2.3. Soil sample extraction and clean-up procedure

The extraction of pesticide residues from soil samples was carried out according to the QuEChERS method with some modifications [23]. Homogenized agricultural soil samples (5 g) and cold purified water (10 mL) were added to a centrifuge tube (50 mL), shaken for 1 min, and allowed to stand for 10 min. Acetonitrile (20 mL) was added and the sample was shaken again for 1 min. A salt mixture composed of 4 g magnesium sulfate, 1 g sodium chloride, 1 g tri-sodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate, were added.

The tubes were immediately shaken for 1 min and vortexed for 5 min. Then, a clean-up dispersive solid-phase extraction step was carried out by adding the supernatant (10 mL) to a centrifuge tube (15 mL) containing magnesium sulfate (1.5 g) and primary secondary amine (0.250 g). After shaking, the mixture was sonicated for 1 min. Centrifugation was carried out for 10 min at 4400 rpm and the supernatant was evaporated to dryness at 40°C. The

residues were then immediately reconstituted by adding 2 mL of n-hexane/acetone (9:1 v/v) and filtered through a disposable 0.45-µm PTFE

membrane filter into an autosampler vial and subsequently analyzed via GC/MS/MS.

Table (1): Agriculture soil samples collected from different governorates

	Governorates		
	Ismailia	**North Sinai**	**South Sinai**
Type of agriculture soil sample	Clay, silty clay, sandy	Sandy	Sandy
Agriculture products grown on sampling cites	Beans, cabbage, cucumber, green pepper, mango, olives, orange, strawberry, wheat	Alfalfa, mango, orange, wheat	Grapes, mango, olives, wheat

2.4. GC/MS/MS analysis

Gas Chromatography system 7890B equipped with tandem mass spectrometer 7010A Quadrupole (Agilent, USA) was used to determine the pesticide residue found in agricultural soil. Instrument control and data acquisition/processing were carried out via Mass Hunter software ver. 7.01. Chromatographic separations were achieved using the HP5MS ultra-inert capillary column (30 mm × 0.25 mm, 0.25 µm). The GC oven temperature was programmed to initially be held at 70 °C for 1 min then ramped to 150 °C at 50 °C/min for 0 min, and raised to 260 °C at the rate of 6 °C/min for 0 min, then ramped from 260 to 310 °C at 20 °C/min for 1.567 min with a total run time of 25 min. Ultra-high purity helium (> 99.999%) served as the carrier gas at a flow rate of 1.654 mL/min. Collision cell gases (helium, quench gas; nitrogen, collision gas) flow rates were 2.25 mL/min and 1.5 mL/min, respectively. Injector temperature, transfer line temperature, ion source temperature, and quadrupole temperature were 250, 280, 300, and 180°C, respectively. The analysis was performed by the Central Laboratory of Residue Analysis of Pesticides and Heavy metals in Food, Agriculture Research Centre (QCAP), Giza, Egypt.

2.5. Method validation

Recoveries, the limit of detection (LOD), and limits of quantification (LOQ) were determined using spiked soil samples. Soil samples that were not contaminated by any pesticides were used for this study. After homogenization, the soil sample was spiked with the standard mixture of pesticides using five replicates of the spiked samples at different concentration levels and equilibrated for 30 min at

room temperature before QuEChERS extraction to allow the pesticides to be incorporated into the soil matrix.

2.6. Statistical analysis

All values were expressed as mean ± SD. Statistical analysis of the data was carried out using Microsoft Excel 2010 statistical program. A one-way analysis of variance (ANOVA) was performed, in which $P<0.05$ was considered statistically significant. Fisher's Protected Least Significant Difference was also used to determine the difference between different means.

3. Results

A total of twenty different pesticide residues (approximately 43% of the tested pesticides) were detected in agriculture soil samples obtained from the three governorates. In Ismailia governorate, azoxystrobin, boscalid, diazinon, difenoconazole, myclobutanil, propiconazole, pyraclostrobin, and thiophanate-methyl were below the limit of detection (<0.001 mg/kg) (Table 2). Data also revealed that chlorfenapyr was detected at a high concentration (0.050 mg/kg), whereas metalaxyl (0.025 mg/kg), propargite (0.020 mg/kg), lambda-cyhalothrin (0.020 mg/kg), methomyl (0.020 mg/kg), and acetamiprid (0.017 mg/kg) were also detected. Meanwhile, flusilazole, imidacloprid, and carbendazim were detected at low concentrations recording 0.005, 0.007, and 0.008 mg/kg respectively (Table 2).

In North Sinai governorate, azoxystrobin, chlorfenapyr, cypermethrin, diazinon, flusilazole, lambda-cyhalothrin, metalaxyl, methomyl, penconazole, and propargite were found to be below the detection limit (<0.001 mg/kg). Meanwhile,

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difenoconazole, myclobutanil, propiconazole, pyraclostrobin, and thiophanate-methyl were found to be below the limit of quantification (<0.01 mg/kg) (Table 2).

Table (2): Pesticide residues (mg/kg dry weight) in agricultural soil samples obtained from different governorates

Pesticides	Governorates			Total	Recovery (%)
	Ismailia	North Sinai	South Sinai		
Acetamiprid (I)	0.017 (0.006)	0.020 (0.028)	<0.01	0.037	82
Azoxystrobin (F)	<0.001	<0.001	0.050 (0.000)	0.050	95
Boscalid (F)	<0.001	0.003 (0.006)	<0.01	0.003	107
Carbendazim (F)	0.008 (0.010)	0.037 (0.035)	0.100 (0.057)	0.145	90
Chlorpyrifos (A, I)	0.010 (0.000)	0.005 (0.006)	<0.001	0.015	127
Chlorfenapyr (A, I)	0.050 (0.000)	<0.001	0.070 (0.000)	0.120	112
Cypermethrin (I)	0.015 (0.010)	<0.001	<0.01	0.015	111
Diazinon (I)	<0.001	<0.001	<0.01	-	121
Difenoconazole (F)	<0.001	<0.01	0.030 (0.000)	0.030	126
Flusilazole (F)	0.005 (0.007)	<0.001	<0.001	0.005	113
Imidacloprid (I)	0.007 (0.012)	0.010 (0.000)	0.120 (0.000)	0.137	86
lambda-cyhalothrin (I)	0.020 (0.000)	<0.001	0.010 (0.000)	0.030	127
Metalaxyl (F)	0.025 (0.021)	<0.001	0.005 (0.007)	0.030	89
Methomyl (I)	0.020 (0.000)	<0.001	0.010 (0.000)	0.030	85
Myclobutanil (F)	<0.001	<0.01	<0.001	-	106
Penconazole (F)	0.010 (0.000)	<0.001	<0.001	0.010	106
Propargite (A)	0.020 (0.000)	<0.001	<0.001	0.020	106
Propiconazole (F)	<0.001	<0.01	<0.001	-	113
Pyraclostrobin (F)	<0.001	<0.01	<0.001	-	97
Thiophanate-methyl (F)	<0.001	<0.01	0.110 (0.156)	0.110	87
Total	0.207	0.075	0.505		

Results are expressed as mean ± (SD)
A: Acaricide; F: fungicide; I: insecticide
LOD: 0.001 mg/kg
LOQ: 0.01 mg/kg
Statistical analysis was carried out for censored numbers (<LOD) given zero.
Within each column, means showed significant difference $P < 0.05$
Within each raw means showed no significant difference $P > 0.05$.

In South Sinai governorate, chlorpyrifos, flusilazole, myclobutanil, penconazole, propargite, propiconazole, and pyraclostrobin were detected below the limit of detection (<0.001 mg/kg). On the other hand, acetamiprid, boscalid, cypermethrin, and diazinon were detected below the limit of quantification (<0.01 mg/kg). The pesticide residue imidacloprid was detected in agricultural soil samples at a concentration of 0.120 mg/kg, followed by thiophanate methyl (0.110 mg/kg), carbendazim (0.100 mg/kg), and chlorfenapyr (0.070 mg/kg) (Table 2). Azoxystrobin, difenoconazole, lambda-cyhalothrin, metalaxyl, and methomyl were also

detected at lower concentrations in agricultural soil samples from South Sinai governorate.

Concerning the total concentration of the pesticide residues in the three governorates, results showed that carbendazim highly contaminated agricultural soil samples for the three governorates with a total concentration of 0.145 mg/kg, followed by imidacloprid (0.137 mg/kg), and chlorfenapyr (0.120 mg/kg) respectively. The comparison between the three governorates revealed that South Sinai governorate was highly contaminated by pesticides with a total concentration of 0.505 mg/kg, followed by Ismailia (0.207 mg/kg) and North Sinai (0.075 mg/kg) governorates respectively (Table 2).

Data in Table (2) displayed the different pesticides groups, which included 5 triazoles (difenoconazole, flusilazole, myclobutanil, penconazole, and propiconazole), 2 organophosphates (chlorpyrifos, and diazinon), 2 neonicotinoids (acetamiprid, and imidacloprid), 2 pyrethroids (cypermethrin, and lambda-cyhalothrin), and 2 carbamates (methomyl, and thiophanate methyl), as well as other groups.

The percentage of pesticide contamination in different agricultural soil samples collected from different Egyptian governorates was shown in Figure (1). Results indicated that the percentage of contamination recorded 60%, 83.33%, and 75% for agriculture soil samples collected from Ismailia, North Sinai, and South Sinai governorates respectively. On the other hand, data in Figure (2) showed the percentage of detected pesticide residues based on their usage in agriculture, whereas 60% of the detected pesticides were fungicides, 35% were insecticides, and 5% of the detected pesticides were Acaricides. Meanwhile, no herbicides were detected in soil samples.
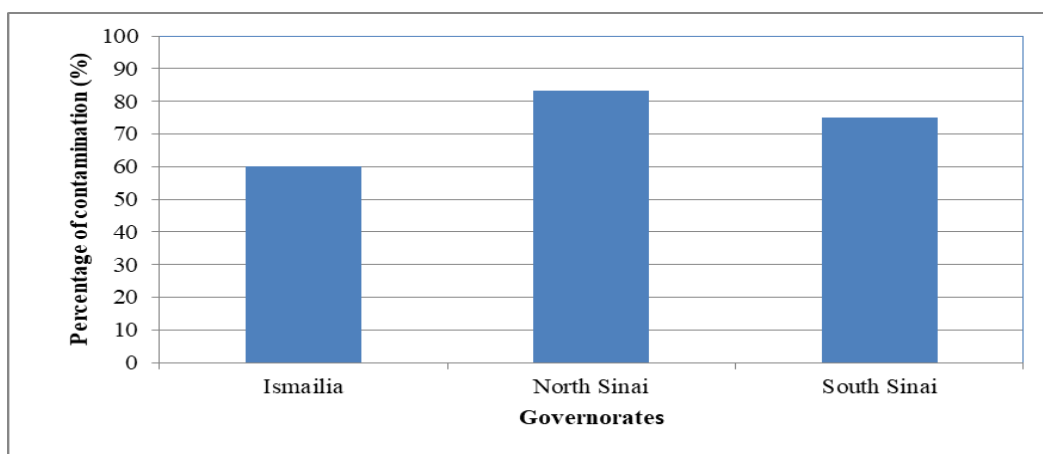

Figure (1): Percentage of pesticide contamination in each governorate
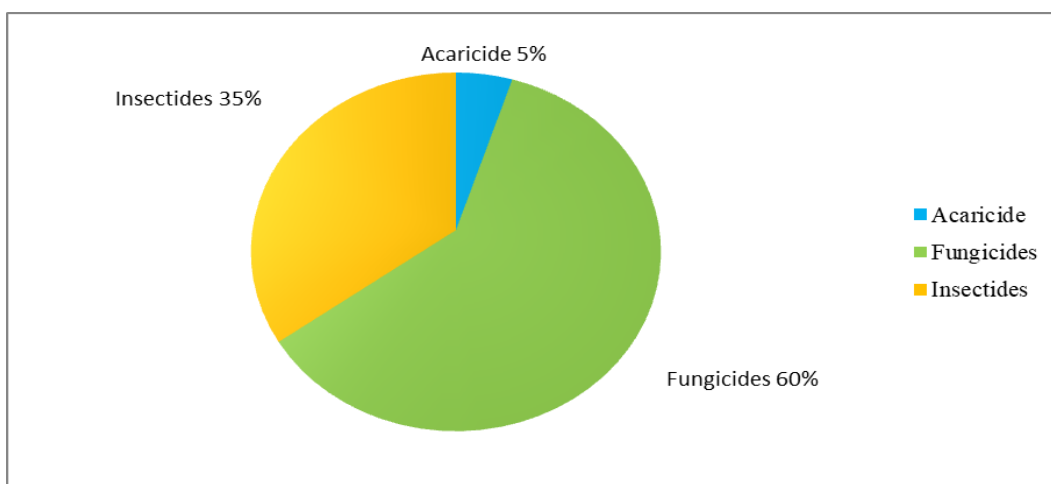

Figure (2): Different types of pesticides detected in agricultural soil samples

Results in Figure (3) presented the percentage of contamination of each pesticide residue in different governorates. In Ismailia governorate, carbendazim was detected in 40% of the agricultural soil samples, followed by imidacloprid (30%), acetamiprid (30%), metalaxyl (20%), and flusilazole (20%). In North Sinai governorate, boscalid (66.66%) and chlorpyrifos (66.66%) were observed in the soil samples, followed by carbendazim (50%), acetamiprid (33.33%), and imidacloprid (33.33%). In South Sinai governorate, thiophanate methyl (50%), metalaxyl (50%), and carbendazim (50%) were detected in soil samples. Meanwhile, each of the following pesticides; methomyl, lambda-cyhalothrin, imidacloprid, difenoconazole, diazinon, chlorpyrifos, boscalid, and azoxystrobin were detected in 25% of the soil samples.
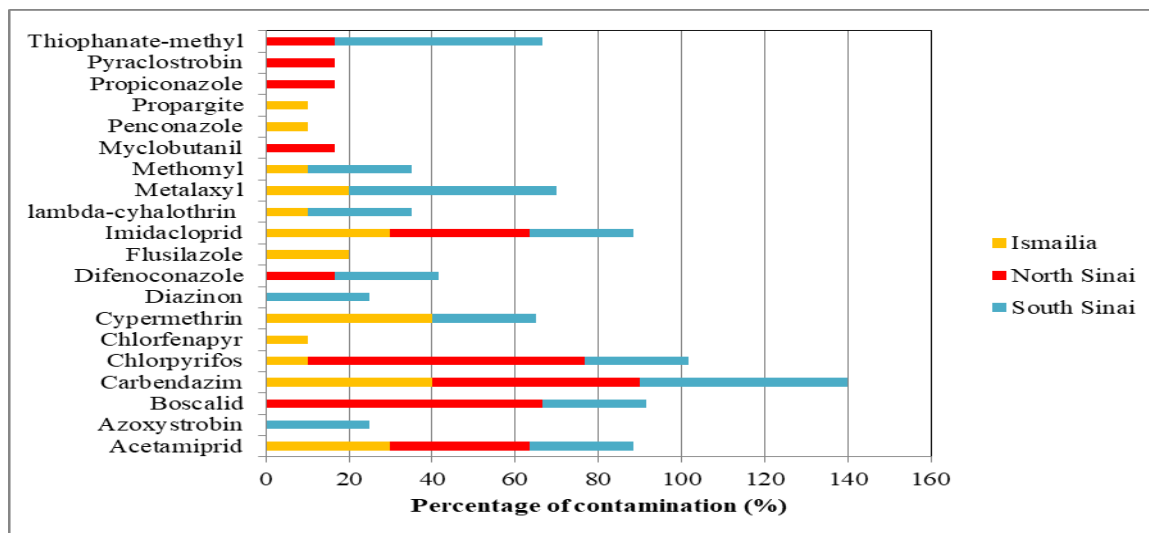

Figure (3): The percentage of pesticide residues contamination in agricultural soil samples obtained from different governorates

Data in Figure (4) revealed the number of pesticide residues in each soil sample. In Ismailia governorate, 3 pesticides were detected in 30% of the soil samples. Meanwhile, a group of different pesticides (4, 5, and 6) was detected in 10% of the soil samples. On the other hand, in about 40% of the soil samples, no pesticides were detected as these pesticides were below the limit of detection (<0.001 mg/kg). In North Sinai governorate, 2 pesticides were detected in 33.33% of the soil samples, whereas a group of pesticides (4, 5, and 7) was detected in 16.66% of the soil samples. For South Sinai governorate, a group of pesticides (2, 4, and 10) was detected in 25% of the soil samples.
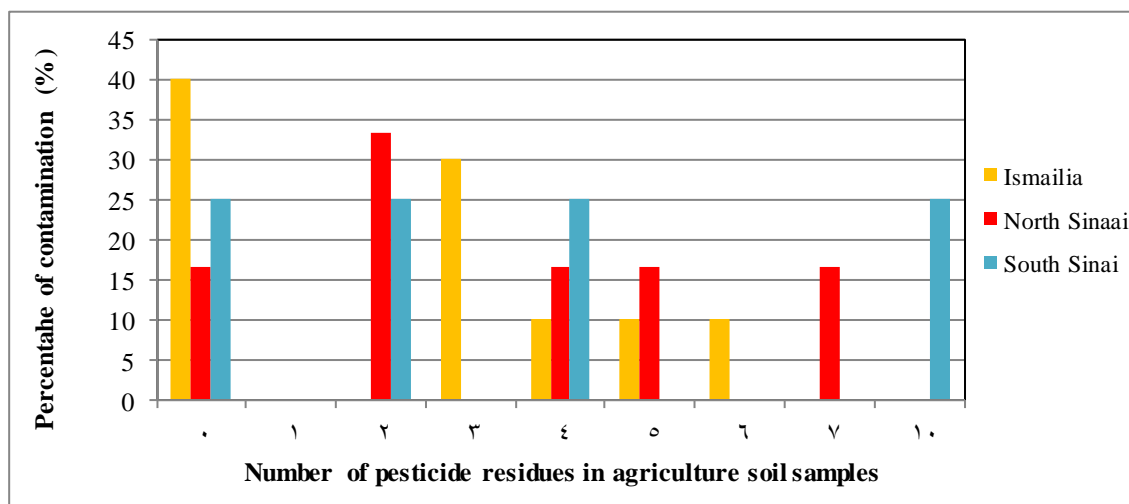
Figure (4): The number of pesticide residues in agricultural soil samples obtained from different governorates

4. Discussion

To measure the efficiency of the analytical method used in this study, recovery, LOD, and LOQ was done by spiking a soil sample (free of any pesticides), by a mixture of pesticide standards, and the mean recoveries ranged from 82 to 127 % demonstrating good performance. The LOD and LOQ recorded 0.001 and 0.01 mg/kg respectively. The most predominant pesticides detected in agricultural soil samples from different governorates were carbendazim, chlorfenapyr, imidacloprid, and thiophanate methyl, and they ranged between 0.008 and 0.100 mg/kg, 0.007 and 0.120 mg/kg, <LOD and 0.070 mg/kg, and <LOD and 0.110 mg/kg respectively. A great variance in the level of a single pesticide from a governorate to another was observed. These variances in pesticide levels at different sites showed variations in application practices [24].

Carbendazim is a broad-spectrum benzimidazole fungicide that is widely used in agriculture for protecting and eliminating diversity of pathogens affecting crops and turf and is also used in post-harvest food storage and as a seed pre-planting treatment [25]. In Nepal, Korimort et al. [26] studied 15 soil samples and found that the samples were contaminated with carbendazim, at levels up to 0.038 mg/kg. Recently, Bhandari et al. [27] reported the detection of carbendazim in conventional farming soil from Nepal, which ranged between 1.03 and 6.45 µg/kg. Soil samples from the southern districts of Jordan contained a higher range of carbendazim between 0.07 and 0.29 mg/kg [28]. Our results were considered higher than those samples obtained from Nepal and similar to those of Jorden. The high occurrence level of

carbendazim might be due to its long persistence in soil, as it is known to have a half-life of 6 to12 months [29].

Chlorfenapyr is a novel broad-spectrum insecticide-miticide for the control of various insects and mite pests on cotton, ornamentals, and several vegetable and fruit crops [30, 31]. The half-life of chlorfenapyr was found to be 11 - 13.5 months in surface-level soil and 20 - 29 months in deeper soil [32]. In Jordan, Kailani et al. [28] reported that chlorfenapyr was detected in soil samples of Karak, Tafila, and Ghor Al-Safi districts at concentrations of 2.09, 1.77, and 12.96 mg/kg respectively. These results were considered higher than those of our study. In Egypt, chlorfenapyr was detected in soil samples from Damietta governorate [33].

Imidacloprid is a neonicotinoid insecticide with efficient toxicity for a wide variety of pests, used to control sucking insects, termites, some soil insects, and fleas on pets [34]. Imidacloprid was detected in soil from both conventional and agricultural farms practicing integrated pest management at a range between 1.02 and 1.17 and between 1.16 and 31.6 µg/kg, suggesting that this farming system could reduce soil pollution in Nepal [35]. He et al. [21] studied the detection of pesticides in the soil of tea plantations of Taiwan, Tibet, Guangdong, and Fujian, and the pesticide imidacloprid was detected at concentrations of 32.0, 41.8, 101.6, and 14.1 µg/kg respectively. Tan et al. [36] reported that the most frequently detected pesticide in Chinese agricultural topsoil was imidacloprid. In agreement, Zhang et al. [37] revealed that imidacloprid was the most dominant neonicotinoid insecticide in agricultural areas.

Thiophanate methyl is a broad-spectrum benzimidazole fungicide usually applied in pre-and post-harvest, for the control of a wide range of fruit

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and vegetable pathogens [38]. Similar results were reported by Salem et al. [39] who detected thiophanate methyl in soil samples from El-Beheira governorate, Egypt. On the other hand, thiophanate methyl was not detected in any soil samples collected from Alexandria, Dammitta, Fayoum, and Menia governorates, Egypt [33].

Results showed that among the pesticides detected in the soil sample, fungicides were the most predominant followed by insecticides, and Acaricides respectively. Similar observations were reported by Manjarres-López et al. [40], and Riedo et al. [41]. The high detection of fungicides has caused it to be the dominant group of pesticide residues in the environment [8].

Data revealed that the chemical groups for the pesticides detected included five triazoles, two organophosphates, two neonicotinoids, two pyrethroids, two carbamates, as well as other groups. Similar results were reported by Marete et al. [42] who showed that in Kenya among the commonly used pesticides for the production of fruits and vegetables, for both export and local consumption, were organophosphates, pyrethroids, and carbamate. García-Hernández et al. [43] indicated that organophosphate showed lower persistence in the environment. On the other hand, Mwevura et al. [44] reported that soils and sediments frequently contained a diversity of pesticide residues including organophosphates among others. Several studies reported that these pesticides are the major contributors to ecotoxicity including; triazoles [45], organophosphates [46], carbamates, and neonicotinoids [47].

Pesticide residues analysis in soils revealed the presence of a variety of pesticide combinations, whereas a mixture of three pesticides was detected in 30% of the samples. Similar results were reported by Bhandari et al. [35] who stated that multiple residues were present in 35% of the soil samples. Studies have shown that mixtures of pesticide residues in the soil are the rule and not the exception [48]. The few studies that examined pesticide mixtures indicated that they may be more toxic than individual pesticides [49].

The results of our study showed that there is a necessity to formulate consistent regulatory guidelines for pesticide contamination in soils that are consistent with environmental and ecotoxicological studies. The combined effects of multiple pesticides are still unclear, creating a high degree of uncertainty about how pesticide residues affect soil fertility crop yield and food safety. This work will contribute to help researchers to focus on the main target which is the removal of these pesticide residues from agricultural soil and crops.

5. Conclusions

In this study, 20 pesticides were detected in agricultural soil samples collected from different Egyptian governorates, whereas fungicides were highly detected. Carbendazim, chlorfenapyr, imidacloprid, and thiophanate methyl were the most significant pesticides identified in soil samples. The differences in the detection of pesticides and their concentration might be due to different pesticides used and different concentrations added, as well as different crops. The results could be considered useful to farmers across Egypt to determine the level of pesticide pollution that affects the quality and health of agricultural land and crops. Future research should focus on crops growing on contaminated agricultural soils to determine the level of contamination by pesticides.

Conflicts of interest

There are no conflicts to declare.

Acknowledgments

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