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# Estimation of the Most Widespread Pesticides in Agricultural Soils Collected from Some Egyptian Governorates

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**Abstract**

Pesticides are usually used in agriculture practice for field and post-harvest protection, and their prolonged persistence in the environment may lead to high toxicity to humans and animals. Therefore, the aim of this study was to investigate the detection of different pesticide residues in agricultural soil samples collected from four Egyptian governorates. A total of forty agricultural soil samples were collected during the period from April to June 2020. Samples were extracted using a QuEChERS method and analyzed using gas chromatography-mass spectrometry. Data revealed that agricultural soil samples from Damietta governorate were highly contaminated (80.00%) by different pesticide residues, followed by Fayoum (40.00%), Menia (36.36%), and Alexandria (10.00%) governorates. The pesticide residues detected in soil samples belonged to the following chemical groups; triazole (21.43%), organophosphate (10.71%), neonicotinoid (10.71%), pyrethroid (10.71%), and others. Among the insecticides detected in soil samples from Damietta governorate were malathion, acetamiprid, and methomyl at concentrations of 10.315, 0.725, and 0.395 mg/kg respectively. The fungicide carbendazim was also detected in soil samples from Damietta governorate at a concentration of 18.303 mg/kg. Meanwhile, in Alexandria governorate, no fungicides were detected in soil samples. The herbicide, oxyfluorfen was detected in soil samples from Menia governorate, whereas pendimethalin and thiobencarb were detected in soil samples from Damietta governorate. Data also revealed that herbicides were not detected in soil samples from both Alexandria and Fayoum governorates. This study shed light on the presence of different pesticide residues in agricultural soil samples in Egypt, which may affect agricultural products grown on contaminated agricultural soil.

***Keywords***: Agricultural soil; pesticide residues; insecticide; fungicide; herbicide; GC/ MS/MS

## 1. Introduction

Soils are a heterogeneous complex matrix with a porous structure that contains both natural organic (humic substances, lipids, carbohydrates, lignin, flavonoids, pigments, resins, and fulvic acids) and inorganic components (sand, silt, and clay) [1]. They are the main natural source for plant life, as well as a vital source for sustaining the survival and development of human existence [2]. Soils are the most vital part of ecosystems, where several studies reported that soils are contaminated by organic and inorganic pollutants including pesticides [3-5].

Contamination of soil with pesticides affects agricultural ecosystems by affecting the microbial community of soils [6, 7], bacterial diversity [8-10], nitrogen transformations [11, 12], soil animals [13], and soil enzymes [14]. The main non-point sources of pollution in agriculture are the increased use of pesticides [15]. Sun [16] revealed that 70% of pesticides used in agriculture end up in the soil, contaminating farmland soil. Therefore, agricultural soil quality is closely related to crop quality and food safety, which are thereby associated with human health.

Pesticides are a group of chemical compounds that are widely spread as they are used in agricultural practice for field and post-harvest protection [17]. A great number of pesticides are commonly used on farms, to reduce the incidence of insects, weeds, fungi, and other pests, as they cause

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a considerable challenge to crop production resulting in adverse consequences for the economy of the country. [18]. The use of pesticides also poses significant environmental and health concerns, regardless of their benefit on crop yields and their importance to the economy [19]. About 0.1% of the pesticides are likely to reach the target organisms, whereas the residual pesticides contaminate the nearby ecosystem (water, air, and soil) eventually entering the food and affecting non-target animals, as well as humans. [20]. It was reported that about 3 million tons of pesticides are applied every year globally [21].

Pesticides are classified based on their chemical nature as organophosphates (OPs), pyrethroid, phenyl amide, carbamate, triazole, neonicotinoid, and others [22]. Organophosphate pesticides are a probable risk to human health and wildlife and thus are considered an increasing concern [2]. Organophosphate pesticides are among the most regularly identified pesticides in contaminated soils [23, 24]. Carbamate and organophosphate pesticides are the most common cause of pesticide poisoning [25, 26]. Following long-term dietary exposure in a group of male and female mice, the fungicide triazole was found to be associated with an increase of carcinomas and hepatocellular adenomas incidence [27]. On the other hand, the presence of neonicotinoids in the environment may lead to a variety of possible adverse effects on human health and the ecosystem [28, 29]. Neonicotinoid insecticides were adopted to replace the pesticides carbamate and organophosphate, as they were considered to be more dangerous to applicators and mammals [30].

Due to their continuous environmental persistence and/or high human/animal toxicity, most of the pesticides have been banned for a long time; and this has led to the request for testing pesticide residues in the environment and food [31]. Therefore, the aim of this study was to investigate the detection of different pesticide residues in agricultural soil samples collected from four Egyptian governorates.

## 2. Materials and Methods

### *2.1. Chemicals and Reagents*

Twenty-eight pesticide standards were from Santa Cruz Biotechnology Inc., (Santa Cruz, CA 95060, USA). Toluene, hexane, acetone, acetonitrile, ethyl acetate, and formic acid were HPLC grade (Merck, Darmstadt, Germany). QuEChERS extraction kits with solvent partitioning salt packets contained 4 g anhydrous magnesium sulphate ($MgSO_4$), 1 g sodium chloride (NaCl), 1 g trisodium citrate dihydrate ($Na_3C_6H_5O_7{\bullet}2H_2O$), and 0.5 g disodium hydrogen citrate sesquihydrate ($Na_2HC_6H_5O_7{\bullet}1.5H_2O$) were used (Agilent, Santa Clara, CA 95051, USA). Centrifuge tubes (15 mL) containing a cleaning up mixture for d-SPE of 150 mg anhydrous magnesium sulphate and 25 mg primary secondary amines (PSA) were also used (Agilent, Santa Clara, CA 95051, USA). Pure water was obtained from a Milli-Q system (Millipore, Billerica, MA 01821, USA), and was cooled to about 4 °C.

### *2.2. Sampling*

Forty agricultural soil samples were collected randomly from four Egyptian governorates (Alexandria, Damietta, Fayoum, and Minia) during the period from April to June 2020. Types of agriculture soil samples and agricultural products grown are shown in Table (1). Soil samples were collected at a depth of 15 cm for vegetable growing areas, and at a depth of 30 cm for fruit growing areas from 10 randomly selected locations in each governorate. Samples were then placed in well-labeled clean plastic polythene bags. The soil samples were then air-dried and sieved using a sieve (2 mm). Sample collection, preservation, and storage were based on the method of USEPA [32].

Table 1: Agricultural soil samples collected from different governorates

| Governorates | Type of agriculture soil samples | Type of agriculture products grown on agricultural soil samples |
|---|---|---|
| Alexandria | Loamy | Onions, tomato, watermelon, wheat |
| Damietta | Clay | Alfalfa, aubergine, guava, mango, green pepper, wheat |
| Fayoum | Clay, loamy, sandy | Corn, beetroot, lemon, onions, mango, molokhia, orange, wheat |
| Menia | Clay, loamy, sandy | Alfalfa, grapes, mango, marjoram, onions, oranges, wheat |

### *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 [33]. Homogenized soil samples (5 g) and cold purified water (10 mL) were added to centrifuge tubes (50 mL), shaken for 1 min, and allowed to stand for 10 min. Twenty mL acetonitrile was added and the samples were shaken for 1 min. Salt mix composed of 4 g magnesium sulphate, 1 g sodium chloride, 1 g tri-sodium citrate dihydrate, and 0.5 g disodium hydrogen citrate sesquihydrate, was added. The tubes were shaken for 1 min and vortexed for 5 min.

A clean-up dispersive solid-phase extraction was performed by adding the supernatant (10 mL) to centrifuge tubes (15 mL) that contained 1.5 g of magnesium sulphate and 0.250 g primary secondary amine. After shaking, the mixtures were sonicated for 1 min. Centrifugation was performed for 10 min. at 4400 rpm and the supernatants were evaporated to dryness at 40°C. The residues were then directly reconstituted by adding n-hexane/acetone (9:1 v/v) (2 mL) and filtered using a disposable PTFE syringe filter (0.45-µm) into an autosampler vial and subsequently analyzed via GC/MS/MS.

### *2.4. GC/MS/MS analysis*

Gas Chromatography system 7890B equipped with tandem mass spectrometer 7010A Quadrupole (Agilent, Santa Clara, CA 95051, USA) was performed to determine the pesticide residues in agricultural soil samples. Under scanning conditions for the confirmation of the pesticides, mass spectral library (NIST 14), ver. 2.0f (Agilent P/N G1033A) was used. Chromatographic separations were achieved using the HP5MS ultra-inert capillary column (30 m × 0.25 mm, 0.25 µm) (Agilent, Santa Clara, CA 95051, USA). The oven temperature was programmed to be initially held at 70°C for 1 min then ramped to 150°C at the rate of 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 the rate of 20°C/min for 1.567 min with a total run time of 25 min [34]. Both the ion ratio and tR of the qualifiers to quantify were performed as the acceptance criteria for correct peak identification. 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 samples with 28 pesticide standards. In this study, we used soil samples that were not contaminated by any pesticides, whereas after homogenization, the soil samples were spiked with the standard mixture of pesticides (28 pesticides) using five replicates of the spiked samples at different levels and equilibrated for 30 min at room temperature before QuEChERS extraction to allow the pesticides to be incorporated into the soil matrix [35]. The recoveries ranged from 76 to 127%, the LOD was 0.001 mg/kg, and the LOQ ranged from 0.01 to 0.05 mg/kg.

### *2.6. Statistical analysis*

Results were demonstrated as mean (95% CI). Statistical analysis was conducted using Microsoft Excel 2010 statistical program. A one-way analysis of variance (ANOVA) was achieved, whereas $P<0.05$ was considered statistically significant. To determine the differences between different means, Fisher's Protected Least Significant Difference was also implemented.

## 3. Results

Data in Figure (1) revealed the percentage of pesticide contamination in different agricultural soil samples collected from different Egyptian governorates. Results indicated that the percentage of contamination recorded was 80.00%, 40.00%, 36.36%, and 10.00% for agriculture soil samples collected from Damietta, Fayoum, Menia, and Alexandria governorates respectively.

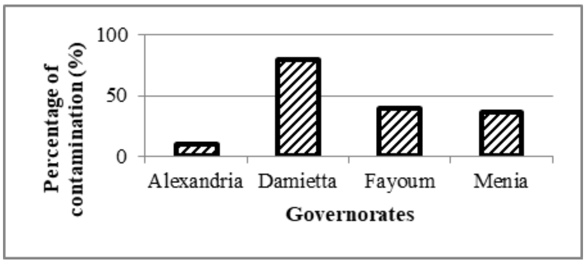


Figure (1): Percentage of pesticide contamination in each governorate

Results in Table (2) showed the different pesticides detected in Egyptian agricultural soil, whereas 28 pesticides were detected, among which 14 were insecticides, 11 were fungicides, and 3 were herbicides. The pesticides detected belonged to different chemical groups including triazole (6 pesticides), neonicotinoid (3 pesticides), organophosphate (3 pesticides), pyrethroid (3 pesticides), strobilurin (2 pesticides), benzoylurea (2 pesticides), benzimidazole (1 pesticide), pyrrole (1 pesticide), carbamate (1 pesticide), and others. It was noticed that triazole was the most detected pesticide in soil samples by 21.43%. Meanwhile, each of the following; organophosphate, neonicotinoid, and pyrethroid were detected in 10.71% of the soil samples. These pesticides were followed by other pesticides at lower detection levels.

Results in Table (2) also showed the frequency occurrence, and mean concentration (mg/kg) of each pesticide in agriculture soil samples collected from all Egyptian governorates. Data indicated that the highest frequency occurrence was for the following pesticides; carbendazim (20.00%), propiconazole (15.00%), followed by chlorfenapyr, cypermethrin, and lambda-cyhalothrin (12.50%). Meanwhile, the frequency occurrence of 2.50% has been recorded for the pesticides; chlorfluazuron, diniconazole, malaoxon, tebuconazole, thiobencarb, tricyclazole, and trifloxystrobin. On the other hand, malathion (10.315 mg/kg), carbendazim (9.160 mg/kg), and acetamiprid (0.487 mg/kg) were detected at high concentrations. Other pesticides for example azoxystrobin, cypermethrin, flusilazole, metalaxyl, methomyl, and Penconazole were detected at low concentrations, although exceeding LOQ, whereas others such as chlorpyrifos (0.007 mg/kg) and chlorfenapyr (0.006 mg/kg) were also detected below LOQ.

The detection of insecticides in agricultural soil samples collected from different Egyptian governorates was recorded in Table (3). Most of the soil samples collected from Damietta governorate were contaminated by pesticide residues at different concentrations. The most detected insecticides at high concentrations were malathion, acetamiprid, and methomyl at a concentration of 10.315, 0.725, and 0.395 mg/kg respectively. The insecticides chlorpyrifos, chlorfenapyr, clothianidin, lambda-cyhalothrin, cypermethrin, emamectin, lufenuron, malaoxon, and thiamethoxam were also detected in Damietta governorate at low concentrations. These results indicated that soil samples from

Damietta governorate was contaminated with more than 12 insecticides. In Menia governorate, acetamiprid, and lambda-cyhalothrin were only detected at a concentration of 0.010, 0.020 mg/kg respectively. On the other hand, the insecticides chlorfluazuron and cypermethrin were detected at a concentration of 0.020 and 0.055 mg/kg respectively in soil samples from Fayoum governorate, whereas lambda-cyhalothrin was also detected below LOQ. Meanwhile, in soil samples from Alexandria governorate, permethrin was the only insecticide detected at a concentration of 0.010 mg/kg.

Table 2: Frequency occurrence and mean concentration (mg/kg dry weight) of each pesticide in agricultural soil collected from all four Egyptian governorates

| Pesticides | Pesticide Type | Substance Group | No. and frequency of positive samples (%) | Mean (95% CI) |
|---|---|---|---|---|
| Acetamiprid | I | Neonicotinoid | 3 (7.50%) | 0.487 (-0.062 - 1.036) |
| Azoxystrobin | F | Strobilurin | 2 (5.00%) | 0.035 (-0.034 - 0.104) |
| Carbendazim | F | Benzimidazole | 8 (20.00%) | 9.160 (-4.699 - 23.019) |
| Chlorfluazuron | I | Benzoylurea | 1 (2.50%) | - |
| Chlorpyrifos | I, A | Organophosphate | 3 (7.50%) | 0.007 (0.000 - 0.014) |
| Chlorfenapyr | I | Pyrrole | 5 (12.50%) | 0.006 (0.001 - 0.011) |
| Clothianidin | I | Neonicotinoid | 2 (5.00%) | 0.010 (0.010 - 0.010) |
| Cypermethrin | I | Pyrethroid | 5 (12.50%) | 0.032 (0.010 - 0.054) |
| Diniconazole | F | Triazole | 1 (2.50%) | - |
| Emamectin | I | Avermectins | 2 (5.00%) | 0.010 (-0.010 - 0.030) |
| Flusilazole | F | Triazole | 3 (7.50%) | 0.030 (-0.004 - 0.064) |
| *Lambda*-cyhalothrin | I | Pyrethroid | 5 (12.50%) | 0.006 (-0.002 - 0.014) |
| Lufenuron | I | Benzoylurea | 2 (5.00%) | 0.045 (-0.024 - 0.114) |
| Malathion | I, A | Organophosphate | 2 (5.00%) | 10.315 ( -2.690 - 23.320) |
| Malaoxon | I | Aliphatic Organophosphate | 1 (2.50%) | - |
| Metalaxyl | F | Phenylamide | 4 (10.00%) | 0.018 (0.003 - 0.033) |
| Methomyl | I | Carbamate | 2 (5.00%) | 0.395 (0.268 - 0.522) |
| Myclobutanil | F | Triazole | 2 (5.00%) | 0.005 (-0.005 - 0.015) |
| Oxyfluorfen | H | Diphenyl ether | 1 (2.50%) | - |
| Permethrin | I | Pyrethroid | 1 (2.50%) | - |
| Penconazole | F | Triazole | 2 (5.00%) | 0.040 (0.001 - 0.079) |
| Pendimethalin | H | Dinitroaniline | 3 (7.50%) | 0.020 (0.000 - 0.040) |
| Propiconazole | F | Triazole | 6 (15.00%) | 0.030 (-0.010 - 0.070) |
| Tebuconazole | F | Triazole | 1 (2.50%) | - |
| Thiamethoxam | I | Neonicotinoid | 2 (5.00%) | 0.040 (0.040 - 0.040) |
| Thiobencarb | H | Thiocarbamate | 1 (2.50%) | - |
| Tricyclazole | F | Triazolobenzothiazole | 1 (2.50%) | - |
| Trifloxystrobin | F | Strobilurin | 1 (2.50%) | - |

Pesticide type and substance group were obtained from Pesticide Properties DataBase (PPDB) http://sitem.herts.ac.uk/aeru/ppdb/en/index.htm
A: Acaricide; F: fungicide; H: herbicide; I: insecticide
The total numbers of agricultural soil samples from the Egyptian governorates are 40 samples
Results are expressed as mean (95% CI); 95% CI: 95% Confidence interval of the mean
[a] Censored number (<LOQ) was given zero.
LOQ: 0.01 mg/kg for all pesticides, and 0.05 mg/kg for oxyfluorfen LOD: 0.001 mg/kg

Data in Table (4) showed the detection of fungicides in agriculture soil samples collected from different Egyptian governorates. Results revealed that carbendazim was detected at a high concentration of 18.303 mg/kg in soil samples from Damietta governorate. The pesticides metalaxyl, propiconazole, and tricyclazole were also detected in soil samples from Damietta governorate at concentrations of 0.010, 0.015, and 0.010 respectively, whereas both azoxystrobin and myclobutanil were detected below LOQ. Meanwhile, soil samples from Fayoum governorate carbendazim, flusilazole, penconazole, and propiconazole were detected at concentrations of 0.018, 0.045, 0.040, and 0.075 mg/kg respectively. Furthermore, azoxystrobin, metalaxyl, and myclobutanil were detected in agricultural soil samples collected from Menia governorate at concentrations of 0.070, 0.040, and 0.010 mg/kg respectively, whereas diniconazole, flusilazole, penconazole, tebuconazole, and trifloxystrobin were detected below LOQ. Data also revealed that fungicides were not detected in soil samples from Alexandria governorate.

The presence of herbicides in agricultural soil samples collected from different Egyptian governorates was shown in Table (5). Data also showed the detection of pendimethalin and thiobencarb at concentrations of 0.020 and 0.010 mg/kg respectively in soil samples from Damietta governorate. Soil samples from Menia governorate, oxyfluorfen was only detected at a concentration of 0.020 mg/kg. Data also revealed that no herbicides were detected in soil samples from both Alexandria and Fayoum governorates.

Results in Table (6) showed the different crops grown on contaminated agricultural soil by pesticides. Crops grown on contaminated soil in Damietta governorate were alfalfa, aubergine, green pepper, guava, mango, and wheat, thus demonstrating that all crops were grown on contaminated soil.

On the other hand, crops grown on contaminated soil in Fayoum governorate were corn, lemon, and mango, whereas beetroot, onions, molokhia, orange, and wheat were grown on soil free from pesticides. Crops grown on contaminated soil in Menia governorate were grapes, mango, and onions; while, the following crops alfalfa, marjoram, oranges, and wheat were grown on soil free from pesticides. In Alexandria governorate, tomato was the only crop grown on contaminated soils, whereas onions, watermelon, and wheat were grown on soil free from any pesticide contamination.

Table 3: Insecticide residues (mg/kg dry weight) in agriculture soil samples collected from different Egyptian governorates

| Pesticides | Governorates | | | | Recovery (%) |
|---|---|---|---|---|---|
| | Alexandria | Damietta | Fayoum | Menia | |
| Acetamiprid | ND | 0.725 (0.225 -1.230) | ND | 0.010 (0.010 -0.010) | 82 |
| Chlorfluazuron | ND | ND | 0.020 (0.020 - 0.020) | ND | 106 |
| Chlorpyrifos | ND | 0.007 (0.002 - 0.014) | ND | ND | 127 |
| Chlorfenapyr | ND | 0.008 (0.004 - 0.012) | ND | ND | 112 |
| Clothianidin | ND | 0.010 (0.010 - 0.010) | ND | ND | 84 |
| Cypermethrin | ND | 0.017 (0.003 - 0.031) | 0.055 (0.026 - 0.084) | ND | 111 |
| Emamectin | ND | 0.010 (-0.009 - 0.0294) | ND | ND | 76 |
| *lambda*-cyhalothrin | ND | 0.003 (-0.004 - 0.010) | <LOQ | 0.020 (0.020 -0.020) | 127 |
| Lufenuron | ND | 0.045 (-0.023 - 0.113) | ND | ND | 97 |
| Malaoxon | ND | 0.010 (0.010 - 0.010) | ND | ND | 96 |
| Malathion | ND | 10.315 (-2.69 -23.3) | ND | ND | 117 |
| Methomyl | ND | 0.395 (0.267 - 0.523) | ND | ND | 85 |
| Permethrin | 0.010 (0.010 - 0.010) | ND | ND | ND | 111 |
| Thiamethoxam | ND | 0.040 (0.040 - 0.040) | ND | ND | 84 |

Results are expressed as mean (95% CI); 95% CI: 95% Confidence interval of the mean; ND: Not detected
LOQ: 0.01 mg/kg for all pesticides
LOD: 0.001 mg/kg
Statistical analysis was carried out for censored numbers (<LOQ) given LOQ/2, whereas ND was given zero.
Within each column, means showed no significant difference $P > 0.05$
Within each raw means showed no significant difference $P > 0.05$.

Table 4: Fungicide residues (mg/kg dry weight) in agriculture soil samples collected from different governorates

| Pesticides | Governorates | | | | Recovery (%) |
|---|---|---|---|---|---|
| | Alexandria | Damietta | Fayoum | Menia | |
| Azoxystrobin | ND | <LOQ | ND | 0.070 (0.070 -0.070) | 95 |
| Carbendazim | ND | 18.303 (-4.318-40.924) | 0.018 (0.001 - 0.035) | ND | 90 |
| Diniconazole | ND | ND | ND | <LOQ | 126 |
| Flusilazole | ND | ND | 0.045 (0.016 - 0.074) | <LOQ | 113 |
| Metalaxyl | ND | 0.010 (0.010 - 0.010) | ND | 0.040 (0.040 -0.040) | 89 |
| Myclobutanil | ND | <LOQ | ND | 0.010 (0.010 -0.010) | 106 |
| Penconazole | ND | ND | 0.040 (0.001 - 0.079) | <LOQ | 106 |
| Propiconazole | ND | 0.015 (0.005 - 0.025) | 0.075 (-0.033-0.183) | ND | 113 |
| Tebuconazole | ND | ND | ND | <LOQ | 114 |
| Tricyclazole | ND | 0.010 (0.010 - 0.010) | ND | ND | 88 |
| Trifloxystrobin | ND | ND | ND | <LOQ | 121 |

Results are expressed as mean (95% CI); 95% CI: 95% Confidence interval of the mean; ND: Not detected
LOQ: 0.01 mg/kg for all pesticides
LOD: 0.001 mg/kg
Statistical analysis was carried out for censored numbers (<LOQ) given LOQ/2, whereas ND was given zero.
Within each column, means showed no significant difference $P > 0.05$
Within each raw means showed no significant difference $P > 0.05$.

Table 5: Herbicide residues (mg/kg dry weight) in agriculture soil samples collected from different Egyptian governorates

| Pesticides | Governorates | | | | Recovery (%) |
|---|---|---|---|---|---|
| | Alexandria | Damietta | Fayoum | Menia | |
| Oxyfluorfen | ND | ND | ND | 0.020 (0.020 -0.020) | 112 |
| Pendimethalin | ND | 0.020 (0.0008 - 0.039) | ND | ND | 115 |
| Thiobencarb | ND | 0.010 (0.010 - 0.010) | ND | ND | 95 |

Results are expressed as mean (95% CI); 95% CI: 95% Confidence interval of the mean; ND: Not detected
LOQ: 0.01 mg/kg for pendimethalin and thiobencarb, and 0.05 mg/kg for oxyfluorfen
LOD: 0.001 mg/kg
Statistical analysis was carried out for censored numbers (<LOQ) given LOQ/2, whereas ND was given zero.
Within each column, means showed no significant difference $P > 0.05$
Within each raw means showed no significant difference $P > 0.05$.

Table 6: Agriculture products grown on contaminated soil samples by different pesticides

| Pesticides | Governorates | | | |
|---|---|---|---|---|
| | Alexandria | Damietta | Fayoum | Menia |
| Acetamiprid | - | Aubergine, green pepper | - | Onion |
| Azoxystrobin | - | Green pepper | - | Mango |
| Carbendazim | - | Aubergine, green pepper, wheat | Corn, lemon, mango | - |
| Chlorfluazuron | - | - | Mango | - |
| Chlorpyrifos | - | Aubergine, green pepper, guava | - | - |
| Chlorfenapyr | - | Alfalfa, green pepper, guava, mango, wheat | - | - |
| Clothianidin | - | Aubergine, green pepper | - | - |
| Cypermethrin | - | Aubergine, green pepper, guava | Corn, mango | - |
| Diniconazole | - | - | - | Grapes |
| Emamectin | - | Aubergine, green pepper | - | - |
| Flusilazole | - | - | Lemon, mango | Grapes |
| *Lambda*-cyhalothrin | - | Aubergine, green pepper, guava | Lemon | onion |
| Lufenuron | - | Aubergine, green pepper | - | - |
| Malathion | - | Aubergine, green pepper | - | - |
| Malaoxon | - | Green pepper | - | - |
| Metalaxyl | - | Aubergine, green pepper, wheat | - | Onion |
| Methomyl | - | Aubergine, green pepper | - | Grapes |
| Myclobutanil | - | Mango | - | |
| Oxyfluorfen | - | - | - | Onion |
| Permethrin | Tomato | - | - | - |
| Penconazole | - | - | Lemon, mango | - |
| Pendimethalin | - | Aubergine, green pepper, wheat | - | - |
| Propiconazole | - | wheat | Lemon, mango | Grapes |
| Tebuconazole | - | - | - | Grapes |
| Thiamethoxam | - | Aubergine, green pepper | - | - |
| Thiobencarb | - | Wheat | - | - |
| Tricyclazole | - | Wheat | - | - |
| Trifloxystrobin | - | - | - | Grapes |

-: Fruits and vegetables that are grown on soil samples that are not contaminated by pesticides

## 4. Discussion

The current results revealed that triazole pesticides were detected in 21.43% of agricultural soil samples, whereas organophosphate, neonicotinoid, and pyrethroid pesticides were detected in 10.71% of the samples. Similar results were reported by Liu et al. [31] who found that the detection of organophosphate pesticides in soil was 8.70%. Meanwhile, Pan et al. [24] stated that organophosphates were detected in 93% of the soil samples, which was considered higher than those stated in this study. On the other hand, Liu et al. [31] indicated that the pyrethroid pesticides were detected in 60.90% of the soil samples, which was considered higher than that mentioned in the present study. In Egypt, Ghabbour et al. [17] detected organochlorines, organophosphorus insecticides, pyrethroids, carbamates, and fungicides in soil samples from two different locations in the AL-Sharqiya governorate.

Results in this study revealed that carbendazim (20.00%), propiconazole (15.00%), followed by chlorfenapyr, cypermethrin, lambda-cyhalothrin (12.50%), and chlorpyrifos (7.50%) were highly detected in soil samples from all four Egyptian governorates. The high-frequency occurrence of carbendazim might be due to the slow degradation of carbendazim, and its long persistence in soil, as carbendazim is known to have a half-life of 6 to12 months [36]. Similar results were reported for propiconazole, which was found to be persistent in soil under anaerobic conditions [37]. Furthermore, Lambda-cyhalothrin was found to have a high potential to bind to soil particles, which may indicate a high-frequency occurrence. Data clearly showed that the frequency occurrence of chlorpyrifos in soil samples was considered to be lower than those reported by Anwar et al. [38] who found that chlorpyrifos was detected in 16.00% of the soil samples collected from Pakistan. Meanwhile, the present study indicated that both malathion (10.315 mg/kg), and carbendazim (9.160 mg/kg), were detected at a high concentration in soil samples from all four Egyptian governorates. Although malathion was detected at high concentrations, it is known that malathion is of low persistence in soil with half-lives of 1 to 25 days [39]. Thus this high concentration could be due to recent spraying of the pesticide in the field.

The current results showed that malathion, acetamiprid, and methomyl were highly detected at a concentration of 10.315, 0.725, and 0.395 mg/kg respectively in soil samples from Damietta governorate. Results also indicated that soil samples from Damietta governorate were contaminated with more than 12 insecticides (chlorpyrifos, chlorfenapyr, clothianidin, lambda-cyhalothrin, cypermethrin, emamectin, lufenuron, malaoxon, and thiamethoxam). The occurrence of multiple pesticide residues in Damietta governorate could be due to the presence of pesticides that have high persistence in the soil, cross-contamination during the processing of the crops, or spray drift from neighboring plots [40]. In a previous study in Egypt, malathion was detected but at a lower concentration in soil samples of conventional strawberry farms [17]. In another study carried out in Egypt, Tchounwou et al. [41] reported that both methomyl and chlorpyrifos were detected in soil samples from eight different locations in Egypt, whereas chlorpyrifos was detected at higher concentrations. Similar results were reported by Liu et al. [31] who detected the pesticides chlorpyrifos, and cypermethrin among other pesticides in soil samples from China. In Thailand, Harnpicharnchai et al. [42] detected chlorpyrifos in soil samples at concentrations of 32.19, and 28.57 mg/kg during summer and winter respectively. These results were considered higher than those reported in this study. In the current study, the neonicotinoid clothianidin was also detected in soil samples collected from Damietta governorate. This is in agreement with that of Ramasubramanian [43] who reported the persistence of clothianidin in the soil of tropical sugarcane. Similar results were stated by Schaafsma et al. [44] who detected clothianidin in soil samples associated with corn. Recently, Zhang et al. [45] detected clothianidin in soil samples from agriculture areas at a concentration of 96 ng/g.

Results indicated the detection of several fungicides in agricultural soil samples collected from Egypt, among which were diniconazole, flusilazole, penconazole, tebuconazole, and trifloxystrobin. Similarly, Tchounwou et al. [41] discovered diniconazole in the soil samples from eight different locations in Egypt. In a similar study carried out in the European Union countries on the presence of pesticide residues in agricultural soil, Silva et al. [19] indicated that fungicide residues (tebuconazole, and others) were common in agricultural soil. This study showed that the herbicides pendimethalin and thiobencarb were detected in agricultural soil samples collected from different Egyptian governorates. Similar observations were reported by Sondhia [46] who revealed that pendimethalin residues recorded 0.02, 0.023, and 0.019 µg/g in the soil planted by tomato, cauliflower, and radish respectively.

The growth of crops on pesticide-contaminated soils is considered a risk to both food safety and human health as some researchers demonstrated that plants could uptake pesticides from soils [47, 48]. In a previous study, Mattina et al. [49] reported the uptake of pesticides by vegetables and fruits. Different plant uptakes depend on root uptake from soil [50], or by other means.

In this study, the occurrence of multiple pesticide residues in soil samples was considered a rule rather than an exception. Therefore, attention is needed to address the toxicity of the mixtures of pesticide residues in soil, particularly the probability of combined effects of different pesticide residues on different taxa, which may result in an indirect effect on the functioning and the structure of the community [51]. It is also essential to screen pesticide residues in the dust, as contaminated dust could be easily released into the atmosphere, and thus could be easily inhaled by humans and animals [52]. The growth and production of foods on pesticide-contaminated soils are of great concern due to the possible uptake of pesticides by the crops [19].

## 5. Conclusions

In the present study, twenty-eight pesticides were detected in agricultural soil samples collected from different governorates in Egypt. There was a difference in the detection of pesticides and their concentration, which may be due to different cultivated crops, different pesticide usage, and different time intervals. The results of the current study could be considered useful for the agricultural extension offices and the farmers across Egypt to determine pesticide contamination levels affecting the quality and health of agricultural lands as well as the crops. In future studies, crops grown on contaminated agricultural soil should also be studied to determine the level of pesticide contamination.

## 6. Conflicts of interest

There are no conflicts to declare.

## 7. Acknowledgments

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## 8. References

[1] Pinto C.G., Martin S.H., Pavon J.L.P. and Cordero B.M., A simplified Quick, Easy, Cheap, Effective, Rugged and Safe approach for the determination of trihalomethanes and benzene, toluene, ethylbenzene and xylenes in soil matrices by fast gas chromatography with mass spectrometry detection. Analytica Chimica Acta, 689, 129-136 (2011). https://doi.org/10.1016/j.aca.2011.01.023.

[2] Sun S., Sidhu V., Rong Y. and Zheng Y., Pesticide Pollution in Agricultural Soils and Sustainable Remediation Methods: a Review. Current Pollution Reports, 4, 240-250 (2018). https://doi.org/10.1007/s40726-018-0092-x.

[3] Fabietti G., Biasioli M., Barberis R. and Ajmone-Marsan F., Soil contamination by organic and inorganic pollutants at the regional scale: the case of Piedmont, Italy. Journal of Soils Sediments, 10, 290-300 (2010). https://doi.org/10.1007/s11368-009-0114-9.

[4] Tang X., Shen C., Chen L., Xiao X., Wu J., Khan M.I., Dou C. and Chen Y., Inorganic and Organic Pollution in Agricultural Soil from an Emerging E-Waste Recycling Town in Taizhou Area, China. Journal of Soils Sediments, 10, 895-906 (2010). https://doi.org/10.1007/s11368-010-0252-0.

[5] Beone G.M., Carini F., Guidotti L., Rossi R., Gatti M., Fontanella M.C. and Cenci R.M., Potentially toxic elements in agricultural soils from the Lombardia region of northern Italy. Journal of Geochemical Exploration, 190, 436-452 (2018). https://doi.org/10.1016/j.gexplo.2018.03.002.

[6] Srinivasulu M. and Ortiz D.R., Effect of pesticides on bacterial and fungal populations in Ecuadorian tomato cultivated soils. Environmental Processes, 4, 93-105 (2017). https://doi.org/10.1007/s40710-017-0212-4.

[7] Satapute P., Kamble M.V., Adhikari S.S. and Jogaiah S., Influence of triazole pesticides on tillage soil microbial populations and metabolic changes. Science of the Total Environment, 651, 2334-2344 (2019).https://doi.org/10.1016/j.scitotenv.2018.10.099.

[8] Sulowicz S., Cycon M. and Piotrowska-Seget Z., Non-target impact of fungicide tetraconazole on microbial communities in soils with different agricultural management. Ecotoxicology, 25, 1047-1060 (2016). https://doi.org/10.1007/s10646-016-1661-7.

[9] Storck V., Nikolaki S., Perruchon C., Chabanis C., Sacchi A., Pertile G., Baguelin C., Karas P.A., Spor A., Devers-Lamrani M., Papadopoulou E.S., Sibourg O., Malandain C., Trevisan M., Ferrari F., Karpouzas D.G., Tsiamis G. and Martin-Laurent F., Lab to field assessment of the ecotoxicological impact of chlorpyrifos, isoproturon, or tebuconazole on the diversity and composition of the soil bacterial community. Frontiers in Microbiology, 9, 1412 (2018). https://doi.org/10.3389/fmicb.2018.01412.

[10] Onwona-Kwakye M., Plants-Paris K., Keita K., Lee J., Van den Brink P.J., Hogarh J.N. and Darkoh C., Pesticides decrease bacterial diversity and abundance of irrigated rice fields. Microorganisms, 8, 318 (2020). https://doi.org/10.3390/microorganisms8030318.

[11] Andersch I., and Anderson J.P.E., Influence of pesticides on nitrogen transformations in soils. Toxicology and Environmental Chemistry, 30, 153-158 (1991).

[12] Crouzet O., Poly F., Bonnemoy F., Bru D., Batisson I., Bohatier J., Philippot L. and Mallet C., Functional and structural responses of soil N-cycling microbial communities to the herbicide mesotrione: a dose-effect microcosm approach. Environmental Science and Pollution Research, 23, 4207-4217 (2016). https://doi.org/10.1007/s11356-015-4797-8.

[13] Wang Y., An X., Shen W., Chen L., Jiang J., Qiang W. and Leiming C., Individual and combined toxic effects of herbicide atrazine and three insecticides on the earthworm, *Eisenia fetida*. Ecotoxicology, 25(5), 991-999 (2016). https://doi.org/10.1007/s10646-016-1656-4.

[14] Tiwari R.K., Singh S., Pandey R.S. and Sharma B., Enzymes of earthworm as indicators of pesticide pollution in soil. Advances in Enzyme Research, 04, 113-124 (2016). https://doi.org/10.4236/aer.2016.44011.

[15] Martha S., UA-CS Pesticide safety-safety update. Cranberry Station Extension meetings, pp. 249 (2017).

[16] Sun W.Z.M., The pesticide pollution problem of food in China. Pesticides, 7(1), 1-4 (2000).

[17] Ghabbour S.I., Zidan Z.H., Sobhy H.M., Mikhail W.Z.A. and Selim M.T., Monitoring of Pesticide Residues in Strawberry and Soil from Different Farming Systems in Egypt. American-Eurasian Journal of Agricultural and Environmental Sciences, 12 (2), 177-187 (2012).

[18] Fosu-Mensah B.Y., Okoffo E.D., Darko G. and Gordon C., Organophosphorus pesticide residues in soils and drinking water sources from cocoa producing areas in Ghana. Environmental Systems Research, 5, 10 (2016). https://doi.org/10.1186/s40068-016-0063-4.

[19] Silva V., Mol H.G.J., Zomer P., Tienstra M., Ritsema C.J. and Geissen V., Pesticide residues in European agricultural soils-A hidden reality unfolded. Science of the Total Environment, 653, 1532-1545 (2019). https://doi.org/10.1016/j.scitotenv.2018.10.441.

[20] Carriger J.F., Rand G.M., Gardinali P.R., Perry W.B., Tompkins M.S. and Fernandez A.M., Pesticides of potential ecological concern in sediment from South Florida canals: an ecological risk prioritization for aquatic arthropods. Soil and Sediment Contamination: An International Journal, 15, 21-45 (2006). https://doi.org/10.1080/15320380500363095.

[21] Pimentel D., Pesticides and pest controls. Ed. Peshin R., Dhawan A.K., Integrated Pest Management. Volume 1: Innovation-Development Process (2009).

[22] Jayaraj R., Pankajshan M. and Sreedev P., Review Article. Organochlorine pesticides, their toxic effects on living organisms and their fate in the environment. Interdisciplinary Toxicology, 9, 90-100 (2016). https://doi.org/10.1515/intox-2016-0012.

[23] Colorado B.E.J., Tobón A.B. and Ballesta I.T., Organophosphorus pesticides degrading bacteria present in contaminated soils. Revista Ciencias Técnicas Agropecuarias, 25 (3), 13-22 (2016). http://dx.doi.org/10.13140/RG.2.2.20023.73126.

[24] Pan L., Sun J., Li Z., Yu Z., Shen X. and Zhu L., Organophosphate pesticide in agricultural soils from the Yangtze River Delta of China: concentration, distribution, and risk assessment. Environmental Science and Pollution Research, 25, 4-11 (2018). https://doi.org/10.1007/s11356-016-7664-3.

[25] Huang H.S., Hsu C.C., Weng S.F., Lin H.J., Wang J.J., Su S.B., Huang C.C. and Guo H.R., Acute Anticholinesterase Pesticide Poisoning Caused a Long-Term Mortality Increase: A Nationwide Population-Based Cohort Study. Medicine, 94(30), e1222 (2015). https://doi.org/10.1097/MD.0000000000001222.

[26] Lim Y.P., Lin C.L., Hung D.Z., Ma W.C., Lin Y.N. and Kao C.H., Increased risk of deep vein thrombosis and pulmonary thromboembolism in patients with organophosphate intoxication: a nationwide prospective cohort study. Medicine, 94(1), e341 (2015). https://doi.org/10.1097/MD.0000000000000341.

[27] EFSA, Conclusion on the peer review of the pesticide risk assessment of the active substance difenoconazole, EFSA J 9 (2011) No. 1967.

[28] Zeng G.M., Chen M. and Zeng Z.T., Risks of neonicotinoid pesticides. Science, 340, 1403 (2013). https://doi.org/10.1126/science.340.6139.1403-a.

[29] Sánchez-Bayo F., The trouble with neonicotinoids. Science, 346, 806-807 (2014). https://doi.org/10.1126/science.1259159.

[30] Elbert A., Haas M., Springer B., Thielert W. and Nauen R., Applied aspects of neonicotinoid uses in crop protection. Pest Management Science, 64, 1099-1105 (2008). https://doi.org/10.1002/ps.1616.

[31] Liu Y., Li S., Ni Z., Qu M., Zhong D., Ye C. and Tang F., Pesticides in persimmons, jujubes and soil from China: Residue levels, risk assessment and relationship between fruits and soils. Science of the Total Environment, 542 (A), 620-628 (2016). https://doi.org/10.1016/j.scitotenv.2015.10.148.

[32] USEPA, Method 1699: Pesticides in Water, Soil, Sediment, Biosolids, and Tissue by HRGC/HRMS, US EPA, (2007) https://www.epa.gov/sites/production/files/2015-10/documents/method_1699_2007.pdf.

[33] Asensio-Ramos M., Hernandez-Borges J., Ravelo-Perez L.M. and Rodriguez-Delgado M.A., Evaluation of a modified QuEChERS method for the extraction of pesticides from agricultural, ornamental and forestal soils. Analytical and Bioanalytical Chemistry, 396, 2307-2319 (2010). https://doi.org/10.1007/s00216-009-3440-2.

[34] Soliman, M., Khorshid, M.A., El-Marsafy, A.M., Abo-Aly, M.M. and Khedr, T., Determination of 10 pesticides, newly registered in Egypt, using modified QuEChERS method in combination with gas and liquid chromatography coupled with tandem mass spectrometric detection. International Journal of Environmental Analytical Chemistry,

99(3), 224-242 (2019). https://doi.org/10.1080/03067319.2019.1588263.

[35] Saleh, I., Khorshed, M., Eshmawy, M.R. and Kandil, M., PESTICIDE RESIDUES IN HORTICULTURAL CROPS FROM DOMESTIC MARKETS OF GIZA, EGYPT: OCCURRENCE AND RISK ASSESSMENT. Plant Archives, 20, Supplement 1, 3862-3869 (2020).

[36] Singh S., Singh N., Kumar V., Datta S., Wani A., Singh D., Singh K. and Singh J., Toxicity, monitoring and biodegradation of the fungicide carbendazim. Environmental Chemical Letters, 14, 317-329 (2016). https://doi.org/10.1007/s10311-016-0566-2.

[37] Gad S.C. and Pham T., Propiconazole. Ed. Wexler, P., Encyclopedia of Toxicology (Third Edition), Academic Press, p 1101-1104 (2014). https://doi.org/10.1016/B978-0-12-386454-3.01203-3.

[38] Anwar T., Ahmed I. and Tahir S., Determination of pesticide residue in soil of Nawabshah district, Sindh, Pakistan. Pakistan Journal of Zoology, 44(1), 87-93 (2012).

[39] Singhal R., Gangadhar B., Basu H., Manisha V., Naidu G. and Reddy A., Remediation of Malathion Contaminated Soil Using Zero Valent Iron Nano-Particles. American Journal of Analytical Chemistry, 3(1), 76-82 (2012). https://doi.org/10.4236/ajac.2012.31011.

[40] Lozowicka B., Health risk for children and adults consuming apples with pesticide residue. Science of the Total Environment, 502, 184-198 (2015). https://doi.org/10.1016/j.scitotenv.2014.09.026.

[41] Tchounwou P.B., Ashour B.A., Moreland-Young C. and Raghb D.A., Health risk assessment of pesticide usage in Menia El-Kamh province of Sharkia governorate in Egypt. International Journal of Molecular Science, 3, 1082-1094 (2002). https://doi.org/10.3390/i3101082.

[42] Harnpicharnchai K., Chaiear N. and Charerntanyarak, L., Residues of organophosphate pesticides used in vegetable cultivation in ambient air, surface water and soil in Bueng Niam subdistrict, Khon Kaen, Thailand. Southeast Asian Journal of Tropical Medicine and Public Health, 44, 1088-1097 (2013).
http://ec.europa.eu/health/scientific_committees/environmental_risks/docs/scher_o_155.pdf.

[43] Ramasubramanian T., Persistence and dissipation kinetics of clothianidin in the soil of tropical sugarcane ecosystem. Water, Air, and Soil Pollution, 224, 1468 (2013). https://doi.org/10.1007/s11270-013-1468-6.

[44] Schaafsma A., Limay-Rios V., Baute T., Smith J. and Xue Y., Neonicotinoid insecticide residues in surface water and soil associated with commercial maize (Corn) fields in Southwestern Ontario. PLoS ONE, 10 (2), e0118139 (2015). https://doi.org/10.1371/journal.pone.0118139.

[45] Zhang C., Yia X., Chen C., Tian D., Liu H., Xie L., Zhu X., Huang M. and Ying G-G., Contamination of neonicotinoid insecticides in soil-water-sediment systems of the urban and rural areas in a rapidly developing region: Guangzhou, South China. Environment International, 139, 105719 (2020). https://doi.org/10.1016/j.envint.2020.105719.

[46] Sondhia S. Harvest time residues of pendimethalin in tomato, cauliflower, and radish under field conditions. Toxicological and Environmental Chemistry, 95(2), 254-259 (2013). https://doi.org/10.1080/02772248.2013.765620.

[47] Trapp S., Fruit tree model for uptake of organic compounds from soil and air. SAR and QSAR in Environmental Research, 18, 367-387 (2007). https://doi.org/10.1080/10629360701303693.

[48] Fantke P., Wieland P., Wannaz C., Friedrich R. and Jolliet O., Dynamics of pesticide uptake into plants: from system functioning to parsimonious modeling. Environmental Modelling and Software, 40, 316-324 (2013). https://doi.org/10.1016/j.envsoft.2012.09.016.

[49] Mattina M.J.I., Berger W.I. and Dykas L., Chlordane uptake and its translocation in food crops. Journal of Agriculture and Food Chemistry, 48, 1909-1915 (2000). https://doi.org/10.1021/jf990566a.

[50] Chiou C.T., Sheng G. and Manes M., A partition-limited model for the plant uptake of organic contaminants from soil and water. Environmental Science and Technology, 35, 1437-1444 (2001). https://doi.org/10.1021/es0017561.

[51] SCHER (Scientific Committee on Health and Environmental Risks), SCCS (Scientific Committee on Consumer Safety), and SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), Opinion on the Toxicity and Assessment of Chemical Mixtures (2012). http://ec.europa.eu/health/scientific_committees/environmental_risks/docs/scher_o_155.pdf.

[52] Bento C.P.M., Goossens D., Rezaei M., Riksen M., Mol H.G.J., Ritsema C.J. and Geissen V., Glyphosate and AMPA distribution in wind-eroded sediment derived from loess soil. Environmental Pollution, 220, 1079-1089 (2017). https://doi.org/10.1016/j.envpol.2016.11.033.