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Original article (Orijinal araştırma)

Determination of insecticide residues in soils from Troia agricultural fields by the QuEChERS method[1]

QuEChERS yöntemi ile Troia tarım alanları topraklarında insektisit kalıntılarının belirlenmesi

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Abstract

Extensive and misuse of pesticides can cause to toxicity to humans and pollution in the environment. The primary objective of this study was to determine insecticide load of agricultural soils of Troia, located in Troia National Park of Çanakkale Province (Türkiye) by the QuEChERS method. For method verification, blank soil samples were spiked at two levels of pesticides. The overall recovery was 84.8% with a relative standard deviation of 13.0% (n = 230), with the values within acceptable recovery (60-140%) and repeatability (≤20%) ranges set by SANTE. Forty-nine soil samples were collected in the study area in 2020. Thirty-six samples had insecticide residues at varying concentrations. Overall, 23 insecticide residues were detected at different frequencies. The most frequent pesticides were: chlorantraniliprole> imidacloprid> pyridaben> clothianidin> indoxacarb (in decreasing order). Mean concentration of insecticide residues in soils varied between 0.99-77.7 µg/kg. Imidacloprid residues were detected in all fields, except cabbage fields. The highest imidacloprid concentration (23.3 µg/kg) was detected in pepper fields. Imidacloprid was detected in 21 samples with a mean concentration of 6.20 µg/kg. Persistent insecticides with the long half-lives, such as chlorantraniliprole, imidacloprid, and clothianidin, were detected in almost all samples.

Keywords: Insecticide residues, pesticide load, soil samples, Troia National Park

Öz

Pestisitlerin yoğun ve yanlış kullanımı, insanlar ve çevre için toksisiteye neden olabilir. Bu çalışmanın temel amacı, Troia Milli Parkı-Çanakkale İli (Türkiye) 'ndeki Troia tarım topraklarının insektisit yükününün QuEChERS metodu ile belirlenmesidir. Yöntem doğrulaması için, pestisit içermeyen toprak numuneleri pestisitler ile 2 seviyede spike edilmiştir. Yöntemin geri kazanımı, SANTE tarafından belirlenen kabul edilebilir geri kazanım (%60-140) ve tekrarlanabilirlik (≤%20) aralıkları içindeki değerler ve %13.0'lük bir RSD (n = 230) ile %84.8 bulunmuştur. 2020 yılında çalışma alanından 49 toprak örneği toplanmıştır. Bunlardan 36 adedinde farklı konsantrasyonlarda insektisit kalıntısı bulunmuştur. Topraklarda toplam 23 adet insektisit kalıntısı farklı sayıda örneklerde tespit edilmiştir. En fazla sayıda örnekte tespit edilme sırası şöyledir; chlorantraniliprole> imidacloprid> pyridaben> clothianidin> indoxacarb. Toprakta insektisit kalıntılarıları ortalama konsantrasyonları 0.99- 77.7 µg/kg arasında değişmiştir. Lahana ekili alan dışında tüm alanlarda imidacloprid kalıntısı bulunmuştur. En yüksek imidacloprid konsantrasyonu (23.30 µg/kg) biber ekili alanlarda bulunmuştur. İmidacloprid tespit edilen örnek sayısı 21 ve ortalama konsantrasyon 6.20 µg/kg olarak bulunmuştur. Chlorantraniliprole, imidacloprid ve clothianidin gibi uzun yarılanma ömrüne sahip kalıcı insektisitler neredeyse tüm örneklerde tespit edilmiştir.

Anahtar sözcükler: İnsektisit kalıntısı, pestisit yükü, toprak örnekleri, Troia Milli Parkı

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Introduction

Pesticides are essential components of modern farming. Pesticides reduce pests-induced losses in agricultural production and then increase yield levels. However, excessive and improper uses of pesticides and their prolonged persistence in environment may lead to soil pollution, toxicity to humans and animals, and undesirable residues in the environment and in living tissues (Tiryaki et al., 2010; Tiryaki & Temur, 2010; Hathout et al., 2022).

Soils are contaminated with pesticides through various means including direct applications, accidental spills, incorporation of pesticide-treated plant residues into the soils, runoff from pesticide-applied surfaces. Herbicides pose a greater risk of pollution on soils. Behavior of pesticides in soil affects complex chemical, physical and dynamic biological systems. These include absorption, desorption, evaporation, degradation, surface runoff and leaching. It has been reported that 14-80% of pesticides used for pests and disease control reached to soil depending on application technique, phenological period of the plant and plant density (Çılgı & Jepson, 1992; Temur et al., 2012). Pesticides can also bioaccumulate in soil, leading to even greater possible risks for environment. European Commission states that soil conservation was vital for long-term sustainable agricultural process. Therefore, soil pesticide levels should systematically be monitored and relevant measures should be taken over time (Karasali et al., 2016; Bhandari et al., 2019).

Pesticides (especially organochlorines) can persist in environment for long durations and may pose serious health risks on human health and environment, thus, several pesticides have been banned for use in agricultural fields. Such prohibitions increased the significance of tests for pesticide residues on foodstuff and in the environment (Liu et al., 2016). Excessive use of pesticides may destroy rich biodiversity, ecological cycles and soil health (Bhandari et al., 2019).

Contamination of soil with pesticides affects agroecosystems. Such contaminations influence soil microbial community, bacterial diversity, microorganisms, nitrogen transformation and soil enzymes (Andersch & Anderson, 1991). Excessive use of pesticides is the primary source of pollution in agricultural lands (Balderacchi et al., 2014). It has been reported that 70% of pesticides used in agriculture end up in the soil and seriously contaminate farmlands (Sun, 2000). Therefore, agricultural soil quality is closely related to crop quality and food safety, which are thereby associated with human health.

Half-lives determine the fate of pesticides in the soil. Half-life (DT_{50}) indicates the time or duration in which a pesticide degrades by half and is usually expressed in days, months or years. With the use of half-life, it is possible to see if a pesticide tends to accumulate in soils. Based on half-lives, pesticides can be divided into three persistence groups as of: low (<16 days), moderate (between 16-59 days) and high (>60 days). Short half-lived pesticides accumulate less in soils than the long half-lived pesticides, with the latter a greater risk to soil and water resources (Anonymous, 2022). Despite their highly toxic nature, organophosphorus insecticides have half-lives of <30 days, thus they do not pose long-term risks to soil and water resources; however, neonicotinoids with quite a long half-life may pose serious risk of pollution especially in soils (Seagraves & Lundgren, 2012; DiBartolomeis et al., 2019).

In Türkiye, annual total pesticide use was 39 kt in 2015, but increased to 54 kt in 2020 (TUIK, 2021), with 8 and 12 kt of that, respectively, being insecticides. The average application of pesticides was about 1.7 kg of active ingredients per ha in 2018. In Çanakkale Province, Türkiye, agricultural activities are largely practiced around and within Troia National Park. Tomato, maize, sunflower, wheat, pepper, rice, cabbage and beans are predominant crops grown in Troia. Considering these products, there is an intensive use of insecticides against many insects. A total of 1.6 kt of solid/liquid pesticides (223 t insecticide) were used throughout Çanakkale in 2021 and 23.4% of the pesticides were used in the Central District (Anonymous, 2021). In the previous study, 1.80 mg/kg of imidacloprid and 2.71 mg/kg of emamectin benzoate residues were found in areas where conventional tomato growing is conducted in Troia. Both residue levels were trace amounts and less than MRL (Polat & Tiryaki, 2019).

In a study conducted by Yıldırım & Özcan (2007) in 2003, 14 soil samples were taken from the borders of Troia National Park, where agricultural production was conducted. Soil samples were analyzed by the standard method 6630 (Greenberg et al., 1998; USEPA, 2007a) and gas chromatography. Captan (100-230 ppb), cypermethrin (20-80 ppb), endosulfan (16.7-230 ppb), ethion (1-6 ppb), mancozeb (2 ppb), trifluralin (20 ppb) pesticides were detected. The residues of endosulfan and captan were higher than the others.

QuEChERS method is generally used to analyze pesticide residues on agricultural commodities (Anastassiades et al., 2003; Lehotay, 2007) and has proven to be efficient in detection of pesticide residues in fruit and vegetables (Çatak & Tiryaki, 2020; Polat, 2021). The method has also proven to be efficient in pesticide residue analyses of soil samples (Nagel, 2009; Temur et al., 2012; Zaidon et al., 2019; Vickneswaran et al., 2021). Analyses were conducted with LC-MS/MS system.

The primary objective of this study was to determine insecticide load of agricultural soils of Troia, located in Troia National Park of Çanakkale Province by the QuEChERS method. Method validation was done by using relevant validation criteria (Hu et al., 2018, SANTE, 2020; Zaidon et al., 2019).

Materials and Methods

Chemicals and reagents

Analytical standards for pesticide analysis were supplied from Chem Service (West Chester, PA, USA) and Dr. Ehrenstorfer GmbH (Wesel, Germany). QuEChERS extraction kits (1.5 g NaOAC and 6 g $MgSO_4$) and QuEChERS clean-up kits [400 mg C_{18}, 400 mg primary secondary amines (PSA, 40 µm particle size), 1.2 g $MgSO_4$] and 0.22 µm nylon syringe filter (Membrane Solutions, Plano, TX, USA) were used. The other solvents and reagents including acetonitrile (MeCN) and acetic acid (HAc) were chromatographic grade.

Apparatus and chromatographic conditions

Insecticide detection was conducted in an LC-MS/MS device. Separation was made with the use of an Acquity UPLC BEH C_{18} column (1.7 mm, 100 x 2.1 mm) under flow rate of 0.35 mL min^{-1}, injection volume of 1 µL, and total run time of 15 min. The gradient program included 10 mM $NH_4CH_3CO_2$ in methanol (B) and 10 mM $NH_4CH_3CO_2$ in water pH 5 (A). Transition groups (precursor and fragment ion) and retention times of insecticide were provided in Table 1.

Study area and sample collection

The study area, Troia, is located in the Central District of Çanakkale Province, where agricultural activities are practiced intensively (Figure 1). The sampling area included six villages: Kumkale, Halileli, Tevfikiye Çıplak, Kalafat and Pınarbaşı. Soil samples were taken from tomato, maize, sunflower, wheat, pepper, rice, cabbage and bean fields. Forty-nine soil samples were collected from 5-25 cm deep after at the growing period (November 2020). Soils in the sampling area have organic matter between 0.49-2.75%, clay 8-54%, pH 7.7-8.2 (Yıldırım & Özcan, 2007). Samples were placed in labeled clean plastic polythene bags (Adeyinka et al., 2019, Zaidon et al., 2019), transported to laboratory in an icebox and kept frozen (-20ºC) until the analyses. Air-dried soils were passed through 2 mm sieve (USEPA, 2007b). Blank soil samples were collected from the study area, which is known to be pesticide free, for recovery experiment and matrix-matched calibration.

Table 1. Retention times (tR) calibration line equations (5 point), concentration ranges and correlation coefficients (R^2)

Insecticide	tR (min)	Precursor ion / Fragment ion (m/z)	Calibration curve equation*	Concentration range (ppb)	R^2
Acetamiprid	5.1	223.1 >125.9 / 223.1 > 55.9	$y =-71.68 x^2 + 108657 x + 1294.5$	1-200	0.99975
Chlorantraniliprole	8.2	482.0 > 283.9 / 482.0 > 450.9	$y = -9.73 x^2 + 14384 x + -708.4$	1-200	0.99987
Clofentezine	10.0	302.9 > 137.9 / 302.9 > 101.9	$y = -37.75 x^2+ 33418.1 x + -61.8$	1-200	0.99987
Clothianidin	4.6	250.0 > 131.9 / 250.0 > 169.0	$y = -11.01 x^2+ 15197.3 x + 2078.3$	1-200	0.99967
Cyhalothrin-lambda	11.3	467.2 > 225.0 / 467.2 > 141.0	$y = -0.03 x^2 +1418.16 x + 1139.4$	10-2000	0.99999
Cypermethrin	11.4	433.1 > 190.9 / 435.1 > 192.9	$y = -0.004 x^2+ 2962.79 x + 1248.4$	10-200	0.99991
Deltamethrin	11.4	523.0 > 280.9 / 523.0 > 506.0	$y = -0.27 x^2 + 3382.47 x + -515.6$	1-200	0.99983
Etoxazole	11.1	360.1 > 140.9 / 360.1 > 112.9	$y = -175.9 x^2 + 237612 x + 16003.1$	1-200	0.99975
Flubendiamide	9.6	680.9 > 253.9 / 680.9 > 274.0	$y = -11.12 x^2+ 11290.5 x + 1704.8$	1-200	0.99884
Hexythiazox	10.9	353.0 > 227.9 / 353.0 > 168.0	$y = -19.65 x^2 + 37913 x + 926.1$	1-200	0.99972
Imidacloprid	4.6	256.0 > 175.0 / 256.0 > 209.0	$y = -5.76 x^2+ 12261.9 x + -36.0$	1-200	0.99982
Indoxacarb	10.3	528.0 > 202.9 / 528.0 > 249.0	$y = -7.27 x^2+ 7726.08 x + -571.2$	1-200	0.99999
Lufenuron	10.8	508.9 > 325.9 / 508.9 > 174.9	$y = -8.63x^2+ 2235.18 x + 422.2$	1-200	0.99988
Metaflumizone	10.7	507.1 > 178.0 / 507.1 > 115.9	$y = 0.10 x^2 + 3653.8 x + 511.9$	10-2000	0.99999
Methoxyfenozide	8.9	369.1 > 149.0 / 369.1 > 313.1	$y = -297.83 x^2+ 82874.9 x + -3970.2$	1-200	0.99999
Novaluron	10.4	493.0 > 158.0 / 493.0 > 141.0	$y = -0.70 x^2+ 6529.42 x + 323.1$	1-200	0.99968
Pirimicarb	7.6	239.1 > 71.9 / 239.1 > 182.1	$y = -86.99 x^2 + 180575 x + -2331.0$	1-200	0.99999
Pymetrozine	3.8	218.0 > 104.9 / 218.0 > 77.9	$y = -53.47 x^2+ 123182 x + -6110.0$	1-200	0.99997
Pyridaben	11.5	365.1 > 147.0 / 365.1 > 309.0	$y = -127.96 x^2+ 116395 x + 8582.8$	1-200	0.99975
Tebufenpyrad	10.7	334.1 > 116.9 / 334.1 > 145.0	$y = -27.83 x^2+ 37081.3 x + 1796.9$	1-200	0.99982
Teflubenzuron	10.8	378.9 > 338.9 / 378.9 > 358.9	$y = -10.64 x^2+ 5571.07 x + 3575.8$	1-200	0.99764
Thiamethoxam	3.9	292.0 > 211.0 / 292.0 > 181.0	$y = -12.48 x^2 + 32248.7 x + -634.9$	1-200	0.99998
Triflumuron	10.0	359.0 > 155.9 / 359.0 > 138.9	$y = - 24.38 x^2+ 29410.2 x + 3210.6$	1-200	0.99963

* Ordinary calibration curve was used.

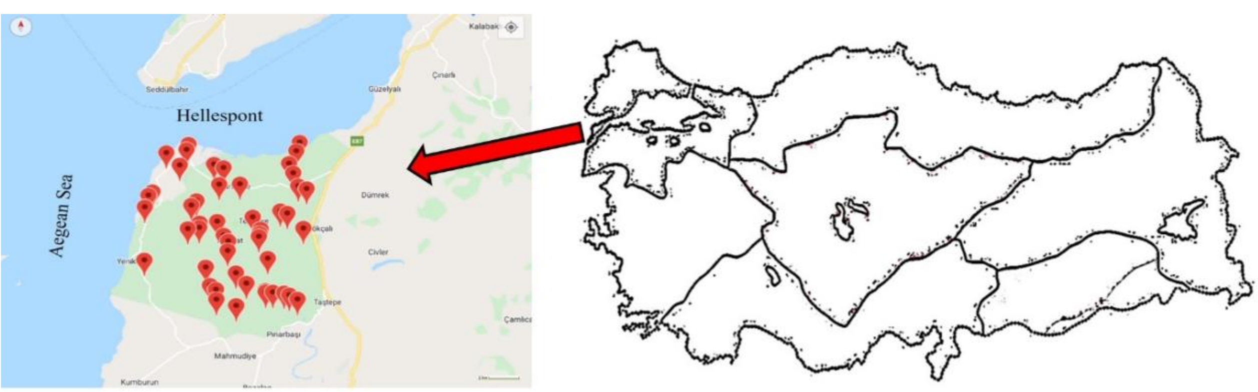

Figure 1. Study area (Troia, Türkiye).

Analyses

Analyses were all completed within three months after sample collection. The modified QuEChERS method was used for the analysis of spiked and sampled soils (Adeyinka et al., 2019; Zaidon et al., 2019; Vickneswaran et al., 2021).

About 10 g sieved sample was placed into 50 mL tubes, supplemented then with 100 µL of HAc and shaken vigorously. Samples were spiked with 100 µL of pesticide spike solutions corresponding 1x LOQ (limits of quantification) and 10x LOQ spike level. Sample tubes were supplemented with 15 mL MeCN and shaken for 15 s. QuEChERS extraction pouch kits (6 g $MgSO_4$ and 1.5 g NaOAC) were then supplemented into the samples and vortexed for 1 min. Resultant extracts were centrifuged at 3.000 rpm for 10 min. Supernatant aliquots (8 mL) were supplemented with QuEChERS clean-up kit (1.2 g $MgSO_4$, 400 mg C_{18} and 400 mg PSA) and shaken for 15 s. Sample tubes were centrifuged again at 3,000 rpm for 10 min, resultant supernatant was filtered through 0.22 µm nylon syringe into 2 mL vials and analyzed in an LC-MS/MS device.

Verification of analysis method

Method verification was performed with the use of linearity, recovery, precision and LOQ parameters. Recovery tests were conducted at two spiking levels (1x LOQ and 10x LOQ) of each pesticide for method accuracy and precision. Tests were conducted in five replicates. Percent recovery (%) was calculated as:

$$Recovery\ (\%) = \frac{Determined\ concentration\ (\frac{\mu g}{kg})}{Spiked\ concentration\ (\frac{\mu g}{kg})} X100 \qquad (1)$$

For accurate results, matrix-matched calibration curve was used to quantify insecticides.

Results and Discussion

Method verification

Calibration curves of 23 pesticide standards were linear over the various concentration ranges (soil matrix-matched calibration), with various correlation coefficient (R^2) (Table 1). Retention times, quantification and confirmation ion and matrix-matched calibration line equations (5-point level), used in MRM mode for pesticide detection, are also shown in Table 1.

Percent recovery together with relative standard deviations (RSDs) and limit of quantification values are provided in Table 2. Percent recoveries varied between 60.6 and 107% with RSDs of between 1.73 and 29.2% (Table 2). Number of recovery data (n) was 10 for each insecticide. Method overall recovery was identified as 84.8% with an RSD of 13.0% (n = 230). These recovery values validated the accuracy of the method as listed in Table 2 and the values were within the acceptable ranges indicated as between 60-140% in SANTE (2020). The LOQ values (Table 2) also revealed that the method could detect pesticide residues lower than the MRL set by the EU (2020). The findings revealed that the QuEChERS method can serve as an accurate and rapid tool for detection of insecticide residues in soil samples.

Table 2. Percent recovery together with RSDs and LOQ values

Insecticide	Spiking level				Mean		LOQ µg/kg
	1xLOQ		10xLOQ				
	Recovery %*	RSD (%)	Recovery %*	RSD (%)	Recovery % (As a tool for trueness)	RSD % (As a tool for precision)	
Acetamiprid	86.8	2.6	91.3	3.4	89.1	3.9	1
Chlorantraniliprole	96.0	4.2	87.9	4.5	92.0	6.2	1
Clofentezine	75.8	3.9	75.3	7.3	75.6	5.5	1
Clothianidin	101	7.1	88.2	4.5	94.4	9.0	1
Cyhalothrin-lambda	88.9	1.7	63.7	29.2	76.3	15.5	10
Cypermethrin	69.5	7.4	82.8	9.1	76.2	8.3	10
Deltamethrin	82.2	2.8	85.0	4.7	83.6	4.1	1
Etoxazole	87.8	2.6	80.4	5.0	84.1	5.9	1
Flubendiamide	78.0	6.9	94.7	5.5	86.3	11.7	1
Hexythiazox	98.2	3.1	88.2	3.2	93.2	6.4	1
Imidacloprid	105	3.5	90.8	3.6	98.1	8.5	1
Indoxacarb	70.6	17.9	80.9	2.6	75.8	13.4	1
Lufenuron	87.0	9.3	91.0	4.5	89.0	7.2	1
Metaflumizone	60.6	2.5	85.0	6.9	72.8	18.5	10
Methoxyfenozide	96.0	2.4	89.4	4.5	92.7	5.0	1
Novaluron	69.6	12.7	90.6	6.7	80.1	16.5	1
Pirimicarb	76.8	5.6	90.7	9.4	83.7	7.5	1
Pymetrozine	60.6	8.2	67.1	11.8	63.9	10.0	1
Pyridaben	107	3.9	99.3	25.0	102.8	17.7	1
Tebufenpyrad	87.4	5.7	88.4	4.7	87.9	5.0	1
Teflubenzuron	88.0	12.9	89.8	5.4	88.9	9.3	1
Thiamethoxam	78.8	3.9	74.5	12.2	76.6	23.1	1
Triflumuron	78.4	9.0	93.9	6.7	86.1	11.9	1
Method overall recovery (accuracy): 84.8 % (n=230; SD=11.00; RSD%=13.0)							

* Mean of 5 replicates (analytical portions).

Analytical results of soil samples

Concentrations of insecticide residues detected in soil samples are provided in Table 3. Of the 49 samples, 36 (~75%) contained insecticide residues at varying concentrations. Overall, 23 insecticide residues were detected in different frequencies. The detection frequencies of 23 insecticides are given in Table 3. The most frequent pesticides (first 10) were: chlorantraniliprole > imidacloprid > pyridaben > clothianidin > indoxacarb > methoxyfenozide > clofentezine > cypermethrin > novaluron > thiamethoxam (in decreasing order). Mean concentration of insecticide residues in soils varied between 0.99 and 77.7 µg/kg with the lowest value (0.90 µg/kg) for acetamiprid and the highest value (204 µg/kg) for pyridaben in soil from tomato fields. Chlorantraniliprole and pyridaben were detected in soil samples sunflower, wheat and rice fields (crops for which they are not licensed).

Acetamiprid, clothianidin, imidacloprid and thiamethoxam residues, included in the neonicotinoid group of IRAC classification (IRAC, 2022), were detected in present samples. Neonicotinoid insecticides have negative effects on non-target organisms and wildlife, thus they have recently been banned in the EU. Use of imidacloprid in greenhouses will be terminated on 1 June 2022 in Türkiye (PPPDA, 2022). Imidacloprid residues were found in all agricultural lands, except for cabbage fields. The greatest imidacloprid concentration (23.3 µg/kg) was seen in pepper fields. Detection frequency of imidacloprid was 21. Acetamiprid residues were detected only in four samples, all from tomato fields, with mean and maximum concentrations of 2.69 µg/kg and 4.41 µg/kg, respectively. Bonmatin et al. (2021) detected at least one neonicotinoid in 80% of the soil samples and three insecticides in 64% of the samples. While imidacloprid was detected in all samples, clothianidin and thiamethoxam were the other common insecticides detected in 69 and 73% of the soil samples, respectively. Amin et al. (2021) detected nine pesticides such as cypermethrin, chlorpyrifos, propachlor, carbofuran, metachlore, endosulfan, cyhalothrin, difenoconazole and acetamiprid in soil samples and reported pesticide concentrations of between 6.77 and 32.0 µg/kg. Clothianidin residues were detected in 14 samples with the mean and maximum concentrations of 4.12 µg/kg and 8.93 µg/kg, respectively. Clothianidin has been banned in the 31 July 2019 in Türkiye (PPPDA, 2022). The presence of clothianidin may due to illegal use or application of previous season. The European Food Safety Authority following clothianidin for all field uses, a high risk was identified in the next crop scenario, or a high risk was not ruled out (EFSA, 2016). Thiamethoxam residues were detected in 5 samples with mean and maximum concentrations of 8.29 µg/kg and 27.6 µg/kg, respectively. Prado-Lu (2015) took soil samples from 26 different farms and detected insecticide residues in 11 samples. Chlorpyrifos, cypermethrin, malathion, profenophos and triazophos residues were detected on four farms.

Chlorantraniliprole, clofentezin, fenbutatin-oxide, flubendiamide, imidacloprid, pyridaben and thiamethoxam insecticides were detected above LOQ levels in soil samples taken from wheat fields. In a previous study, p,p'-DDE, diazinon, chlorfenapyr, difenoconazole pesticides were detected above LOQ in soil samples taken from wheat fields (Salem et al., 2021).

Persistence of pesticides in soil is an important factor in such studies. The DT_{50} of the studied insecticides are provided in Table 3 (PPDB, 2022). DT_{50} varied between 3 days (acetamiprid) and 204 days (chlorantraniliprole). Chlorantraniliprole, imidacloprid and clothianidin are the insecticides with the longest half-lives in soil and were detected in almost all fields (Figure 2). In addition to soil, imidacloprid has been identified as one of the more persistent pesticides in water systems (Braschi et al., 2022). Pyridaben (moderate half-life of 29 days) residues were also detected in almost all agricultural fields. These residues may be resulted from insecticides applied in previous seasons.

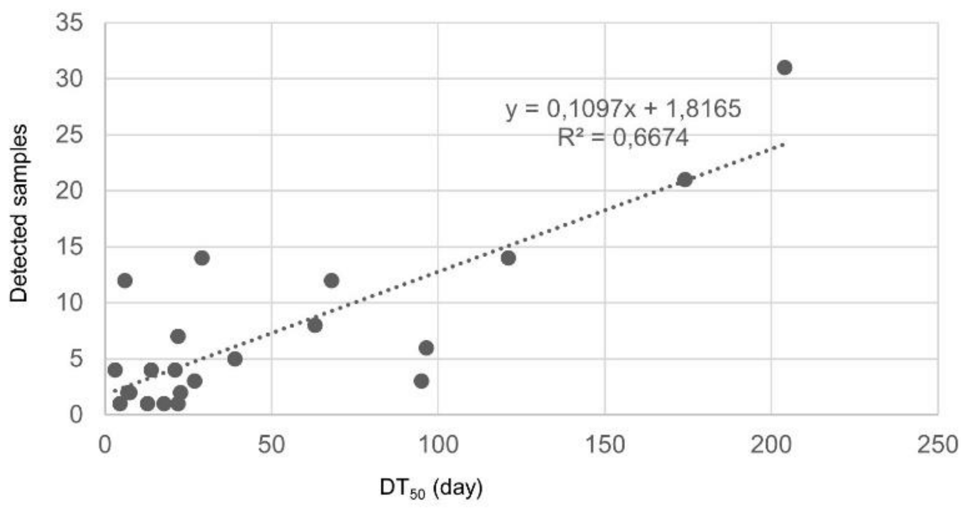

Figure 2. Relationship between number of detected samples and DT_{50}.

Table 3. Insecticide residues (µg/kg) in soils sampled from various cultivation areas

Insecticide	Type of agriculture products grown on agricultural lands								Mean conc.
	Tomato (8)*	Corn (10)	Sunflower (9)	Wheat (7)	Pepper (5)	Rice (4)	Cabbage (3)	Beans (3)	
Acetamiprid	2.69;0.9-4.4;4**								2.69
Chlorantraniliprole	23.8; 2.27-78.7;7	5.34; 1.72-15.3; 7	1.42;1.3-1.5;1	8.73;0.8-93; 6	3.33;0.8-11.8;3	1.31;1. 5-1.3; 2	5.65;1.7-13.0; 3	1.62;1. 2-2.2; 2	6.40
Clofentezine	25.1;9.2-41;2	5.43;0.9-20; 4		1.06;0.9-1.1; 1	5.92;5.4-6.2;1				9.38
Clothianidin	3.96;3.3-4.41	2.87;0.9-7.0; 7	2.95;1.8-4.2; 2		8.55;8.3-8.9;1		2.27;1.4-3.5; 3		4.12
Cyhalothrin-lambda	19.9;14.2-24.4;2						10.7; 8.5-12.5; 1		6.12
Cypermethrin	113;25-243;6						23.1;18.2-32; 1		68.1
Deltamethrin	4.56;1.1-10.3;4								4.56
Etoxazole	4.19;3-5.8;1							0.93;0. 8-1.1; 1	2.56
Fenbutatin-oxide		9.67; 1.4-20.6; 2		1.07; 0.9-1.1; 1					5.37
Fenpyroximate	1.2;0.9-1.3;1				0.97; 0.7-1.1;1				1.08
Flubendiamide	79.6;1.5-177;7	7.43; 2.45-13.2; 3		5.82; 5.4-6.0; 1		39.2;38.8-39.4; 1			33.0
Hexythiazox						0.99; 0.9-1.04;1			0.99
Imidacloprid	5.2;1.6-11.5;4	3.12; 1.3-6.1; 6	9.85; 9.3-10.2; 1	1.9; 1.4-2.6; 3	11.9; 2.4-23.3;4	3.92; 3.4-4.2; 2		7.52;7. 2-7.6; 1	6.20
Indoxacarb	26.5;1.3-83.5;7				3.06; 2.1-4.1;2	9.22; 8.7-10; 1	1.18; 0.7-1.4; 2		9.99
Metaflumizone	77.7; 12-203; 4								77.7
Methoxyfenozide	74.8;10.4-146; 5	11; 2.49-18.95; 5				22; 20.8-23.4; 1	33.5;33-34; 1		35.32
Novaluron	16.9;3.09-39.3;6								16.90
Pymetrozine					18.2; 1.1-39.6;2				18.20
Pyridaben	59.3;1.9-204;6	1.91; 0.7-4.7; 2	2.13; 1.6-2.4; 1	66; 2.61-192; 1	28.5; 0.2-160;3	22; 16.8-26.1; 1			30.0
Tebufenpyrad					2.69; 2.5-2.8;1				2.69
Teflubenzuron						3.25; 3.1-3.4 ;1			3.25
Thiamethoxam			0.98; 0.9-1.0; 1	2.38; 2.3-2.4; 1	2.49; 0.6-10.2;2		27.3; 27-27.6; 1		8.29
Triflumuron	2.77;2.4-3.1;1								2.77

*Number of soil samples taken from tomato fields;

** Mean residue; min. residue-max. residue; number of soil samples with pesticide residue.

Conclusion

In this study, QuEChERS analytical method was verified for pesticide residue detection in soil samples using an LC-MS/MS system. Present linearity, limit of quantification, accuracy, precision and matrix effect parameters revealed that QuEChERS analytical method may offer an accurate and rapid tool for pesticide residue detection in soils.

Neonicotinoids with negative impacts on non-target organisms and wildlife were also detected in varying concentrations in the soil samples. Insecticides with the longest half-lives were detected in soil samples taken from almost all fields. Based on these findings, it is concluded that the environmental risk of pesticides with high persistence should be given greater consideration. The higher the DT_{50}, the more environmental risk occurs.

Insecticide load of soil either comes from the application of the current year or from accumulation from previous years. Therefore, farmers need to be more aware of the effects of pesticides on environment and human health. They should also be encouraged to practice more judicious and conscious pesticide application.

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