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Original article (Orijinal araştırma)

Investigation of insecticide residues in the soil of agricultural areas and around water resources and associated risk assessment[1]

Tarımsal alanlar ve su kaynakları çevresindeki topraklarda insektisit kalıntılarının araştırılması ve ilgili risk değerlendirmesi

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Abstract

Pesticides are the important contaminants for the environment. In this study, insecticide residues of the soils, taken from agricultural lands and around water resources in the Çanakkale-Central district were investigated. The Quick-Easy-Cheap-Efficient-Rugged-Safe (QuEChERS) method was employed to determine residues. Method verification was performed by spiking blank samples at 1 and 8 times the limit of quantification. 54 soil samples were taken from study area in 2020 and subjected to residue analyses. Of these samples, 44 had insecticides at various concentrations. Twenty insecticides were detected at various frequencies. Insecticide residue levels were between 1.01 and 760.01 µg/kg. Maximum etoxazole was detected as 760.01 µg/kg in one sample. This sample was sampled from the nearby fields where wastes were seen. In addition, 17 insecticides were found at various concentrations in the same sample. Risk assessments revealed low hazard for children and adults. In terms of hazard quotient (HQ) levels, maximum values were encountered for pyridaben ($445.00*10^{-7}$ for children and $59.33*10^{-7}$ for adults). The sum of HQs for all insecticides was $1310.00*10^{-7}$ for children and $174.67*10^{-7}$ for adults. It was concluded that farmers should be encouraged to use insecticides with low HQ values to mitigate soil contamination in places where insecticides are detected.

Keywords: Hazard quotient, health risk assessment, neonicotinoid, persistence of insecticide

Öz

Pestisitler çevre için önemli kirleticilerdir. Bu çalışmada Çanakkale-Merkez ilçedeki tarımsal alanlardan ve su kaynakları çevresinden alınan topraklarda insektisit kalıntıları araştırılmıştır. Kalıntıları belirlemek için Hızlı-Kolay-Ucuz-Etkili-Sağlam-Güvenli (QuEChERS) yöntemi kullanılmıştır. Metot doğrulaması, hesaplama limitinin 1 ve 8 katı seviyelerinde pestisit standardı eklenmesi ile yapılmıştır. Çalışma alanlarından 2020 yılında 54 toprak örneği alınmış ve kalıntı analizine tabi tutulmuştur. Bu örneklerden 44'ü çeşitli konsantrasyonlarda insektisit kalıntısı içermiştir. Farklı sıklıklarda 20 insektisit tespit edilmiştir. İnsektisit kalıntı seviyeleri 1.01 ila 760.01 µg/kg arasında değişmektedir. Maksimum etoxazole bir örnekte 760.01 µg/kg olarak tespit edilmiştir. Bu örnek pestisit atıklarının görüldüğü tarlaların yakınından alınmıştır. Ayrıca, aynı numunede çeşitli konsantrasyonlarda 17 insektisit bulunmuştur. Risk değerlendirmeleri, çocuklar ve yetişkinler için düşük düzeyde tehlike ortaya koymuştur. Tehlike katsayısı (HQ) seviyeleri açısından, pyridaben için maksimum değerlere rastlanmıştır (çocuklar için $445.00*10^{-7}$ ve yetişkinler için $59.33*10^{-7}$). Tüm insektisitler için toplam HQ değerleri çocuklar için $1310.00*10^{-7}$ ve yetişkinler için $174.67*10^{-7}$'dir. İnsektisit tespit edilen yerlerde toprak kirliliğini azaltmak için çiftçilerin düşük HQ değerlerine sahip insektisitlerin kullanmaya teşvik edilmesi gerektiği sonucuna varılmıştır.

Anahtar sözcükler: Tehlike katsayısı, sağlık risk değerlendirmesi, neonikotinoid, insektisit kalıcılığı

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Introduction

Pesticides are an important part of intensive agriculture. Pesticides potentially reduce pests-induced yield losses and increase production levels. Despite various advantages, pesticides also have some disadvantages, since only a small proportion of these pesticides reach the target organisms and the rest pollute the environment, affecting animals and humans (Kaur et al., 2023). Excessive and unintentional use of pesticides cause soil and water pollution and toxicity to living organisms. Pesticide residues may also generate serious damage on ecosystems and penetrate into the food chain (Tiryaki & Temur, 2010; Lewis et al., 2016; Kaur et al., 2024).

Soils around agricultural fields, orchards and animal drinking water sources can easily be contaminated with pesticides. Direct applications, runoff from pesticide-treated surfaces, accidental spills and the incorporation of plant residues treated with pesticides into the soil may result in soil contamination. The fate of pesticides in soil is affected by various physico-chemical, dynamic and biological processes. Such processes include adsorption-desorption, runoff, leaching, evaporation and degradation. Previous literature revealed that 14- 80% of applied chemicals reach the soil depending on the method and rate of application, plant growth stages and varieties (Çılgı & Jepson, 1992; Temur et al., 2012). Furthermore, Pimentel (1995) indicated that only 0.3% of applied pesticides reached the targeted pest and the rest (99.7%) dispersed into the surrounding environment. Just because of soil-environment and soil-plant interactions, soils constitute an important source of pesticides for plants (Li, 2025). Pesticides can also bioaccumulate in the soil due to previous years' applications, leading to greater environmental risk. Soil health is very important for sustainable agriculture. Therefore, the pesticide content of agricultural soils should regularly be assessed. Appropriate measures should be taken if there is a risk of pesticide contamination or accumulation (Karasali et al., 2016). Introducing restrictions on fertilizer or pesticide use without providing alternatives can destabilase food security (Futa et al., 2024). Persistent agrochemicals may exert serious health risks for both humans and the environment. Unconscious uses of these agrochemicals potentially destruct biodiversity, soil health and ecological processes (Liu et al., 2016; Bhandari et al., 2019). Therefore, several agrochemicals have been banned. These prohibitions have already raised an awareness of pesticide residues on foodstuffs.

Soil contamination with agrochemicals adversely affects agricultural fields. The widespread use of pesticides in agriculture could affect many non-target organisms and their succession in the ecosystem by altering the interaction between soil microbes and plants (Liu et al., 2025). The overuse and misuse of pesticides may result in contamination of agricultural fields (Balderacchi et al., 2014). These contaminants then exert serious health risks on humans, soils and groundwater. Such contaminations require integrated management and monitoring systems (Mariappan & Tamilarasan, 2025). Measurement of pesticide residues in agricultural soils is important to maintain environmental health standards and thereby minimize the harmful effects of pesticides on soil and water resources (Faraj et al., 2024).

The fate and behavior of a pesticide is designated by its solubility, degradation, half-life and partition coefficient (Li et al., 2025). Manufacturers usually provide half-life (DT_{50} days) values to indicate persistence of pesticides (Mangold et al., 2024). DT_{50} indicates whether pesticide tends to accumulate in the soil. Pesticides can be divided into 4 groups according to their half-life (days): <20 - readily degradable, 20-60 - fairly degradable, 60-180 - slightly degradable and >180 - very slightly degradable. Those with shorter DT_{50} tend to accumulate less in soil. Those with longer DT_{50} pose a greater risk in agricultural areas (Anonymous, 2025). Organochlorines and neonicotinoids with long half-lives can pose a serious contamination risk, especially in soils. Although organophosphate insecticides are highly toxic, they usually have DT_{50} values of <30 and therefore do not exert a long-term risk to soils and agricultural lands (Seagraves and Lundgren, 2012; Di Bartolomeis et al., 2019). However, residues of persistent pesticides can generate a source of chronic soil contamination (Mangold et al., 2024).

Total annual pesticide use in Türkiye is 57.7 kt in 2023 (TUIK, 2024). Pesticides constitute about 12.3 kt of this sum. The average pesticide consumption is about 2300 g a.i. per hectare. Fresh fruits and vegetables of different varieties are cultivated in Central District of Çanakkale province, Türkiye. Pesticides (especially insecticides) are used intensively to protect crops from pests. In 2023, 2.2 kt pesticides (243 t insecticides) were utilized on agricultural fields of Çanakkale province. Of this sum, 27% was utilized in Central District (Anonymous, 2024).

Various studies have confirmed that the Quick-Easy-Cheap-Efficient-Rugged-Safe (QuEChERS) method could also be safely used for pesticide residue analysis of soils (Nagel, 2009; Temur et al, 2012; Balkan, 2021; Polat & Tiryaki, 2022; Top et al., 2023). In the borders of Troia National Park, captan, endosulfan, ethion, cypermethrin, trifluralin, mancozeb, pesticides were detected with the range of 100-230 ppb, 16.7-230 ppb, 1-6 ppb, 20-80 ppb, 20 ppb and 2 ppb, respectively (Yıldırım & Özcan, 2007). In another study, the insecticide load of Troia was determined using the QuEChERS method. Detected pesticides were ordered as chlorantraniliprole > imidacloprid > pyridaben > clothianidin > indoxacarb (Polat & Tiryaki, 2022).

Insecticide residue levels of the soil samples, taken from agricultural lands and around water resources in the Çanakkale - Central district were investigated in present study. Health risk assessments were also performed for adults and children.

Materials and Methods

Chemicals and reagents

Pesticides were supplied by Chem Service (USA) and Dr. Ehrenstorfer GmbH (Germany). Chemicals and reagents used in present experiments included QuEChERS cleanup and extraction kits and nylon syringe filters. Other reagents and solvents, such as acetic acid (AcOH), acetonitrile (ACN), ammonium acetate, methanol and sodium chloride (NaCl) were supplied by Merck in Darmstadt, Germany. All reagents and solvents were analytical grade with a purity of 99%.

Equipment and chromatography

Insecticide detection was performed with the use of an LC-MS/MS instrument equipped with an Acquity UPLC BEH C_{18} column (1.7 µm, 2.1 mm x 100 mm). The flow rate, injection volume and the total run time were 0.35 mL/min, 1 µL, and 15 minutes, respectively. The current gradient programme consists of 10 mM ammonium acetate ($NH_4CH_3CO_2$) in pH 5 water (A) and 10 mM $NH_4CH_3CO_2$ in methanol (B). Fragment and precursor ions and retention times (t_R) are listed in Table 1.

Sampling and analysis of the soil

Soils were sampled from a depth of 5 to 25 cm in agricultural areas in Çanakkale Central District. In Autumn of 2020, 54 samples were taken from the study area, located between 39°57’24” N latitudes and 26°14’48″E longitudes. The samples were transported to the laboratory in an ice box and kept frozen (-20°C) until the analyses were performed (Zaidon et al., 2019; Polat & Tiryaki, 2022). The soils were dried in the air and sieved through 2 mm sieves (EPA, 2007). Insecticide-free samples (confirmed by chromatographic analysis) were also taken from the same sites. Modified QuEChERS method was employed for analyses of blank and spiked samples (Adeyinka et al., 2019; Polat, 2021; Vickneswaran et al., 2021; Polat & Tiryaki, 2022). Approximately 10 g air-dried sample was supplemented with 100 µL AcOH, then with 15 mL ACN and mixed thoroughly for 15 seconds. Extraction kits were added to the mixture and vortexed for 1 min. The mixture was centrifuged at 3000 rpm for 10 min. After centrifugation, the supernatant was taken into a 50 mL centrifuge tube (including QuEChERS Cleanup Kits), vortexed for 15 s and centrifuged again at 3000 rpm for 10 min. The supernatant was then filtered through a 0.22 µm syringe into 2 mL vials and analysed by LC-MS/MS instrument.

Table 1. LC-MS/MS parameters and calibration parameters (5 -point calibration levels) for the insecticide

Insecticide	t_R*	Precursor ion m/z	Fragment ion, m/z (CE) **	Calibration range (ppb)	Calibration curve equation***	R^2
Acetamiprid	5.05	223.09	125.95 (21)	1-200	$y=-71.6832 x^2 + 108657 x + 1294.52$	0.9997
Bifenthrin	11.97	440.08	181.05 (20)	1-200	$y=-1.75921 x^2 + 10550.5x + 745.791$	0.9999
Chlorantraniliprole	8.19	482.00	283.94 (10)	1-200	$y= -9.73986 x^2+14384 x- 708.385$	0.9999
Clofentezine	9.99	302.98	137.96 (12)	1-200	$y=-37.7542 x^2+ 33418.1 x + -61.8424$	0.9998
Clothianidin	4.58	250.04	131.93 (16)	1-200	$y= -11.008 x^2+ 15197.3 x + 2078.26$	0.9996
Cyhalothrin-lambda	11.26	467.22	225.04 (10)	10-2000	$y= -0.03035 x^2 +1418.16 x +1139.43$	0.9999
Deltamethrin	11.39	523.04	280.92 (15)	1-200	$y= -0.274504 x^2 + 3382.47 x+-515.595$	0.9998
E. benzoate	4.02	886.60	158.11(36)	1-200	$y = -44.8434 x^2 + 114086 x +15623.8$	0.9999
Etoxazole	11.09	360.19	140.99 (48)	1-200	$y= -175.839 x^2 + 237612 x + 16003.1$	0.9997
Flubendiamide	9.60	680.99	253.99 (30)	1-200	$y=-11.112x^2+11290.5x+ 1704.8$	0.9988
Hexythiazox	10.93	353.08	227.99 (16)	1-200	$y=-19.6547 x^2 + 37913 x + 926.07$	0.9997
Imidacloprid	4.57	256.03	175.05 (15)	1-200	$y= -5.76398 x^2+ 12261.9 x + -35.9641$	0.9998
Indoxacarb	10.27	528.04	202.99 (24)	1-200	$y= -7.27211 x^2+ 7726.08 x + -571.225$	0.9999
Metaflumizone	10.69	507.13	178.04 (36)	10-2000	$y= 0.106122 x^2 + 3653.8 x + 511.94$	0.9999
Methoxyfenozide	8.87	369.19	149.02 (16)	1-200	$y= -297.829 x^2+ 82874.9 x + -3970.18$	0.9999
Novaluron	10.40	493.05	158.01 (18)	1-200	$y= -0.704415 x^2+ 6529.42 x + 323.143$	0.9997
Pirimicarb	7.58	239.15	71.99 (22)	1-200	$y= -86.9902 x^2 + 180575 x + -2330.9$	0.9999
Pymetrozine	3.80	218.09	104.94 (24)	1-200	$y= -53.4778 x^2+ 123182 x + -6110.02$	0.9999
Pyridaben	11.46	365.14	147.08 (28)	1-200	$y= -127.957 x^2+ 116395 x + 8582.84$	0.9997
Thiamethoxam	3.86	292.01	211.04 (13)	1-200	$y= -12.4825 x^2 + 32248.7 x + -634.857$	0.9999

* t_R, retention time (minutes); ** CE, collision power (V); *** matrix matched calibration; R^2, Correlation coefficients.

Method verification

Method verification was conducted to prove the method employed for a specific sample provided reliable outcomes (Aysal et al., 2007; Yolci Omeroğlu et al., 2015; Balkan & Karaağaçlı, 2023). Recovery, linearity, precision and LOQ were used to verify the method (Yolci Omeroğlu et al., 2013; SANTE, 2021). For recovery testing, 100 µL of insecticide fortification solutions were added to blank samples (10 g) at 1 and 8 times of LOQ levels. Analyses were performed in five repetitions. Calibration ranges of insecticides were provided in Table 1. A matrix-matched calibration curve was utilized for insecticide quantification.

Health risk assessment

Humans are exposed to insecticides by ingestion, inhalation and direct contact. The health risks of insecticides were assessed based on the residue levels found in insecticide-contaminated areas. Health risks were estimated based on previously described methods (EPA, 1998; Chen et al., 2011; Sadeghi-Yarandi et al., 2020; Polat & Tiryaki, 2023). LADD (life- time average daily dose, mg/kg bw day), HI (hazard index) and HQ (hazard quotient) were estimated using the below formulas (EFSA, 2007; Jing et al.,2021; Tadesse, 2021).

$$LADD=\frac{Cs \times IR \times CF \times EF \times ED}{BW \times AT} \quad (1)$$

$$HQ=\frac{CDI}{RfD} \quad (2)$$

$$HI=\sum HQ \quad (3)$$

where Cs is insecticide concentration (mg/kg or mg/L), IR is ingestion rate (for soil: 200 mg/day for children and 100 mg/day for adults; for water: 0.87 L/ day for children and 1.4 L/day for adults, CF is conversion factor (10^{-6} kg/mg). ED is exposure duration, EF is exposure frequency (350 days), BW is body weight, AT is averaging time (EF × ED days) and RfD is reference dose. CDI also known LADD is chronic daily intake (mg/ kg day) for a single compound.

The LADD values less than 10^{-6} for insecticides in soil indicate an acceptable risk limit (EPA, 1998). The HQ was calculated for each insecticide using the LADD and the reference dose (RfD) value. The HQ≥1 indicates a potential risk to human health and the HQ<1.0 indicates an insignificant hazard (EFSA, 2007; Jing et al., 2021). The total exposure to all insecticides was estimated using an HI. HI values less than 1 indicate that the consumer is protected, whereas HI values greater than 1 represent an unreasonable health risk (Yeladi et al., 2024). This comment gives an indication of which compound contributes most to the hazard. Together with the HQ for the individual insecticide, the HI values provide an indication of which pesticides would be most appropriate to reduce the risk from the insecticide (EFSA, 2007).

Results and Discussion

Method verification

Calibration curves of 20 insecticides over the various concentration ranges, retention times and equations for matrix-matched calibration lines are provided in Table 1. Correlation coefficients (R^2) were all greater than 0.999. Insecticides were quantified with the use of relevant analytical functions (Tiryaki et al., 2008). Recovery rates and LOQs are provided in Table 2.

Table 2. Recoveries with RSDs values, and LOQs

Insecticide	LOQ (µg/kg)	Spiking level						Mean	
		1×LOQ			8×LOQ				
		Found (µg/kg)	Recovery (%)*	RSD (%)	Found (µg/kg)	Recovery (%)*	RSD (%)	Recovery (%) (As a tool for trueness)	RSD (%) (As a tool for precision, repeatability)
Acetamiprid	1	0.88	87.79	4.5	8.30	103.76	1.58	95.77	9.28
Bifenthrin	1	0.65	64.56	3.27	7.48	93.50	4.70	79.03	19.73
Chlorantraniliprole	1	0.89	88.64	6.39	7.91	98.84	1.13	93.74	7.05
Clofentezine	1	0.80	80.12	4.98	7.46	93.25	14.34	86.69	13.37
Clothianidin	1	0.92	92.48	5.39	7.99	99.91	0.83	96.19	5.37
Cyhalothrin- L.	10	8.95	89.48	5.33	46.43	116.07	3.38	102.77	14.21
Deltamethrin	1	1.49	76.40	13.42	9.94	62.14	2.25	68.37	13.76
E. benzoate	1	0.52	51.95	15.60	3.59	48.85	3.97	48.40	13.79
Etoxazole	1	0.88	87.80	2.60	6.63	82.86	1.10	85.33	3.60
Flubendiamide	1	0.79	78.83	5.12	7.91	96.40	1.52	87.61	11.06
Hexythiazox	1	0.80	80.32	1.51	8.89	111.10	3.88	95.71	17.23
Imidacloprid	1	0.95	94.61	7.55	8.09	101.13	2.47	97.87	6.24
Indoxacarb	1	0.66	65.60	11.19	6.65	83.11	3.25	74,35	14.25
Metaflumizone	10	7.38	73.81	10.32	83.67	104.59	2.28	89.2	19.14
Methoxyfenozide	1	0.86	85.97	5.50	7.85	98.15	2.36	92.06	7.94
Novaluron	1	0.86	85.87	10.65	7.77	97.07	3.65	91.32	9.75
Pirimicarb	1	0.83	83.31	5.57	7.84	98.04	2.71	90.67	9.42
Pymetrozine	1	0.61	60.59	8.20	5.90	73.71	3.91	67.15	11.97
Pyridaben	1	0.94	93.88	4.42	8.55	106.92	8.88	100.40	9.71
Thiamethoxam	1	0.79	89.92	3.88	8.53	106.62	3.11	92.71	16.72
Method overall recovery (accuracy): 86.77 % (n=200; SD=16.54; RSD%=19.06)									

* Average of 5 repetitions.

Insecticide recovery rates ranged from 60.59 to 115.50 % with RSDs of between 3.6 - 19.73%, all of the values were within the acceptable range for SANTE (2021) (60-140%). Overall recovery ratio was determined to be 86.77% with an RSD of 19.06 % (SD= 16.54; n=200). LOQ values showed that present method could detect insecticide residues lower than the MRL set by the EU (EU, 2025; Polat & Tiryaki, 2023). The modified QuEChERS method has proven to be an accurate, reliable and rapid tool for the detection of insecticide residues in soil. In previous studies (Lesueur et al., 2008; González-Curbelo et al., 2022), the QuEChERS method for pesticide residue analyses in soil has been compared with other extraction methods such as accelerated solvent extraction (ASE), pressurized liquid extraction (PLE), microwave-assisted extraction (MAE), solid-liquid extraction (SLE), solid-phase extraction (SPE), Soxhlet extraction and ultrasonic solvent extraction (USE). Although MAE, ASE and USE have been developed as faster, more practical and environmentally friendly methods than the Soxhlet method, the QuEChERS method is the first choice because of its high performance and ease of modification for specific pesticide and matrix combinations. The QuEChERS method provides the best recoveries with reliability on a QA/QC basis.

Residues in samples

An LC-MS/MS system was used for analyses of insecticides and detected residues above the LOQ were assessed. The max-min and mean insecticide residues are shown in Table 3. Of 54 samples collected from the study area, 44 samples (81.48%) contained different concentrations of insecticide and residues of 20 insecticides were detected at different frequencies. The environmental risk characteristics and hazard classifications of the pesticides are shown in Table 4. The most frequent insecticides were in the following order: chlorantraniliprole (27 samples) > pyridaben (22 samples) > clothianidin and imidacloprid (19 samples) > thiamethoxam (14 samples) > indoxacarb (13 samples) > flubendiamide (10 samples) > deltamethrin and methoxyfenozide (9 samples). The other insecticides were found in less than 9 samples. The concentration of insecticide residues varied from 1.01 µg/kg for deltamethrin, imidacloprid and flubendiamide to 760.01 µg/kg for etoxazole. Etoxazole was detected at a concentration of 760.01 µg/kg in the sample with the highest level. This sample was collected from the nearby fields where pesticide waste was encountered. In addition, 17 insecticides were detected at various concentrations in the same sample. Thiamethoxam was also detected (230.30 µg/kg) in this sample.

Chlorantraniliprole residues ranged from 1.10 to 153.53 µg/kg, pyridaben residues varied between 1.02 - 104.61 µg/kg, clothianidin between 1.02 - 14.07 µg/kg and imidacloprid between 1.01 - 32.37 (Table 3). Clothianidin was banned in Türkiye on 31 July 2019 (PPPD, 2024). EFSA has not ruled out a high risk for clothianidin (EFSA, 2016).

Table 3. Concentrations of insecticides (in triplicate analysis) in soil samples from different cropping areas

Insecticide	Residue, µg/kg											
	Agricultural land (empty)			Vegetable			Orchard			Around water source		
	Min.	Max.	Mean/ F.D*	Min.	Max.	Mean/ F.D*	Min.	Max.	Mean/ F.D*	Min.	Max.	Mean/ F.D*
Acetamiprid	2.10	47.60	24.40 / 2							1.69	1.81	1.70 / 1
Bifenthrin	13.13	14.36	13.60 / 1									
Chlorantraniliprole	1.10	153.53	14.10 / 18	1.57	73.29	28.9/4	2.00	12.80	6.45 / 2	2.66	4.52	3.50 / 3
Clofentezine	3.98	65.55	20.50 / 5							1.15	2.63	1.70 / 1
Clothianidin	1.02	14.07	3.70 / 14	1.56	4.08	2.4 / 4				5.70	6.32	6.02 / 1
Cyhalothrin-L.	106.10	113.39	108.80 /1							113.67	129.48	121.70 / 1
Deltamethrin	1.01	71.90	16.80 / 5	3.77	5.75	4.8 / 2	1.28	1.38	1.34 / 1	7.29	13.22	9.70 / 1
E. benzoate	3.15	5.16	3.90 / 1									
Etoxazole	159.00	760.01	376.40 /1	3.14	7.89	5.3 / 1						
Flubendiamide	1.02	117.81	23.44 / 8							1.01	12.18	6.60 / 2
Hexythiazox	1.44	73.43	25.30 / 3							1.05	1.29	1.10 / 1
Imidacloprid	1.01	12.29	3.55 / 13	1.49	32.37	11.7 / 3				1.86	6.36	4.77 / 3
Indoxacarb	1.02	256.86	25.50 / 9	5.13	9.36	7.5 / 2				1.20	13.16	3.50 / 2
Metaflumizone	9.90	25.25	15.80 / 2	12.95	19.43	15.7 / 1						
Methoxyfenozide	3.54	194.51	44.10 / 6	1.25	3.24	2.2 / 2				5.19	7.32	6.20 / 1
Novaluron	1.29	149.00	38.90 / 4							2.55	3.42	3.10 / 1
Pirimicarb	1.47	42.89	18.72 / 2									
Pymetrozine	58.64	65.60	63.27 / 1									
Pyridaben	1.02	104.61	19.41 /14	2.12	39.84	15.2 / 3	16.25	39.63	26.50 / 2	1.14	56.76	10.10 / 3
Thiamethoxam	1.08	230.30	32.72 / 9	1.65	34.11	15.8 / 3	15.54	34.61	24.30 / 2			

* Frequency of detection.

Table 4. Hazard classifications and environmental risk characteristics (decimal digit point)

Insecticide	Chemical category*	Persistency*	DT_{50} (field), day*	WHO Classification**
Acetamiprid	Neonicotinoid	Non-persistent	3.0	II
Bifenthrin	Pyrethroid	Moderately persistent	86.8	II
Chlorantraniliprole	Diamide	Persistent	204.0	U
Clofentezine	Tetrazine	Moderately persistent	63.0	III
Clothianidin	Neonicotinoid	Persistent	121.2	II
Cyhalothrin-lambda	Pyrethroid	Non-persistent	26.9	II
Deltamethrin	Pyrethroid	Non-persistent	21.0	II
E. benzoate	Micro-organism derived substance	Non-persistent	1.1	II
Etoxazole	Diphenyl oxazoline	Non-persistent	7.3	III
Flubendiamide	Phthalamide	-	-	III
Hexythiazox	Carboxamide	Non-persistent	17.7	U
Imidacloprid	Neonicotinoid	Persistent	174.0	II
Indoxacarb	Oxadiazine	Non-persistent	5.9	II
Methoxyfenozide	Carbohydrazide compound	Moderately persistent	68.0	U
Metaflumizone	Semicarbazone compound	Non-persistent	13.8	U
Novaluron	Benzoylurea	Moderately persistent	96.5	U
Pirimicarb	Carbamate	Non-persistent	9.0	II
Pyridaben	Pyridazinone	Non-persistent	29.0	II
Pymetrozine	Pyridine	Non-persistent	22.6	III
Thiamethoxam	Neonicotinoid	Moderately persistent	39.0	II

* From the IUPAC-PPDB (PPDB, 2024) **III, low hazardous; II, modera hazard; U, probably not an acute health hazard; (WHO, 2019).

A total of 4 neonicotinoid and 3 pyrethroid insecticides were detected in soil samples (Tables 3 & 4). According to the WHO classification (WHO, 2019), 11 out of 20 insecticides were moderately hazardous (Class II). Neonicotinoids, which can be used against aphids, whiteflies and thrips, kill the insects with their neurotoxic effect by binding to acetylcholine receptors (PPDB, 2024; IRAC, 2025). Pyrethroid pesticides are bound to the sodium channel, immobilize and paralyze insects (Ahamad & Kumar, 2023). Pyrethroid pesticides are also linked to neurologic and cardiovascular diseases of humans (Bao et al., 2020; Xue et al., 2021; Ahamad & Kumar, 2023). Pyrethroid pesticides include cypermethrin, deltamethrin and cyhalothrin-lambda (Yang et al., 2020). The mean insecticide residues of bifenthrin, cyhalothrin- lambda, deltamethrin and were found to be 14 μg/kg, 115 μg/kg, 8 μg/kg, respectively (Figure 1).

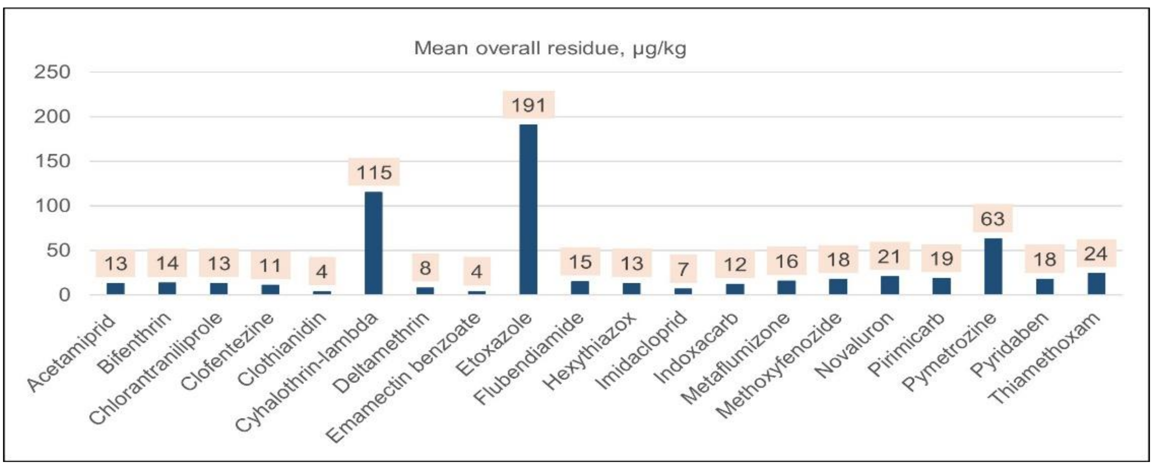

Figure 1. The mean insecticide residues.

The half-life (DT_{50}) of insecticides provides information on the persistence of insecticides in soil and the environment. Chlorantraniliprole (DT_{50}=204 days), clothianidin (DT_{50}=121.2 days) and imidacloprid (DT_{50}=174 days) were detected in 65 samples as persistent insecticides. These persistent insecticides and pyridaben (DT_{50}=29 days) were found in almost all of the agricultural lands (Table 3). The relationship between DT_{50} and frequency of detection of insecticides is shown in Figure 2. Present DT_{50} values varied from 3 days (acetamiprid) to 204 days (chlorantraniliprole).

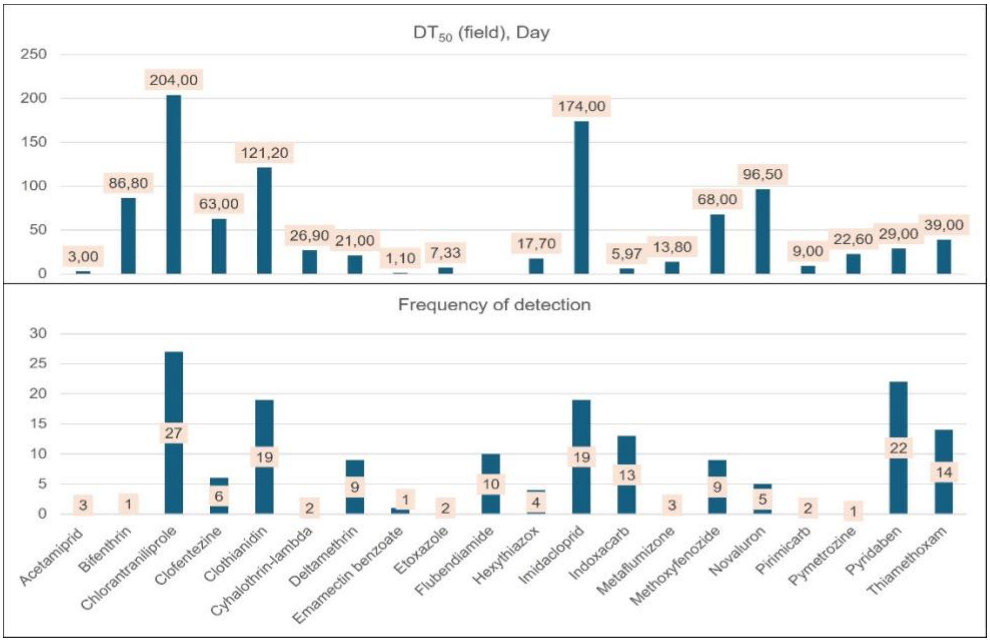

Figure 2. The relationship between half-lives and detection frequencies of insecticides.

The study identified the insecticides emamectin benzoate, acetamiprid, indoxacarb, etoxazole and pirimicarb with DT_{50} values less than 10 days. Mariappan & Tamilarasan (2025) showed that indoxacarb (DT_{50}= 5.97 days) was readily degradable and therefore did not exert a risk of contamination for groundwater. Indoxacarb had a limited mobility in soil, thus posed a slight risk of groundwater contamination.

Health risk assessment

Health risk assessments were performed for insecticides (10 insecticides in total) that were most frequently detected (more than 5 samples) in soil samples. The HQs of individual insecticides, calculated with LADD (mg/ kg bw per day) and RfD values, and the cumulative hazard of all insecticides (HI) for soil samples are presented for children and adults in Table 5. Current HQ and HI values for soil samples were < 1, indicating insignificant hazards. The highest mean HQ value for pyridaben was identified as $445.00*10^{-7}$ (with a range of $2.55\text{-}2615.25*10^{-7}$) for children and $59.33*10^{-7}$ (with a range of $3.40\text{-}348.7*10^{-7}$) for adults (Table 5). Similarly, the lowest mean HQ values for chlorantraniliprole were found to be $1.05*10^{-7}$ (with a range of $0.09\text{-}12.15*10^{-7}$) and $0.14*10^{-7}$ (with a range of $0.01\text{-}1.62*10^{-7}$) for children and adults, respectively. The mean HQs for both children and adults were ordered as pyridaben > thiamethoxam > novaluron > deltamethrin > indoxacarb > clothianidin. The sum of hazard ratios (HQ) for all the insecticides was $1310.00*10^{-7}$ (with a range of $100.54\text{-}10689.00*10^{-7}$) for children and $174.67*10^{-7}$ (with a range of $13.405\text{-}1425.28*10^{-7}$) for adults. But HQ for an individual insecticide indicates which insecticide should be used to decrease the risks for a specific location. In present cases, pyridaben (FD=22) had greater risk than clothianidin and imidacloprid. Pyridaben is non-persistent with a DT_{50}= 29 days. Clothianidin and imidacloprid (FD=19) are persistent with a DT_{50}= 121.2 and 174 days, respectively. Pyridaben is used to control spider mite and whiteflies insects. Clothianidin and imidacloprid are used against the aphids, thrips and plant hopper insects, respectively. In this case, farmers should prefer insecticides with less environmental risk. The risks of human exposure to insecticides in the study soils were within acceptable limits. However, the levels of insecticides in agricultural soils should be monitored regularly, especially for environmental risks arising from their transfer to the surface waters.

Table 5. Hazard Quotients [HQ ($x10^{-7}$)] and Hazard Indexes [HI ($x10^{-7}$)] for children and adults in soil

Insecticide	F.D*	Children				Adult			
		HQ**		HI***		HQ**		HI***	
		Range	Average	Range	Average	Range	Average	Range	Average
Chlorantraniliprole	27	0.09-12.15	1.05	100.54-10689.00	1310.00	0.01-1.62	0.14	13.405-1425.28	174.67
Pyridaben	22	2.55-2615.25	445.00			3.40-348.7	59.33		
Clothianidin	19	13.01-179.46	51.28			1.73-23.93	6.84		
Imidacloprid	19	2.21-70.99	14.61			0.30-9.46	1.95		
Thiamethoxam	14	11.25-2398-96	252.71			1.50-319.86	33.69		
Indoxacarb	13	6.38-1605.38	75.98			8.50-214.05	10.13		
Flubendiamide	10	0.63-73.63	9.38			0.08-9.81	1.25		
Deltamethrin	9	2.53-1797.50	200.00			3.37-239.66	26.66		
Methoxyfenozide	9	1.56-243.14	21.38			0.21-32.42	2.92		
Novaluron	5	14.66-1693.18	238.13			1.95-225.76	31.75		

* Frequency of detection; **Hazard quotient (HQ); ***Hazard index (HI).

Conclusion

Experimental findings showed that the QuEChERS combined with an LC-MS/MS device could provide a reliable, accurate and rapid tool for insecticide analysis in soils. Twenty insecticides were detected at various concentrations in soil samples. The most abundant insecticides were in the following order: chlorantraniliprole (27 samples) > pyridaben (22 samples) > clothianidin and imidacloprid (19 samples) > thiamethoxam (14 samples) > indoxacarb (13 samples) > flubendiamide (10 samples) > deltamethrin and methoxyfenozide (9 samples). The DT_{50} values of insecticides were high, indicating different persistence classes. The maximum residue of etoxazole was found in one sample at 760.01 µg/kg. This sample was taken from the nearby fields with pesticide wastes. HIs and HQs were mostly < 1.0 for both adults and children. Despite safe levels of existing insecticides, precautions might be taken against potential toxicity of insecticides. The environmental and human health impacts of pesticide residues in soil, rather than degradation products, should not be neglected. These residues can remain in the environment for long periods of time, potentially leading to bioaccumulation and trophic transfer along the food chain. Furthermore, the behavior of agricultural producers also plays a critical role in determining residue levels. Therefore, targeted education programs and awareness campaigns are essential to promote responsible pesticide use and reduce soil contamination.

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