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Experimental study on photodegradation and leaching of typical pesticides in greenhouse soil from Shouguang, Shandong Province, East China

Li-Ting Hua^{1†}, Rui-Lin Wu^{2†}, Cun-Lu Li¹, Chao-Nan Wang¹, Yi-Long Li¹ and Fu-Liu Xu^{1*} 

Abstract

Background Pesticide use contributes to national food security. The dissipation pathways and degradation mechanisms of pesticides have been widely studied and pesticide residues have remained a focus of public concern. However, studies on the migration and transformation behaviors of pesticide residues in real-world greenhouse soils are insufficient. Therefore, in this study, we collected greenhouse soil from Shouguang, Shandong Province, and investigated the photodegradation and leaching of 17 common pesticides, which leave residues in the soil and are the most frequently used pesticides in Shouguang. The environmental behavior of pesticides in greenhouse soils will provide new information on pesticide residues in the real environment and provide a scientific basis for the prevention and control of pesticide pollution in greenhouse soils.

Results The photodegradation of trifloxystrobin followed a first-order kinetic equation, whereas those of emamectin benzoate, chlorantraniliprole, buprofezin, difenoconazole, pyraclostrobin, boscalid, tebuconazole, isoprothiolane, metalaxyl, and oxadixyl followed second-order kinetics. The half-lives of 17 pesticides under light and dark conditions ranged from 2.5–104 (mean: 36.2) and 2.6–110 (mean: 31.4) days, respectively. The half-lives of emamectin benzoate, pyraclostrobin, and metalaxyl in the light were 86.6%, 68.5%, and 94.5% of their half-lives in the dark, respectively. Chlorantraniliprole, metalaxyl, nitenpyram, diethofencarb, acetamiprid, carbendazim, and oxadixyl were leached to $\geq 90\%$ in aqueous solution. Six pesticides, avermectin B1A, emamectin benzoate, trifloxystrobin, difenoconazole, pyraclostrobin, and buprofezin, were difficult to leach from aqueous solutions.

Conclusions The degradation rate of some pesticides was higher in the light environment than in the dark. The leaching potential of the leachable pesticides was nitenpyram \gg metalaxyl $>$ acetamiprid $>$ carbendazim $>$ diethofencarb \approx chlorantraniliprole $>$ isoprothiolane $>$ oxadixyl $>$ boscalid \approx tebuconazole $>$ hexaconazole. Pesticides that are easy to leach but not easily degraded, such as chlorantraniliprole and metalaxyl, have a high potential risk of groundwater pollution, and additional degradation technologies should be used to reduce their pollution risk. The study of the photodegradation and vertical migration behavior of various pesticides is conducive to providing references for the agricultural use and pollution control of pesticides.

Keywords Pesticides, Photodegradation, Half-life, Leaching, Vertical migration

[†]Li-Ting Hua and Rui-Lin Wu share first authorship.

*Correspondence:

Fu-Liu Xu

xufl@urban.pku.edu.cn

Full list of author information is available at the end of the article

Introduction

Pesticides, as a type of artificially synthesized chemicals, have wide applications in reducing losses in food production owing to pests and diseases. China is a traditional agricultural power, and the largest producer and user of pesticides worldwide. The production of chemical pesticide raw materials in China reached a peak of 2.5 million tons in 2022 (NBSC 2022). The production of herbicides, insecticides, and fungicides in China in 2016 was 1.773, 0.507, and 0.199 million tons, respectively (CCPIA 2017). Subsequently, in response to the “Action Plan for Zero Growth in Pesticide Use by 2020,” the production of pesticides decreased annually, with only 2.148 million tons produced in 2020, a decrease of approximately 43%. The usage of pesticides in China was above 1.5 million tons from 2010 to 2018, but decreased to below 1.4 million tons in the following two years. Owing to their low mobility and difficulty of degradation, the continuous accumulation of certain pesticides in the soil causes environmental pollution problems or transmission via crops containing pesticide residues through the food chain, which may have an impact on human health (Singh et al. 2016; Wang et al. 2019). Therefore, the use of pesticides has gradually developed from organochlorine pesticides, which are highly toxic to humans, to low toxicity, high efficiency, and easily degradable pesticides such as organic nitrogen phosphorus, carbamate, neonicotinoid, and pyrethroid pesticides.

Vegetable planting in China is highly dependent on the greenhouse mode, which has high yield and economic benefits; pesticides are often sprayed to prevent plant diseases and insect pests and to improve crop yields (Song et al. 2018). However, because of the input of fertilizers and pesticides into greenhouses, the properties of greenhouse soils undergo significant changes, such as degradation, acidification, salinization, imbalance, and accumulation of pesticide residues (Hu et al. 2017). Easily leachable pesticides can also pollute groundwater (Li et al. 2018). Seventy-six pesticide residues were detected in 317 agricultural topsoils across the European Union, among which tebuconazole and boscalid were two of the most common with the highest residual pesticides in soil, having median and maximum concentrations of 0.02 and 0.19 mg/kg and 0.04 and 0.41 mg/kg, respectively (Silva et al. 2019). Pesticide monitoring of 75 cultivated lands in the Czech Republic found that 11% of the soil contained tebuconazole exceeding the limit of 0.01 mg/kg (Hvezdova et al. 2018). Tao et al. (2021) monitored 206 pairs of wheat field soil samples in suburban areas of Beijing in 2018–2020 and found that the detection rates of carbendazim (range: 71.4–98.5%) and neonicotinoids (e.g., imidacloprid range: 90.0–98.5%) were high. The mean concentrations of acetamiprid, carbendazim,

tebuconazole and hexaconazole were 4.5, 10.3, 36.8, and 114.2 $\mu\text{g}/\text{kg}$, with maximum values of 121.5, 179, 476.5, and 1035.6 $\mu\text{g}/\text{kg}$, respectively, and the maximum value of difenoconazole was 19 $\mu\text{g}/\text{kg}$ (Tao et al. 2021). High levels of pesticide residue are present in multiple agricultural regions. The pesticide residue content in 80% of greenhouse soils collected from 20 provinces in China was significantly higher than that in nearby open-field soils (Dou et al. 2020). Our previous research found that the total residual concentration of neonicotinoid pesticide in tomato greenhouse soils in Shouguang ranged from 0.731 to 11.383 $\mu\text{g}/\text{kg}$ (Wu et al. 2020). Therefore, attention should be paid to the environmental changes in residual pesticides in greenhouse soils.

Residual free dissolved pesticides in greenhouse soil undergo environmental behaviors such as migration and transformation through degradation and leaching processes (Rani and Sud 2022). Pesticides migrate easily under conditions such as rainfall and irrigation (Wu et al. 2013). The effect of leaching into deep soil owing to rainfall was found to be greater than that of degradation on the dissipation of paclobutrazol and uniconazole (Wu et al. 2013). Soil pesticides are prone to degradation under the influence of light (Konstantinou et al. 2001). For example, the degradation rate of triazophos is faster in moist soil than in dry soil, and an increase in light intensity increases its degradation rate (Rani and Sud 2015). Plastic film coverings in greenhouses can effectively reduce light intensity, and thus reduce the photolysis rate of photosensitive pesticides. In addition, irrigation promotes the vertical migration of pesticides in the soil. Considering that current research on pesticides mainly focuses on their efficacy and residues (Houbraken et al. 2017; Menon et al. 2021; Sultana et al. 2018), little research has been conducted on their environmental behavior characteristics; moreover, the types of pesticides are constantly increasing. Therefore, we conducted environmental behavior studies on multiple pesticides to provide a basis for improving food safety and reducing the risk of ecological pollution.

The purpose of this study was to analyze the influence of light on pesticide degradation in soil through photodegradation experiments and to clarify whether the vertical migration behavior of target pesticides has an effect on groundwater pollution according to the content of pesticides leached from different volumes and polarities of the leaching solution. In addition, the key aspects of environmental behavior were explored based on the classification characteristics of pesticides with different properties. Furthermore, the photodegradation and leaching experiments were conducted with the aim of clarifying the characteristics of different residual pesticides in greenhouse soils in Shouguang.

Materials and methods

Chemicals

Seventeen pesticides were included in this study, including six insecticides and 11 fungicides. The target pesticide standards used in this study were purchased from Accu-Standard (USA), Chem Service (USA), Dr. Ehrenstorfer (Germany), Anpel (China), O2si (USA), and Toronto Research Chemicals (Canada), all with a purity higher than 99%. Isotope-labeled internal standards, including imidacloprid- d_4 , clothianidin- d_3 , and thiamethoxam- d_3 with a purity of 99.5% were purchased from C/D/N Isotopes (Canada). The physicochemical properties, structural formulas, and registered quantities of the target pesticides are presented in Table 1 and Additional file 1: Figure S1 and Additional file 1: Table S1, respectively. Chromatographically pure acetonitrile, formic acid, and ammonium formate were purchased from Fisher Scientific (USA) and CNW (China). Ultrapure water was prepared using a Hitech Ultrapure Water Purifier system. Centrifuging was performed using a Shanghai Anting® low-speed refrigerated multi-tube centrifuge.

Soil collection

This study was conducted in Shouguang, Shandong Province, China. Shandong Province is located in the mid-latitude zone and has a continental climate of a warm temperate monsoon region. Tomatoes are a primary variety of greenhouse vegetables in Shouguang and have a long history of cultivation. Soil samples were collected from tomato greenhouses in Shouguang between September 2018 and early January 2019. To eliminate spatial differences in soil sample collection, surface soil was collected at a depth of 10 cm using a five-point sampling method and then mixed. The evenly mixed samples were placed into sample bags and stored in a refrigerator at $-20\text{ }^{\circ}\text{C}$.

Photodegradation experiment

Impurities (gravel and plant tissues) were removed from the soil samples prior to the photodegradation experiment. After the samples were air-dried at room temperature ($25\text{ }^{\circ}\text{C}$), they were screened through a 40-mesh sieve, mixed evenly, and used for the soil degradation experiments. Degradation of target pesticides in the soil was simulated in the laboratory using an artificial climate chamber under dark and light conditions (dark/light intensity of 0/2000 lx with a 24/12 h cycle, temperature constant of $25\text{ }^{\circ}\text{C}$, relative humidity of 60%) for 6 and 14 d, respectively. Soil (150 mg) was placed into a 1.5 mL centrifuge tube and 100 μL of 1.5 mg/L of pesticide mixture standard (pesticide concentration in soil: 1000 ng/g) was added. For the blank control, 100 μL deionized water was added. The photodegradation experiment was

preceded by time zeroing to rule out background concentrations of pesticides, that is, soils that may contain previously applied pesticides. A total of 31 and 71 samples were collected for the dark condition and light degradation experiments, respectively. Three spiked parallel samples and one blank control sample were collected from each sample. Acetonitrile (1 mL) was added to each sample for extraction, which was then rotated, mixed for 10 min, and centrifuged at 10,000 rpm. Internal standard (10 ng) was added to approximately 1 mL of the removed supernatant, passed over a 0.22 μm organophilic polytetrafluoroethylene filter, and stored in a 1.8 mL brown bottle for testing.

Leaching experiment

Leaching experiments were conducted using fresh soil from a tomato greenhouse before the autumn and winter planting seasons. Two parallel samples and one blank sample were prepared; 1 mL of 1 mg/L pesticide was added to each parallel sample, and 1 mL of deionized water was added to the blank sample. Considering that irrigation follows pesticide application in the greenhouse, we took approximately 1 mL of surface soil and filled it into an empty 6 mL solid phase extraction column after achieving an equilibrium between the pesticide and soil, and a vacuum filter device was used. One milliliter of aqueous solution was added at a time to the column and the eluent collected immediately. We considered that the water-soluble pesticides were almost completely eluted when the elution efficiency of the last milliliter of the added aqueous solution for all the pesticides was less than 3%. Next, organic reagents with different elution capacities (methanol, acetonitrile, and isopropyl alcohol) were used to elute the pesticides and their elution effects were compared. After collecting each milliliter of eluent, 10 ng of internal standard was added, and the sample was then stored in a 1.8 mL brown bottle after passing through a 0.22 μm hydrophilic or organophilic polytetrafluoroethylene filter.

Determination of target pesticides

The target pesticides were determined using a Xevo TQ-XS/ACQUITY UPLC-Class (Waters, USA) ultra-high-pressure liquid chromatography-triple quadrupole mass spectrometer with an ACQUITY BEH C18 column (1.7 μm , $2.1\times 100\text{ mm}$). An ACQUITY BEH C18 VAN-GUARD (1.7 μm , $2.1\times 5\text{ mm}$) protective column and an online filter (model: 205000343) were used in front of the column. The liquid phase conditions were as follows: column temperature, $40\text{ }^{\circ}\text{C}$; mobile phase flow rate, 0.4 mL/min; and injection volume, 2 μL . Mobile phase A was a 0.1% formic acid aqueous solution containing 5 mmol ammonium formate and mobile phase B was 100%

Table 1 Physicochemical properties of 17 typical pesticides commonly used in tomato greenhouses in Shouguang

Category	Pesticide	CAS number	Molecular formula	Molecular weight	Water solubility* (mg/L)	Vapor pressure# (Pa)	Henry constant* (Pa·m ³ /mol)	logKow* (pH=7)	GUS	logKoa	Koc (mL/g)
Insecticide	Nitenpyram	150824-47-8	C ₁₁ H ₁₅ ClN ₄ O ₂	270.72	5.90E+05	1.10E-06	3.54E-13	-0.66	2.01	7.83	60
	Acetamiprid	135410-20-7	C ₁₀ H ₁₁ ClN ₄	222.67	2.95E+03	1.73E-07	5.30E-08	0.8	0.94	6.35	343
	Chlorantraniliprole	500008-45-7	C ₁₈ H ₁₄ BrCl ₂ N ₃ O ₂	483.15	8.80E-01	6.30E-12	3.20E-09	2.86	3.51	-	330
Enamectin benzoate	Enamectin benzoate	155569-91-8	C ₅₆ H ₈₁ NO ₁₅	1008.24	2.40E+01	4.00E-10	-	-	-	-	283
	Buprofezin	69327-76-0	C ₁₆ H ₂₃ N ₃ OS	305.44	4.60E-01	4.20E-05	2.80E-02	4.93	0.45	8.7	-
	Avermectin B1A	65195-55-3	C ₄₈ H ₇₂ O ₁₄	873.08	1.00E-02	2.00E-07	-	4.48	-	29.75	5638
Fungicide	Carbendazim	10605-21-7	C ₉ H ₉ N ₃ O ₂	191.19	8.00E+00	9.00E-05	3.60E-03	1.48	2.21	10.54	350
	Oxadixyl	77732-09-3	C ₁₄ H ₁₈ N ₂ O ₄	278.30	5.96E+02	2.70E-05	5.86E-07	1.4	3.89	10.3	169
	Metalaxyl	57837-19-1	C ₁₅ H ₂₁ NO ₄	279.33	8.40E+03	7.50E-04	1.60E-05	1.75	2.06	8.67	163
	Diethofencarb	87130-20-9	C ₁₄ H ₂₁ NO ₄	267.32	2.76E+01	9.94E-06	9.12E-05	2.89	1.09	7.36	271
	Boscalid	188425-85-6	C ₁₈ H ₁₂ Cl ₂ N ₂ O	343.21	4.60E+00	7.20E-07	5.18E-05	2.96	2.68	12.72	772
	Tebuconazole	107534-96-3	C ₁₆ H ₂₂ ClN ₃ O	307.82	3.60E+01	1.30E-06	1.00E-05	3.7	1.86	11.93	1000
	Isoprothiolane	50512-35-1	C ₁₂ H ₁₈ O ₄ S ₂	290.40	5.40E+01	1.88E-02	1.00E-01	3.3	-	8.69	1352
	Hexaconazole	79983-71-4	C ₁₄ H ₁₇ Cl ₂ N ₃ O	314.21	1.80E+01	1.80E-05	3.33E-04	3.9	2.31	10.77	1040
	Difenoconazole	119446-68-3	C ₁₉ H ₁₇ Cl ₂ N ₃ O ₃	406.26	1.50E+01	3.33E-08	9.00E-07	4.36	0.83	13.88	6120
	Pyraclostrobin	175013-18-0	C ₁₉ H ₁₈ ClN ₃ O ₄	387.82	1.90E+00	2.60E-08	5.31E-06	3.99	0.05	17.32	9300
Trifloxystrobin	141517-21-7	C ₂₀ H ₁₉ F ₃ N ₂ O ₄	408.37	6.10E-01	3.40E-06	2.30E-03	4.5	0.15	9.86	2377	

Above data are from PPBD database (<https://sitem.herts.ac.uk/aeru/ppbd/index.htm>); * represents the defined value of the parameter at 20 °C; # represents the defined value of the parameter at 25 °C; GUS represents groundwater ubiquity score, GUS < 1.8 indicates difficulty in leaching, GUS between 1.8 and 2.8 indicates possible leaching, GUS > 2.8 indicates easy leaching; GUS and Koc data were collected from <https://www.pesticideinfo.org/>; logKoa from EPI Suite software; "-" indicates that no valid data was found

acetonitrile. The gradient elution conditions are listed in Additional file 1: Table S2. The mass spectrum conditions were as follows: electrospray ion source, positive ion mode; capillary voltage, 3200 V; ion source temperature, 150 °C; desolvation and cone gases, high-purity nitrogen gas; desolvation gas flow rate, 1000 L/h; and cone gas flow rate, 150 L/h. The mass spectrum parameters such as retention time, quantitative and qualitative ion pairs, and voltage of the targets are listed in Additional file 1: Table S3.

Quality assurance and quality control

The limits of detection (LODs) and limits of quantitation (LOQs) were defined as signal-to-noise ratios of 3 ($S/N=3$) and 10 ($S/N=10$), respectively. The LODs and LOQs of the pesticides were in the ranges of 0.02–1.5 ng/g and 0.05–4.0 ng/g, respectively. Concentrations below the LOQ were calculated as $LOQ/2$. The recovery (samples spiked with 20 ng of the standard solution) for most pesticides in the soil samples ranged from 74.4% (oxadixyl) to 105.8% (boscalid) (Additional file 1: Table S4). Evaluation of the matrix effects showed ionization enhancement of diethofencarb (100.1%) and ionization suppression of the other compounds (between 77.9% and 98.1%). During the sample pretreatment process, every 30 samples were considered a batch, with two method blanks and two solvent blanks. A 20 ng/mL mixed pesticide standard was inserted between every 10 samples to ensure the stability and reliability of the analytical method during instrumental analysis.

Statistical analysis

Zero-order, first-order, and second-order reaction fitting of the pesticide degradation data in soil was performed to obtain the adjust R^2 and select the optimal reaction kinetics model. The zero-order (Eqs. 1, 2), first-order (Eqs. 3, 4), and second-order (Eqs. 5, 6) reaction rate constants and half-lives of the pesticide photodegradation were calculated as follows (Xi et al. 2021):

$$c_t = c_0 - kt \quad (1)$$

$$t_{1/2} = \frac{c_0}{2k} \quad (2)$$

$$\ln c_t - \ln c_0 = -kt \quad (3)$$

$$t_{1/2} = \frac{\ln 2}{k} \quad (4)$$

$$\frac{1}{c_t} - \frac{1}{c_0} = kt \quad (5)$$

$$t_{1/2} = \frac{1}{kc_0} \quad (6)$$

where k is the reaction rate constant of pesticide photodegradation (h^{-1}) and C_0 and C_t are the concentrations ($\mu\text{g/g}$) of pesticides in soil samples before and after exposure time, respectively.

The IBM® SPSS Statistics 26.0 software (SPSS Inc., USA) was used to analyze the normality and variability of the data. Relevant images were drawn using Microcal™ Origin 2020 software.

Results

Degradation kinetics in soil and half-lives

Photodegradation of pesticides was investigated in tomato greenhouse soil in Shouguang City, Shandong Province. The changes in pesticide residual concentration in the soil over time under dark and light conditions are shown in Figs. 1 and 2, and the half-life and residual rate after degradation are listed in Table 2. Under both dark and light conditions, the degradation of trifloxystrobin in greenhouse soil followed the first-order kinetic equation, with a photodegradation half-life of 3.0 d and degradation half-life of 4.8 d in the dark. Similarly, the degradation of the insecticides emamectin benzoate, chlorantraniliprole, and buprofezin and the fungicides difenoconazole, pyraclostrobin, boscalid, tebuconazole, isoprothiolane, metalaxyl, and oxadixyl followed second-order kinetics with photodegradation half-lives of 16.1, 56.3, 22.8, 61.1, 23.3, 41.1, 99.1, 80.3, 104 and 17.9 d, respectively, and half-lives of 18.6, 53.5, 18.8, 46.1, 34.0, 30.4, 29.8, 44.4, 110, and 9.8 d, respectively, in the dark. The photodegradation half-lives of the insecticide emamectin benzoate and fungicides pyraclostrobin and metalaxyl were 86.6, 68.5, and 94.5%, respectively, of their half-lives in the dark.

Among the remaining pesticides that exhibited different levels of photodegradation and dark reaction kinetics, the photodegradation half-lives of avermectin B1A and diethofencarb were shorter than their half-lives in the dark. The half-lives of two neonicotinoid pesticides, nitenpyram (light, 4.1 d; dark, 4.1 d) and acetamiprid (light, 2.5 d; dark, 2.6 d), were similar and shorter, respectively, under the different light conditions.

Leaching potential of pesticides in soil

Soil chromatography was used to simulate pesticide leaching from the soil. In the elution process using the aqueous solution, the elution efficiency of the seventh addition of 1 mL aqueous solution for each pesticide was less than 3%, at which point the water-soluble pesticides were considered close to being completely eluted. The pesticides in the column were then sequentially eluted with 1 mL of methanol, 1 mL of acetonitrile, and 1 mL

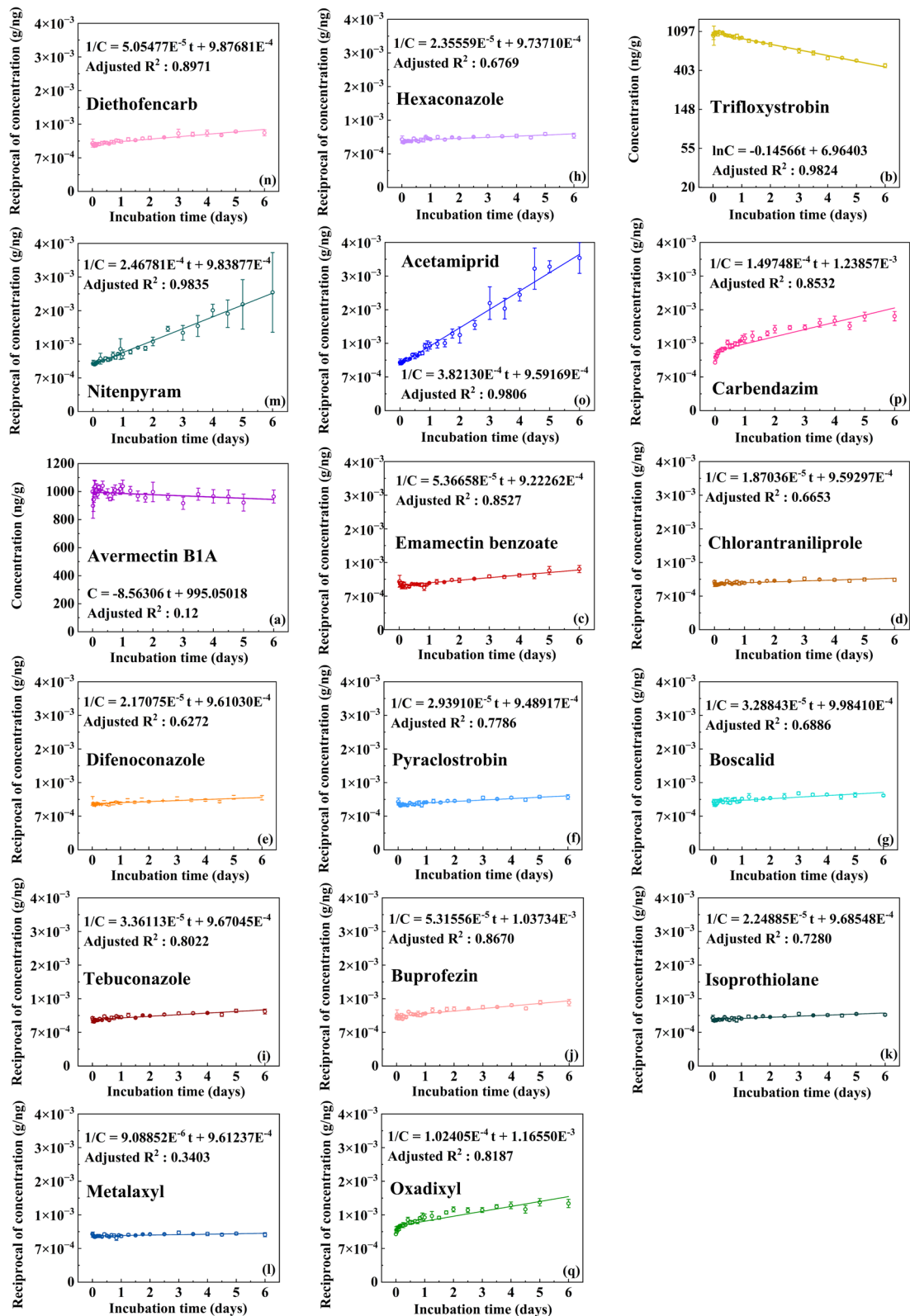


Fig. 1 Changes in the concentrations of 17 pesticides in soil over time under dark conditions. The degradation of avermectin B1A follows a zero-order fit, that of trifloxystrobin follows a first-order fit, and the remaining pesticides follow a second-order fit

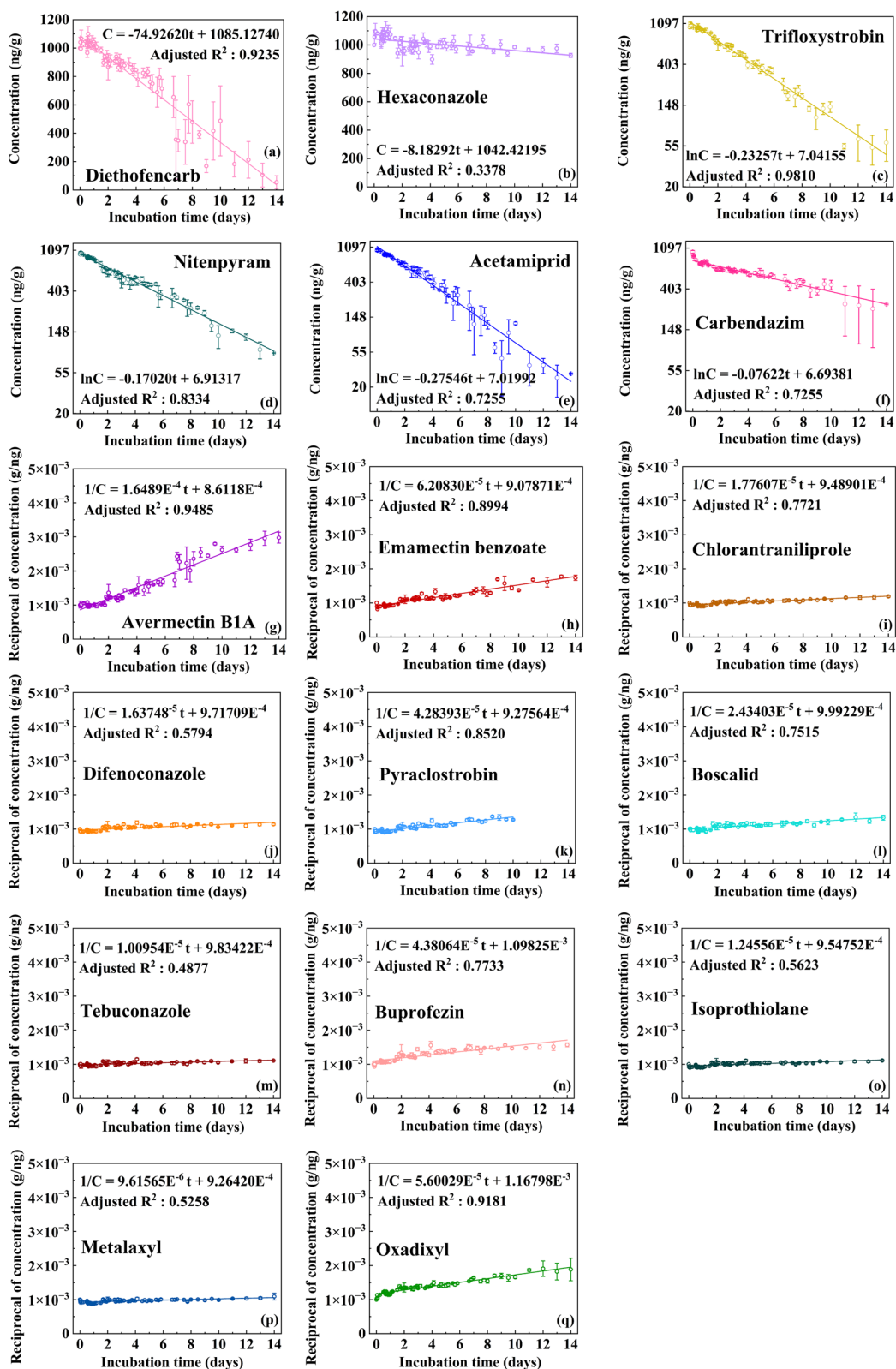


Fig. 2 Changes in the concentrations of 17 pesticides in soil over time under light conditions. The degradation of diethofencarb and hexaconazole follows a zero-order fit, that of nitenpyram, acetamiprid, carbendazim, and trifloxystrobin follow a first-order fit, and the remaining pesticides follow a second-order fit

Table 2 Half-lives of the target pesticides in soil under dark and light conditions

Category	Pesticide	Dark			Light		
		Dynamic level	Half-life (d)	Residual rate after 6 days (%)	Dynamic level	Half-life (d)	Residual rate after 14 days (%)
Insecticide	Nitenpyram	Second-order	4.1	40.3	First-order	4.1	8.8
	Acetamiprid	Second-order	2.6	31.5	First-order	2.5	2.9
	Chlorantraniliprole	Second-order	53.5	96.3	Second-order	56.3	84.1
	Emamectin benzoate	Second-order	18.6	79.1	Second-order	16.1	57.6
	Buprofezin	Second-order	18.8	75.8	Second-order	22.8	63.7
	Avermectin B1A	Zero-order	58.4	96.4	Second-order	6.1	33.6
Fungicide	Carbendazim	Second-order	6.7	50.9	First-order	9.1	30.9
	Oxadixyl	Second-order	9.8	61.1	Second-order	17.9	53.1
	Metalaxyl	Second-order	110	101.4	Second-order	104	91.7
	Diethofencarb	Second-order	19.8	82.0	Zero-order	6.7	5.5
	Boscalid	Second-order	30.4	88.4	Second-order	41.1	74.9
	Tebuconazole	Second-order	29.8	88.1	Second-order	99.1	90.1
	Isoprothiolane	Second-order	44.4	93.8	Second-order	80.3	90.0
	Hexaconazole	Second-order	42.4	92.9	Zero-order	61.1	92.7
	Difenoconazole	Second-order	46.1	92.3	Second-order	61.1	87.6
	Pyraclostrobin	Second-order	34.0	90.8	Second-order	23.3	78.5
	Trifloxystrobin	First-order	4.8	45.7	First-order	3.0	5.9

The degradation of pyraclostrobin under light conditions was only simulated for 10 days

of isopropanol. The pesticides remaining in the column were finally eluted with isopropanol.

More than 90% of seven target pesticides, chlorantraniliprole, metalaxyl, nitenpyram, diethofencarb, acetamiprid, carbendazim, and oxadixyl, were leached by the aqueous solution (Table 3). Among them, only 25% of the oxadixyl was leached by organic solvents, and the proportions of the other six pesticides leached by organic solvents were less than 5%. More than 38% of the target compounds isoprothiolane, boscalid, tebuconazole, and hexaconazole were leached out in the aqueous solution. The aqueous leaching percentages of hexaconazole and tebuconazole were 38.1% and 41.9%, respectively, and those of the other two pesticides were over 60%. However, among the six pesticides that were difficult to leach in aqueous solution, less than 20% of the target compounds avermectin B1A and emamectin benzoate were leached by organic solvents, whereas 32.6% of trifloxystrobin was leached, and more than half of difenoconazole, pyraclostrobin, and buprofezin was leached.

In this study, the ratio of the volume of the aqueous solution to that of the organic solvents required for leaching was used as an indicator of the leaching potential of the pesticides. The higher the ratio of the aqueous solution to organic solvents, the easier is the infiltration and the stronger is the transferability of the pesticides. Among the 17 pesticides evaluated, the leaching

potentials of avermectin B1A, emamectin benzoate, trifloxystrobin, difenoconazole, pyraclostrobin, and buprofezin were not evaluated because of the difficulty of leaching in aqueous solution. The leaching potential of the remaining 11 pesticides was nitenpyram >> metalaxyl > acetamiprid > carbendazim > diethofencarb \approx chlorantraniliprole > isoprothiolane > oxadixyl > boscalid \approx tebuconazole > hexaconazole. The leaching potential of pesticides was closely related to their physicochemical properties.

Discussion

Photodegradation experiments were conducted to investigate the effect of light on pesticide degradation in greenhouse soils. For trifloxystrobin, the half-life of the photodegradation and dark reactions showed that the degradation in soil was fast and its half-life was short. This is consistent with the results of Wang et al. (2015), where the half-life of trifloxystrobin in soil ranged from 0.54 to 8.8 d. Trifloxystrobin has extremely low mobility (2000 mL/g < K_{oc} = 2377 mL/g < 5000 mL/g; K_{oc} : organic carbon normalized sorption distribution coefficients) in soil and low volatility (vapor pressure = 3.40×10^{-6} Pa); therefore, photolysis may be an important factor affecting trifloxystrobin dissipation in soil (Wang et al. 2015). The degradation rate of trifloxystrobin was higher in the dark. From the EE configuration of the acid metabolites

Table 3 Percentage of target pesticides leached by aqueous and organic solvents

Solvent	Volume	Nitenpyram	Acetamiprid	Chlorantraniliprole	Emamectin benzoate	Buprofezin	Avermectin B1A	Carbendazim	Oxadixyl	Metalaxyl
Water solution	1	67±0.2	744±1	53.1±0.3	0±0	0±0	0±0	53.6±2.8	41.5±1.2	64±1.5
	2	28.4±1.9	33.5±2.1	25.2±4.2	0±0	0±0	0±0	23.7±2.5	22.2±2.8	30.8±1.4
	3	5.1±2.6	8.5±3.4	7.9±3.2	0±0	0±0	0±0	8.2±2.7	11.6±1.1	6.9±3.8
	4	1.8±1.1	4±2.5	3.9±2.1	0±0	0±0	0±0	4.5±2.5	8±2.5	2.7±1.9
	5	0.6±0.3	1.7±0.8	1.9±0.9	0±0	0±0	0±0	2.3±1	5.2±1.4	1±0.6
	6	0.3±0.1	0.9±0.3	1.2±0.4	0±0	0±0	0±0	1.4±0.5	3.8±0.7	0.5±0.2
	7	0.2±0.1	0.6±0.2	0.8±0.3	0±0	0±0	0±0	1±0.3	3±0.4	0.3±0.1
Methanol	8	0.1±0	0.5±0	1.1±0.3	3.3±0.7	24.3±9.8	6.6±3.3	0.8±0.2	5.5±2.4	0.2±0
Acetonitrile	9	0.1±0	0.8±0.2	1.3±0.4	2.5±0.5	17.7±6.4	4.4±2.1	1.1±0.4	6.6±2.7	0.2±0.1
Isopropanol	10	0±0	0.8±0.2	1.4±0.5	2±0.8	16.3±2.6	3.7±0.1	1.2±0.4	7.5±1.5	0.2±0
	11	0±0	0.3±0.2	0.5±0.5	0.4±0.4	6.5±5.6	1.2±1	0.4±0.3	2.7±2.3	0.1±0.1
	12	0±0	0.2±0.2	0.3±0.3	0.1±0.1	3±3.3	0.6±0.7	0.2±0.2	1.5±1.7	0.1±0.1
	13	0±0	0.1±0.1	0.2±0.2	0.1±0	1.7±1.8	0.3±0.3	0.1±0.1	0.7±0.8	0±0
	14	0±0	0.1±0.1	0.1±0.2	0.1±0	1.6±1.9	0.4±0.4	0.1±0.1	0.6±0.7	0±0
Subtotal	Water solution	103.4±2.1	123.8±6.2	94±2.4	0±0	0.1±0	0±0	94.5±1.6	95.3±2.1	106.1±6.5
	Organic solvent	0.1±0	2.6±0.6	4.9±1	8.4±0.2	71.1±1	17.2±2.8	3.9±0.7	25±1.9	0.9±0.1
Total	Water solution/organic solvent	103.6±2.1	126.4±6.8	98.9±3.4	8.4±0.2	71.2±1	17.2±2.8	98.4±2.2	120.4±4	107±6.6
		799.16	46.74	19.22	0	0	0	24.36	3.81	121

Solvent	Volume	Diethofencarb	Boscalid	Tebuconazole	Isoprothiolane	Hexaconazole	Difenoconazole	Pyraclostrobin	Trifloxystrobin
Water solution	1	48.6±1	24.4±0.3	12.6±0.4	29.9±0.6	9±0.8	0±0	0±0	0±0
	2	28.4±3.8	16.2±4.9	10.4±3.5	24.9±6.3	8.4±2.9	0±0	0±0	0±0
	3	10.3±4.3	9.3±1.5	7.5±2.2	14.5±3.7	7.7±1.4	0±0.1	0±0	0±0
	4	5±2.7	5.5±1.3	4.4±1	8.3±3.2	4.5±0.4	0±0	0±0	0±0
	5	2.3±1.1	3.7±0.7	3±0.6	5.1±1.9	3.5±0.2	0±0	0±0	0±0
	6	1.4±0.5	2.7±0.6	2.3±0.4	3.5±1.2	2.8±0.2	0±0	0±0	0±0
	7	1±0.4	2.2±0.4	1.7±0.4	2.5±0.9	2.3±0.4	0±0	0±0	0±0
Methanol	8	1.2±0.3	6±2.6	4.9±1.4	4±0.6	7.8±2.7	16.7±7.8	15.4±7.8	11.3±4.3
Acetonitrile	9	1.4±0.3	6.1±2.2	4.9±1	4.2±0.4	7±1.4	13.8±5.2	12.5±5.6	8.1±2.1
Isopropanol	10	1.3±0.6	6.1±2.1	4.8±2.2	3.9±1.9	6.8±2.9	13.6±1.9	11.5±0.3	7.3±2
	11	0.5±0.5	2.4±2.4	2.1±2.1	1.6±1.6	2.9±2.8	5.6±5.1	5.2±4.9	2.8±2.7
	12	0.3±0.3	1.4±1.6	1.2±1.4	0.9±1.2	1.5±1.8	2.7±3.1	2.8±3.3	1.5±1.7
	13	0.2±0.2	0.7±0.8	0.6±0.7	0.4±0.6	0.8±0.9	1.5±1.7	1.5±1.8	0.8±0.9
	14	0.1±0.1	0.6±0.7	0.5±0.7	0.4±0.5	0.7±0.9	1.4±1.8	1.5±2	0.8±1

Table 3 (continued)

Solvent	Volume	Diethofencarb	Boscalid	Tebuconazole	Isoprothiolane	Hexaconazole	Difenoconazole	Pyraclostrobin	Trifloxystrobin
Subtotal	Water solution	97.1 ± 4.2	64 ± 0.8	41.9 ± 1.4	88.7 ± 3.9	38.1 ± 0.5	0.1 ± 0.1	0 ± 0	0 ± 0
	Organic solvent	4.9 ± 1	23.3 ± 2.8	19 ± 4.7	15.5 ± 4.8	27.5 ± 5.2	55.3 ± 0.8	50.3 ± 0.9	32.6 ± 1.8
Total		102 ± 5.2	87.2 ± 1.9	60.9 ± 6.1	104.2 ± 8.7	65.7 ± 5.7	55.4 ± 0.8	50.3 ± 0.9	32.6 ± 1.8
Water solution/organic solvent		19.71	2.75	2.21	5.72	1.38	0	0	0

of trifloxystrobin, hydrolysis was inferred as the main pathway for the dark degradation reaction (Banerjee et al. 2006).

The large differences between the half-lives of emamectin benzoate, pyraclostrobin, and metalaxyl in the soil under light and dark reaction conditions indicated that their residues in the soil were greatly affected by light. As the active site of emamectin benzoate, the diene chromophore easily leads to the photodegradation of emamectin benzoate (Shang et al. 2012). Pyraclostrobin is prone to photolysis (Gao et al. 2021), which is its primary degradation pathway in the natural environment (Zeng et al. 2019). Similarly, photolysis plays a more important role in the dissipation of metalaxyl than in the adsorption between pesticides and soil particles (Bermúdez-Couso et al. 2013).

Compared to the half-lives in the dark, the low photodegradation half-lives of avermectin B1A and diethofencarb indicate that light may promote pesticide degradation. Avermectin B1A exhibits limited soil migration ($K_{oc}=5638 \text{ mL/g} > 5000 \text{ mL/g}$) and low volatility (vapor pressure = $2.00 \times 10^{-7} \text{ Pa}$); therefore, photodegradation is the main pathway for the dissipation of avermectin B1A. Similar to avermectin B1A, diethofencarb has moderate mobility in soil ($150 \text{ mL/g} < K_{oc} = 271 \text{ mL/g} < 500 \text{ mL/g}$) and its volatility is low (vapor pressure = $9.94 \times 10^{-6} \text{ Pa}$). Both the dark and photodegradation half-lives of nitenpyram and acetamiprid demonstrate that neonicotinoid pesticides degrade more easily in soil than most pesticides. In addition, the half-lives of biogenic pesticides (avermectin B1A) and benzimidazole fungicides (carbendazim) were both less than 10 d, indicating that their degradation rates were relatively fast under light conditions. However, different from carbendazim, the half-life of avermectin B1A was 58.4 d in the dark, whereas its half-life in the light was 10.4% of that in the dark, illustrating that light could accelerate the degradation of avermectin B1A in soil.

The half-lives of the insecticides avermectin B1A, emamectin benzoate, buprofezin, nitenpyram, and acetamiprid, and the fungicides trifloxystrobin, pyraclostrobin, diethofencarb, carbendazim, and oxadixyl were all less than 30 d; hence, they are classified as easily degradable pesticides (Li 2020). Chlorantraniliprole, difenoconazole, boscalid, hexaconazole, tebuconazole, isoprothiolane, and metalaxyl are difficult to degrade (half-life greater than 30 d). After 14 d of photodegradation, the residue rates of nitenpyram and acetamiprid among insecticides and trifloxystrobin and diethofencarb among fungicides were lower than 10%, at 8.8%, 2.9%, 5.9%, and 5.5%, respectively. These four pesticides can reasonably be assumed to achieve good degradation under light conditions. The residue rates of hexaconazole, tebuconazole,

isoprothiolane, and metalaxyl after photodegradation were higher than 90% (92.7%, 90.1%, 90.0%, and 91.7%, respectively) and the rates were also very high in the dark. This finding is consistent with the results of the difficulty of pesticide degradation based on their half-lives, indicating that the residues of these four fungicides in the soil are persistent.

Leaching experiments help to study the vertical migration of pesticides during processes such as greenhouse soil irrigation. Chlorantraniliprole, metalaxyl, nitenpyram, diethofencarb, acetamiprid, carbendazim, and oxadixyl were easily leached by aqueous solutions, which was related to their high water solubility or groundwater ubiquity score (GUS) and high mobility in the soil (K_{oc} range: 60–343 mL/g). The seven pesticides with a high leaching proportion in aqueous solution were neonicotinoid (nitenpyram and acetamiprid), o-formamide benzamide (chlorantraniliprole), benzimidazole (carbendazim), phenylamide (oxadixyl), benzamide (metalaxyl), and carbamate (diethofencarb) pesticides. Neonicotinoid insecticides are widely used owing to their high water solubility (water solubility of nitenpyram: $5.70 \times 10^5 \text{ mg/L}$; water solubility of acetamiprid: $2.95 \times 10^3 \text{ mg/L}$) and rapid degradation characteristics (half-life: 2.5–4.1 days). The amount of neonicotinoid insecticides leached generally increases with increasing soil moisture content (Radolinski et al. 2018). Highly water-saturated soil is conducive to the leaching of neonicotinoid insecticides, which then migrate vertically and penetrate soil aquifers (Menon et al. 2021). Metalaxyl also has high leaching mobility (GUS = 2.06), but its degradation efficiency in soil is low (half-life: 104–110 d), indicating a high possibility of groundwater pollution (Kookana et al. 1995).

Emamectin benzoate, buprofezin, avermectin B1A, difenoconazole, pyraclostrobin, and trifloxystrobin were difficult to leach out of aqueous solutions, which is related to their low GUS values (range: 0.05–1.21). In addition, the high K_{oc} values of these six pesticides (range: 2377–283,000 mL/g) indicate high absorption rates and extremely weak mobility in the soil. Therefore, we speculated that these six pesticides remained on the surface of the soil after application and would not enter the deep soil. Avermectin B1A is strongly adsorbed onto various types of soil, especially soil rich in organic matter and clay, illustrating a low probability of avermectin B1A leaching from soil and contaminating groundwater (GUS: – 1.10–0.08) (de Oliveira Ferreira et al. 2019). Similarly, the water solubility of emamectin benzoate (24 mg/L) is extremely low, in addition to the characteristic of being difficult to leach in soil (Takai et al. 2001). The solvent extraction of emamectin benzoate can be promoted by adding organic solvents (e.g., ether, acetone, ethyl acetate, or water) that are miscible with water (Zhang et al. 2013).

Pesticides applied in fields are likely to be absorbed by soil particles or dissipated through microbial degradation, chemical hydrolysis, or photodegradation (Kaur et al. 2021). In the present study, we found that the residues of many pesticides in the soil, such as avermectin B1A and diethofencarb, were greatly affected by light. In addition, direct photolysis was found to be the main degradation mode of pyraclostrobin (Fan et al. 2020), and sunlight irradiation improved the degradation rate of buprofezin (Fenoll et al. 2011). The photodegradation rates of pesticides in soil are affected by various factors. For example, the half-life of avermectin B1A in the dark in four types of Brazilian soils with different textures (clay, sandy-clay, sandy, and sandy-clay-loam) was between 9 and 13 d, which may be related to the soil texture (de Oliveira Ferreira et al. 2019). Microbial degradation is extremely important in greenhouses with suitable temperatures and moist soils. The maximum time required to reduce the content of avermectin B1A by 50% in non-sterile soil was 4 d, whereas the concentration of avermectin B1A in sterile soil did not decrease after 37 d under dark conditions, suggesting that aerobic microbial degradation may be an important mechanism leading to the degradation of avermectin B1A in soil (Dionisio and Rath 2016). In addition, the environmental behavior of pesticides in soils under greenhouse conditions differs from that in the open. Dimethomorph, imidaclothiz, lufenuron, methoxyfenozide, pyridaben, and spinetoram degrade rapidly under open-field conditions and their residual levels are much lower than those under greenhouse conditions (Tang et al. 2021). Paclobutrazole and uniconazole were also more persistent in greenhouses than in the open soil. Light and the leaching effect of rainfall in an open environment are the reasons for differences in dissipation under greenhouse and open field conditions (Wu et al. 2013). However, pesticides in greenhouse soils can evaporate into the air or leach into groundwater (Liu et al. 2021), and pesticide residues may pose a threat to drinking water sources and have adverse health effects (Swartjes and Van der Aa 2020). Many factors affect groundwater infiltration by pesticides, including the physical and chemical properties of the pesticides, soil texture, organic matter content, soil permeability, microbial content, application methods and amounts, and climate change (Li 2018). The present study found that 11 out of 17 pesticides studied had a residual rate exceeding 50% after 14 d of light degradation, and six out of 17 pesticides were difficult to leach by aqueous solution. This indicates that there may be severe pesticide residues in greenhouse soil in Shouguang and further explains our previous monitoring results for pesticide residues in greenhouse soil in Shouguang (Wu et al. 2020). For example, the residual concentrations of

neonicotinoid insecticides (nitenpyram and acetamiprid) exhibited the following trend: top > middle > lower soil layers. The potential risk of groundwater contamination increases when certain pesticide properties overlap, such as highwater solubility (> 30 mg/L), high persistence (half-life > 3 months), and low soil adsorption ($\log K_{oc} < 2$) (Aliste et al. 2021; Gavrilesco 2005).

In the present study, nitenpyram, diethofencarb, acetamiprid, carbendazim, and oxadixyl were found to be easily leachable and degradable pesticides, and their degradation in soil may produce toxic chemicals. Density functional theory calculations and ecological risk evaluations of carbendazim showed that when oxidized by hydroxyl radicals in aqueous solution, the acute toxicity of the obtained degradation products decreased to varying degrees compared with that of carbendazim (Liu et al. 2022). A new non-thermal technology (dielectric barrier discharge cold plasma) was used to degrade carbendazim in an aqueous solution, and the toxicity of its four degradation products (including one oxidation degradation product and three cleavage products of the benzimidazole heterocyclic ring) was much lower than that of carbendazim (Wang et al. 2023). After prolonged irradiation by a solar simulator, the toxicity of the photoproducts of carbendazim, the carbendazim N-C5 dimer, and other low-molecular-weight products was lower than that of carbendazim (Jornet et al. 2013). Photodegradation can reduce the toxicity of carbendazim; however, the photodegradation products of many pesticides are more toxic. Approximately 50% of the degradation products of imidaclothiz (a neonicotinoid pesticide) are more toxic to aquatic organisms such as *Daphnia magna* and *Danio rerio* than is the parent chemical (Ma et al. 2021). Therefore, more attention should be paid to the toxicity of the degradation products of easily leachable and degradable pesticides in soil.

Chlorantraniliprole and metalaxyl are pesticides that are easily leached but not easily degraded, whereas boscalid, hexaconazole, tebuconazole, and isoprothiolane are not easily leachable and do not easily degrade, and their potential risk of contaminating groundwater is high. Among different drinking water sources (surface water, groundwater, water at public pumping stations, surface water chemically treated at household level, harvested rainwater, and bottled water) in rural areas of the Mekong River delta in Vietnam, isoprothiolane (maximum concentration: 8.49 $\mu\text{g/L}$) was detected in almost all water samples analyzed (Chau et al. 2015). On monitoring groundwater in northwestern Italy, the concentrations of seven monitored pesticides, including chlorantraniliprole and metalaxyl, in 30% of wells were found to be higher than the environmental quality standard for groundwater (0.1 $\mu\text{g/L}$) (Marsala et al. 2020). The most frequently

detected pesticides in groundwater in a vineyard area of La Rioja (Spain) were metalaxyl, tebuconazole, and boscalid (Manjarres-Lopez et al. 2021). Metalaxyl exhibited a moderately mobile or mobile potential in 86% and 14% of natural soils, respectively, and tended to migrate to deeper soil layers, suggesting that the continuous application of metalaxyl could result in its leaching from the soil to groundwater (Andrades et al. 2001). The presence of metalaxyl in shallow groundwater (<40 m below the surface) collected from 54 monitoring wells across Long Island, New York, indicated its intensive use in agricultural environments (Fisher et al. 2021). The highest detected concentration of metalaxyl (89.58 ng/L) was in different water samples (groundwater, Wenyu River, sewage treatment plants, and hospitals) in Beijing, with a detection rate of 100% (Zhang et al. 2021). Fortunately, at their current concentrations, pesticides found in groundwater in multiple regions worldwide do not pose a potential health risk to humans.

Avermectin B1A, emamectin benzoate, trifloxystrobin, pyraclostrobin, and buprofezin are easily degraded but not easily leachable pesticides, and their degradation processes (photolysis, hydrolysis, and biodegradation) often occur in the upper soil layer. Avermectin B1A and its metabolites do not migrate easily in soil owing to their low solubility and strong adsorption with organic matter ($K_{oc} \geq 4000$ mL/g). They are mostly degraded in the environment through photodegradation and aerobic decomposition by soil organisms (Wratten and Forbes 1996). In all experimental soils originating from India and Germany, the high partition coefficient for trifloxystrobin demonstrated its strong adsorption (Banerjee et al. 2006). Field leaching data showed that trifloxystrobin remained in the top 80 cm after 16 weeks of treatment, indicating that the possibility of trifloxystrobin leaching was extremely low (Dusek et al. 2010). Another field study on trifloxystrobin in soil at different latitudes found that photolysis may be the primary dissipation route of trifloxystrobin, and sunshine hours may have a significant effect on trifloxystrobin dissipation (Wang et al. 2015). Similarly, most pyraclostrobin residues remain in the topsoil even under high rainfall conditions; therefore, the migration potential of pyraclostrobin to lower soil depths is almost negligible (Reddy et al. 2013). Many studies have focused on the biodegradation of non-leachable but easily degradable pesticides in topsoil. Trifloxystrobin, buprofezin, and pyraclostrobin can be degraded by *Hyphomicrobium* sp. (bacterial strain B1) (Jiang et al. 2022), *Rhodococcus* sp. (YL-1) (Li et al. 2012), or *Pseudomonas* sp. (DFS35-4) (Chen et al. 2011), HI2, and HI6 (Chen et al. 2018), respectively. Among them, the DFS35-4 strain could degrade 50 mg/L buprofezin by over 70% in 3 d (under conditions of pH 5.0–10.0

and temperature 20–30 °C) (Chen et al. 2011), and the microorganisms HI2 and HI6 degraded more than 99% of pyraclostrobin within 5 d ($C_0 = 100$ mg/L) (Chen et al. 2018), exhibiting excellent microbial degradation effects. The toxic effects of the products formed by various pesticide degradation reactions on the soil surface are also of concern. The results of field experiments in Beijing and Shandong Province showed that the main residual compound in tomatoes was trifloxystrobin, whereas its metabolite trifloxystrobin acid (CGA321113) was the primary compound in the soil (Wang et al. 2014). The final residual levels of trifloxystrobin and its metabolites in tomatoes were lower than the EU maximum residue limit (0.5 mg/kg), and the residue of the metabolites in the soil samples was higher than that of its parent compound (Wang et al. 2014). The simulation of molecular docking suggested that the CDocker interaction energy of pyraclostrobin (-44.71) was lower than that of its intermediate products (> -30.00), Methyl N-phenyl-carbamate and 1-(4-chlorophenyl)-3-hydroxy-1H-pyrzole, indicating that the intermediates were less toxic than pyraclostrobin (Fan et al. 2020). Avermectin B1A in soil is not easily taken up by plants and is not bioconcentrated by fish (calculated steady-state bioconcentration coefficient of 52, indicating rapid depuration) (Halley et al. 1993). Overall, further research is required on the degradation process of these non-leachable but easily degradable pesticides in soil and the physicochemical properties of the degradation products.

Difenoconazole is a pesticide that is difficult to leach and degrade; therefore, it can easily accumulate in crops. Difenoconazole was absorbed and accumulated in rice plants (*Oryza sativa* L.) under soil-treated conditions; the concentrations of difenoconazole in roots (15.6 and 79.1 mg/kg dw) were much higher than that in leaves (0.23 and 3.4 mg/kg dw) (Ge et al. 2017). The deposition amount of difenoconazole increased gradually with increasing dosage, and its accumulation order was upper leaf > lower leaf > upper stem > lower stem > cultivated soil > fruit (Chen et al. 2021). Following excessive accumulation in plant tissues, difenoconazole is rapidly degraded by glutathione S-transferase or oxidative damage is reduced by increasing the content of flavonoids and anthocyanins in leaves, thereby achieving self-protection (Li et al. 2023).

In the present study, the photodegradation and leaching of typical pesticides in tomato greenhouse soils located in Shouguang, Shandong Province, East China, were investigated. The effect of light on pesticide degradation was explored by comparing the half-lives of pesticides under light and dark conditions, and the degree of pesticide degradation in the soil was analyzed based on the residual rate after treatment. Aqueous solutions and

organic solvents were used to leach pesticides present in the greenhouse soils. The vertical migration ability of various pesticides in the soil was analyzed according to the leaching content of pesticides in different volumes and types of leaching solutions, and the potential risk of groundwater pollution from pesticides applied in tomato greenhouses was explored. In addition, this study combined the degradation and migration of pesticides in soil to analyze the environmental behavior and toxicity of different types of pesticides, thereby providing a scientific basis for the agricultural application of pesticides. However, this study had some limitations. First, only the effects of dark and natural light environments on pesticide degradation were considered when conducting the photodegradation research, and UV photodegradation experiments were excluded. However, the natural light design is consistent with the reality of conventional agricultural production in tomato greenhouses. Second, the half-lives of certain pesticides in the dark were shorter than those in light, which may be because the simulation time under dark conditions was shorter, and therefore, may not adequately reflect the long-term changes in pesticides in soil. Further experiments should extend the dark reaction time, better fit the kinetic equation of pesticide degradation, and provide more accurate data on the photodegradation of pesticides in greenhouse soils. Finally, as mentioned previously, many factors affect the degradation and leaching of pesticides, such as soil texture and organic matter content. The lack of analyses of these parameters in this study made it impossible to determine the extent to which pesticide degradation and leaching processes were affected. However, the samples used for inter-comparison in this study were all from the same well-mixed soil sample, which strictly maintained the consistency of variables other than the independent variables. The results of this study will be useful for studying the environmental processes of pesticides in greenhouse soils.

Conclusion

To study the migration and degradation behavior of pesticides, photodegradation and leaching experiments were conducted using 17 common pesticides in tomato greenhouse soils in Shandong Province, East China. The half-lives of avermectin B1A, emamectin benzoate, buprofezin, nitenpyram, acetamiprid, trifloxystrobin, pyraclostrobin, diethofencarb, carbendazim, and oxadixyl were less than 30 d, and these pesticides were easily degradable. The residue rates of nitenpyram, acetamiprid, trifloxystrobin, and diethofencarb were all lower than 10% after 14 d of photodegradation, indicating that these pesticides could achieve good

degradation effects under light conditions. The half-lives of emamectin benzoate, pyraclostrobin, and metalaxyl under light conditions were 86.6%, 68.5%, and 94.5%, respectively, of their half-lives in the dark, indicating that their photodegradation rates in soil were high. More than 90% of chlorantraniliprole, metalaxyl, nitenpyram, diethofencarb, acetamiprid, carbendazim, and oxadixyl were leached using an aqueous solution. Avermectin B1A, emamectin benzoate, trifloxystrobin, difenoconazole, pyraclostrobin, and buprofezin, were difficult to leach from aqueous solutions and may not enter the deep soil. The leaching potential of leachable pesticides was nitenpyram >> metalaxyl > acetamiprid > carbendazim > diethofencarb \approx chlorantraniliprole > isoprothiolane > oxadixyl > boscalid \approx tebuconazole > hexaconazole. The environmental behavior analysis of pesticides indicates that the toxicity of the degradation products of pesticides that are easily leachable and degradable should be given more attention. The potential risks of groundwater pollution should be explored for leachable pesticides that are not easily degradable. Further research should be conducted on the accumulation in crops of pesticides that are difficult to leach and degrade.

Abbreviations

LOD	Limit of detection
LOQ	Limit of quantitation
GUS	Groundwater ubiquity score

Supplementary Information

The online version contains supplementary material available at <https://doi.org/10.1186/s13717-024-00503-x>.

Additional file 1: Table S1. Commonly used pesticides and registered quantities of pesticides in vegetable areas in Shouguang facilities. **Table S2.** Elution gradient of the mobile phase in liquid chromatography. **Table S3.** Instrumental analysis parameters of the target pesticides. **Table S4.** Recovery of typical pesticides in soil. **Figure S1.** Structural formulas of the 17 target pesticides.

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Author contributions

LH wrote the paper and performed the formal analysis. RW designed the sampling and methodology, conducted experimentation, and performed the formal analyses. CL collected samples and conducted experiments. CW and YL collected the samples. FX reviewed and supervised this study. All the authors have read and approved the final version of the manuscript.

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Availability of data and materials

All data generated or analyzed in this study are available from the corresponding author upon reasonable request.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

All authors agreed and approved the manuscript for publication in *Ecological Processes*.

Competing interests

The authors declare that they have no competing interests.

Author details

¹MOE Laboratory for Earth Surface Processes, College of Urban and Environmental Sciences, Peking University, Beijing 100871, China. ²Department of Ecology and Environment of Shanxi Province, No. 7, North Section of Binhe West Road, Taiyuan 030024, Shanxi, China.

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