Environ Monit Assess (2016) 188: 363
DOI 10.1007/s10661-016-5372-6

Desorption and mobilization of three strobilurin fungicides in three types of soil

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Received: 26 December 2015 / Accepted: 16 May 2016 / Published online: 24 May 2016

Abstract Phenamacril (JS399-19 with independent intellectual property developed by China), azoxystrobin, and kresoxim-methyl are strobilurin fungicide. Due to their broad spectrum and good control of most of known fungi, strobilurin fungicide has been widely used in agriculture management. Thus, it is important to evaluate their environmental behaviors particularly in soils and underground water. In this study, the sorption/desorption and mobility of strobilurin fungicides in three Chinese soils (Jiangxi red soil, Taihu paddy soil, and Northeast China black soil) were conducted using comprehensively analytic approaches including batch experiment and soil thin-layer chromatography. The strobilurin fungicides were hard to be adsorbed in Jiangxi red soil but had medium adsorption capability in Tanhu paddy soil and Northeast China black soil, while the desorption of three strobilurin fungicides ranked in the order of Jiangxi red soil > Taihu paddy soil > Northeast China black soil. Soil properties including soil organic matter (SOM), pH, and cationic exchange capacity (CEC) affected the adsorption/desorption of the fungicides. Azoxystrobin and kresoxim-methyl had weak mobility in the soils. JS399-19 was moderately mobile in Jiangxi red soil but was not easily moved in Taihu paddy soil and Northeast China black soil. Due to their weak mobility in soils, these strobilurin fungicides tended to remain in the soil phase but not to shift downward to underground water. As azoxystrobin and JS399-19 had a long retention period in soil, there may become persistent residues in the soil environment.

Keywords Soil · Strobilurin fungicide · Adsorption · Desorption · Mobility

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Introduction

Strobilurins were first discovered in 1977 by a group of German scientists. Since then, strobilurin fungicides have taken an important position in pesticide chemistry and become one of the most important classes of fungicides due to their stronger biological activities and lower toxicity (Gullino et al. 2002; Wang et al. 2015). Strobilurin is a group of agricultural fungicides for its unique mechanism, good environmental compatibility, and actual application to improve crop yield and quality (de Souza et al. 2009; Xu et al. 2014). They have a wide fungicidal spectrum and show good control of almost all known fungi. Recently, strobilurin fungicides have become the largest fungicide family in production and agronomic practice (Reuveni 2000; Sudisha et al. 2005). For example, azoxystrobin and kresoxim-methyl are among the typical strobilurin fungicides, and phenamacril (or JS399-19) is also a strobilurin fungicide with independent intellectual property developed by China (Li et al. 2008).

As the market share and widespread application of strobilurin fungicides are progressively rising, the negative influence of the fungicides on the environment has been emerging. The residues of some strobilurin fungicides in environment and soil were detected (Flores et al. 2007; Campillo et al. 2010; Dornellas et al. 2013; Abdelraheem et al. 2015). But, little is known about its environmental behaviors (e.g., the adsorption/desorption, leaching, and degradation as well as other environmental factors), particularly for azoxystrobin, kresoxim-methyl, and phenamacril. Hence, there is an urging need to investigate the fate of azoxystrobin, kresoxim-methyl, and phenamacril in agronomic soil and to develop strategies to minimize its residues and toxic effects on crop production.

As more than 80 % of the chemical pesticides eventually reside in soil after field application, even sprayed on the leave of crops and weeds, soil becomes the major sink for bulk of globally applied pesticides (Arias-Estévez et al. 2006; Fang et al. 2009; Pateiro-Moure et al. 2013). The environmental risk of pesticides mainly depends on its mobility in the soil (Rodríguez-Cruz et al. 2006; Jiang et al. 2011). The process of adsorption, desorption, and leaching plays a critical role in the environmental behavior of chemical pesticides in natural environments (Pateiro-Moure et al. 2010; González-Rodríguez et al. 2011). The efficiency of the process is dependent on many factors such as properties of the pesticide used, dissolved organic matter, soil properties, and environmental conditions (Kah and Brown 2006; Margoum et al. 2006; Pateiro-Moure et al. 2009a, b; Chen et al. 2010; Ding et al. 2011). Among the parameters, soil properties such as soil organic matter, clay content, pH, and CEC are predominant (Rodríguez-Cruz et al. 2006; Jiang et al. 2011). In this study, we investigated three Chinese soils with their different capabilities of adsorption, desorption, and mobility of JS399-19, azoxystrobin, and kresoxim-methyl. Influence of soil properties on adsorption and desorption was analyzed. Thus, the aim of the work was to figure out the mobility behavior of three strobilurin fungicides in the soils. These results may help our assessment of environmental risks or safety and efficient employment of the fungicides in agricultural practice.

Materials and methods

Materials and instruments

Strobilurin fungicides azoxystrobin, kresoxim-methyl, and phenamacril (or JS399-19) were used with a purity of 95.0, 97.5, and 95.0 %, respectively. Standard stock solutions of the strobilurin fungicides at 1000.0 mg L^{-1} were prepared with methanol. When used, each stock solution was diluted and merged. The tested soils including Jiangxi red soil, Taihu paddy soil, and Northeast black soil in China were collected, dried, ground, and sieved with 0.25 mm screen. Each type of soil was sterilized. The physical and chemical characteristics of each soil were presented in Table 1.

Analytical grade calcium chloride and ethyl acetate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Acetonitrile (analytically pure) was purchased from Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). Methanol and acetonitrile of high-performance liquid chromatography (HPLC) grade were purchased from Merck Chemical Co., Ltd. (Darmstadt, Germany).

HPLC measurements were performed using Waters 2695 liquid chromatography with 2996 photodiode array detector (HPLC-PAD) (Waters Technologies, USA). Excella-E24 constant-temperature vibrator (Excella E24 Incubator Shaker Series, USA) and CR22GII high-speed centrifuge (Hitachi, Japan) were employed for sorption/desorption test. N-1001 rotary evaporator (EYELA, Japan) was used to concentrate solvents. Chromatographic tank (5 L) was used for thin-layer chromatography (TLC).

Sorption and desorption experiments

The sorption and desorption experiments were carried out using a batch equilibrium method according to the Organization for Economic Co-operation and Development Testing Guideline 106 (OECD 2000). Five grams of each soil sample was mixed with 50 mL of 0.01 M $CaCl_2$ solution with the three strobilurin fungicide-merged concentrations (C_0) ranging from 0.5, 1.0, 1.5, and 2.0 mg L^{-1} in 150-mL conical flasks with stopper. The conical flasks with stopper were agitated in a

Table 1 Basic properties of the soils used in this study

Soil type	pH	Organic matter (g/kg)	Cation exchange capacity (cmol(+)/kg)	Soil particle composition			Texture
				Clay (%)	Silt (%)	Sand (%)	
Jiangxi red soil	5.29	9.94	10.6	15.9	67.2	16.9	Clay loam soil
Taihu paddy soil	6.23	12.6	17.4	19.4	75.8	4.8	Loam soil
Northeast China black soil	7.86	17.0	22.9	15.6	73.1	11.3	Loose sand soil

Soil particle composition represents quality score

horizontal shaker at 200 rpm and 25 ± 1 °C for 24 h. The soil suspensions were moved into the centrifuge tubes for centrifugation at 6000 rpm min^{-1} for 20 min. The supernatants were passed through 0.45-μm membrane filters and were determined for contents of pesticides by HPLC. Desorption experiments were performed immediately after the sorption experiments. All supernatants were thoroughly removed immediately. The remaining soils were used for desorption studies. Three strobilurin fungicide-free fresh $CaCl_2$ solution (0.01 M, 40 mL) was added to each remaining soil. Shaking, subsequent separation of soil and aqueous phase, and quantification analyses of three strobilurin fungicides by HPLC were conducted as described above. The sorption and desorption experiments were repeated in triplicate. After sorption/desorption tests, the amount of three strobilurin fungicides sorbed on the soil was calculated from the difference between the initial and final solution concentrations (Cao et al. 2008).

Soil thin-layer chromatography

Ten grams of soil were mixed with 12 mL distilled water and spread onto 20 × 10 cm glass plates. The thickness of the soil layer was within 0.5–0.7 mm. The air-dried plates were marked with two horizontal lines in a distance of 2 cm (baseline) and 18 cm (foreland) from the base. A 10-μL droplet of 300 mg L^{-1} fungicide-mixed solution prepared in acetone was spotted onto the baseline of plate with the aid of a microsyringe. The plates were placed in closed individual glass chromatographic chambers and with the gradient in about 30°. Distilled water was used as developing solvents. After the developing solvents migrated to the distance of 18 cm from the baseline, the plates were taken out from glass chromatographic chambers and laid flat to dryness at room temperature. Soil thin layer was divided into eight segments from baseline to foreland. The strobilurin residues in each soil segment were extracted and quantified. The mobility distribution coefficient (R_f) and recovery (Re) of each fungicide on plate were calculated as the following formulas:

$$R_f = L/L_{\max} \tag{1}$$

where L is the moving distance of fungicide from the start point to chromatographic spot center (mm) and $L_{\max}$ is the moving distance of developing solvent from the start point (mm).

$$Re(\%) = \sum_{i=1}^{n} m_i \Big/ M_0 \times 100 \tag{2}$$

where m_i is the amount of fungicide residue in each segment (mg); M_0 is the total amount of added pesticides (mg); i is the number of segments, i = 1, 2, 3, 4, 5, 6, 7, and 8, representing soil segment at 0~2, 2~4, 4~6, 6~8, 8~10, 10~12, 12~14, and 14 ~ 18 cm, respectively.

Determination of three strobilurin fungicides

Water sample was passed through 0.45-μm membrane filters and determined directly for pesticide content by HPLC. Soil sample was added with 30 mL acetonitrile and shaken at 200 rpm and 25 ± 1 °C for 1 h. Soil sample was centrifugated and filtrated. The process was performed for three times. Extracting solution was concentrated by rotary evaporation to remove organic solvent. The rest aqueous phase was extracted with 30 mL ethyl acetate for two times. The extracting solution was concentrated to dry by rotary evaporation. The residue was dissolved with acetonitrile, filtrated through a 0.45-μm microporous membrane, and measured by HPLC.

HPLC measurement of samples was performed using Waters HPLC-PAD with an XterraRRP18 column (250 × 4.6 mm, 5 μm) at 25 ± 5 °C. Acetonitrile/water (55:45, *v*/*v*) was used as mobile phase with a constant flow of 0.80 mL min^{-1}. Aliquots of 10 μL sample extract were injected. Under detectable conditions, the retention times and detection wavelengths of JS399–19, azoxystrobin and kresoxim-methyl were 5.77 min and 290 nm, 8.95 min and 220 nm, 8.95 min and 220 nm, respectively.

Results and discussion

Analysis of three strobilurin fungicides in soil

To ensure that JS399-19, azoxystrobin, and kresoxim-methyl were well separated from environment matrix, the spiked recoveries of three strobilurin fungicide samples in soil were investigated. Under optimal operating conditions of HPLC-PAD, the spiked recoveries of JS399-19, azoxystrobin, and kresoxim-methyl at 0.05~5.00 mg kg^{-1} were 85.0~89.8, 85.4~89.3, and 86.7~91.0 % and the relative standard deviations (RSDs) were 0.16~6.01, 2.13~3.46, and 5.11~8.02 %, respectively. These results indicated that the developed method could be used for accurate quantification of three strobilurin fungicides in soil.

Adsorption of three strobilurin fungicides

Adsorption of three strobilurin fungicides in different soils

To investigate the environmental behavior and fate of three strobilurin fungicides in different soils, the sorption and desorption behaviors of three strobilurin fungicides were investigated. If a pesticide is weakly adsorbed in soil, it usually has strong mobility and diffusivity in soil and, thus, easily goes downward and contaminates ground water and surrounding environment (Liu et al. 2010; Ding et al. 2011). The batch equilibrium method provides a basis for environmental safety assessment and registration of pesticide and is used to determine the adsorption of three strobilurin fungicides in soil.

Sorption kinetics study indicated that a 24-h period of equilibration was adequate to attain the sorption equilibrium for the three strobilurin fungicides. The isotherm model of Freundlich was chosen to evaluate the sorption process of the strobilurin fungicides on soil, as shown in the following equation:

$$Cs = K_d \times Ce^{1/n} \tag{3}$$

where K_d (mL g^{-1}) is the Freundlich sorption coefficient; $1/n$ is the linearity factor, Cs (mg kg^{-1}) is the adsorption concentration of pesticide on soil; and Ce (mg L^{-1}) is the equilibrium concentration of pesticide in solution. The values of K_d and $1/n$ from Eq. (3) were calculated by regression for the sorption of three strobilurin fungicides on the three different soils. The adsorption isotherms and coefficients of the strobilurin fungicides in three soils were given in Table 2 and Fig. 1. The regression coefficient R^2 ranged from 0.9205 to 0.9857, indicating that Freundlich isotherms were appropriate to describe the sorption of three strobilurin fungicides on the soils.

Adsorption coefficient (K_d) represents adsorption degree and capability of pesticide in soil (Tang et al. 2009; Liu et al. 2010; Gao et al. 2014). The higher K_d value indicates the strong pesticide adsorption and weak mobility of the pesticides. The three strobilurin fungicides show much different adsorption capabilities on the three different soils. The adsorption Freundlich coefficients (K_d) for the strobilurin fungicides on the soils were sorted as follows: Northeast China black soil > Taihu paddy soil > Jiangxi red soil. The coefficients varied from 3.65 to 46.5 (Table 2). According to the pesticide adsorption grades stated in Test Guidelines on Environmental Safety Assessment for Chemical Pesticides (USEPA. 2008a; USEPA. 2008b), when K_d is less than 5, it is very difficult to adsorb; when K_d is 5~20, it is difficult to adsorb; when K_d is 20~50, it is medium adsorption. Under the conditions, JS399-19 (K_d 5.20) and kresoxim-methyl (K_d 5.77) were difficult to adsorb on to the Jiangxi red soil and had medium adsorption capability in Tanhu paddy soil and Northeast China black soil (K_d 29.4~46.5). Azoxystrobin was very difficult to adsorb in Jiangxi red soil (K_d 3.65) and had medium adsorption capability in Taihu paddy soil (K_d 20.0) and Northeast China black soil (K_d 35.5) (Table 2).

Effect of soil property on adsorption

The correlation between the pesticide adsorption coefficient (K_d) in soil and the soil physicochemical property (Xu et al. 2005; Porfiri et al. 2015) can be used to predict

Table 2 Parameters of Freundlich equation of three strobilurin fungicides adsorbed in soils

Pesticide variety	Soil type	K_d	n	R^2
JS399-19	Jiangxi red soil	5.20	0.7065	0.9857
	Taihu paddy soil	29.4	0.9217	0.9470
	Northeast China black soil	46.5	0.9024	0.9733
Azoxystrobin	Jiangxi red soil	3.65	0.874	0.9685
	Taihu paddy soil	20.0	1.070	0.9726
	Northeast China black soil	35.5	0.954	0.9732
Kresoxim-methyl	Jiangxi red soil	5.77	1.241	0.9346
	Taihu paddy soil	35.8	1.265	0.9567
	Northeast China black soil	46.1	1.1805	0.9205

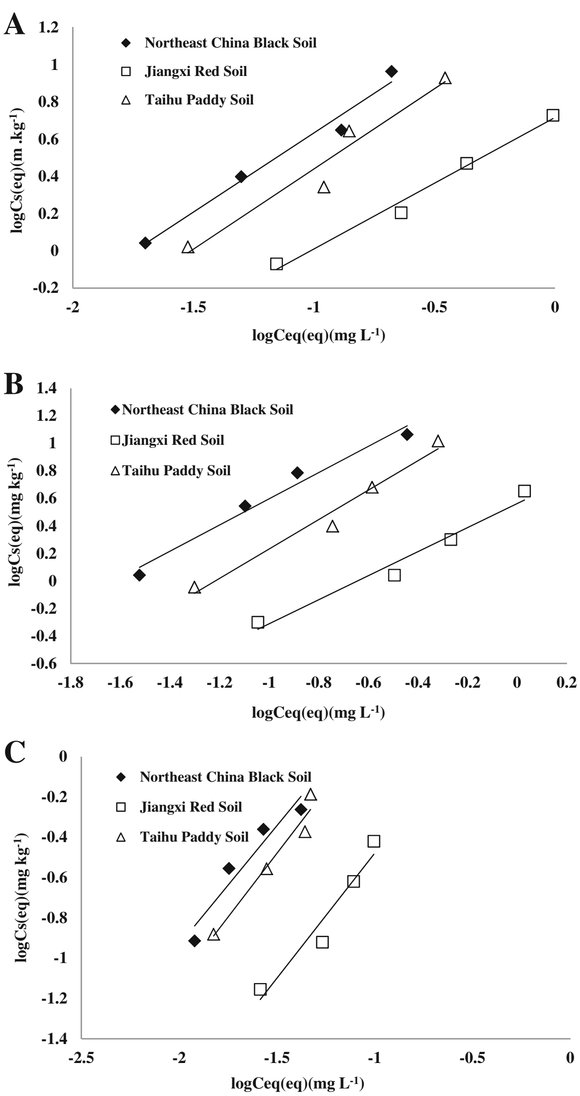

Fig. 1 Sorption isotherms of JS399-19 (**a**), azoxystrobin (**b**), and kresoxim-methyl (**c**) on soil

the influence of soil property on the adsorption of the strobilurin fungicides in different soils. The values of soil pH, soil organic matter (SOM), and cation exchange capacity (CEC) were close to the correlation values of adsorption coefficient (Kd) for the three pesticides (Table 3), suggesting that the influences of soil pH, SOM content, and CEC on the adsorption of three strobilurin fungicides were close to each other in soil. In the strobilurin fungicides, the linear correlation of Kd with SOM, soil pH, and CEC was better for JS39-199 and azoxystrobin than for kresoxim-methyl (Table 3). Compared with soil pH, the correlation of Kd with CEC and SOM was better for the strobilurin fungicides.

Pesticide adsorption in soil was primarily related to soil physicochemical property and pesticide property, of which soil organic matter (SOM) content is an important factor that influences pesticide adsorption (Cao et al. 2008; Liu et al. 2012). SOM usually contains a certain amount of active functional groups, such as carboxyl, phenolic hydroxyl, carbonyl, ethanol-hydroxyl, methyl, etc. Nearly all organic pesticide molecules can react with the active functional groups in SOM to produce hydrogen bonds (Cao et al. 2008; Jiang et al. 2011). Besides, the results of IR, ESR, and fluorometric analyses indicated that there also exists other action mechanisms between pesticides and organic matters, such as

Table 3 The linear correlation (R^2) of F adsorption parameter and soil properties

Chemical	JS399-19	Azoxystrobin	Kresoxim-methyl
pH	0.9375	0.9716	0.8269
Organic matter	0.9902	0.9998	0.9261
CEC	0.9986	0.9979	0.9548

Table 4 Free energy change for adsorption of three strobilurin fungicides in soils

Pesticide variety	Soil type	K_d	K_{oc}	ΔG/kJ mol^{-1}
JS399-19	Jiangxi red soil	5.20	902	−16.86
	Taihu paddy soil	29.4	4023	−20.56
	Northeast China black soil	46.5	4716	−20.96
Azoxystrobin	Jiangxi red soil	3.65	633	−15.98
	Taihu paddy soil	20.0	2737	−19.61
	Northeast China black soil	35.5	3600	−20.29
Kresoxim-methyl	Jiangxi red soil	5.77	1001	−17.12
	Taihu paddy soil	35.8	4898	−21.05
	Northeast China black soil	46.1	4675	−20.94

covalent bond, ionic bond, coordinate bond, van der Waals' force, charge dipole-dipole bond, etc. (Deng et al. 2007). In the tested soils, SOM content ranks in the order of Northeast China black soil > Taihu paddy soil > Jiangxi red soil (Table 1). The adsorption of the strobilurin fungicides was strongest in Northeast China black soil, weakest in Jiangxi red soil, and moderate in Taihu paddy soil (Fig. 1). The adsorptions of the strobilurin fungicides were positively related to the SOM content. The results were consistent with the previous reports (Rütters et al. 1999; Schwab et al. 2006; Wang and Keller 2009). In general, if the content of soil clay was higher, the soil particle was smaller and the specific surface area was larger and the adsorption quantity of pesticide was higher (Kim et al. 2012). In our study, the soil clay content was consistent with the ranking of adsorption quantity for Taihu paddy soil and Jiangxi red soil (Table 1 and Fig. 1). However, the soil clay content was lower in Northeast China black soil than that in Jiangxi red soil, but the adsorption capability was stronger in Northeast China black soil than that in Jiangxi red soil (Table 1 and Fig. 1), suggesting that SOM was a more influential factor than the soil clay content for the adsorption of strobilurin fungicides in Northeast China black soil.

Adsorption free energy ($\triangle G$) of three strobilurin fungicides

Adsorption free energy ($\triangle G$) is an important parameter that reflects adsorption property in soil. The $\triangle G$ value was used to evaluate the adsorption type of the strobilurin fungicides on soil. The relation between $\triangle G$ of pesticide in soil and organic adsorption coefficient (K_{oc}) is presented by the following equation: $\triangle G = -\mathrm{RTln}K_{oc}$. The sorption coefficient normalized to the organic carbon content of the soil (K_{oc}) in unit soil was also calculated by the equation: $K_{oc} = K_f/\mathrm{SOM} \times 100$. When the absolute value of $\triangle G$ is ≤40 kJ mol^{-1}, it implicates a physical adsorption. Otherwise, it is a chemical adsorption. A pesticide with physical adsorption usually has a high adsorption equilibrium speed and its adsorption is reversible, while a pesticide with chemical adsorption has a low adsorption

Table 5 Mobility of three strobilurin fungicides in soils

Soil type	GUS (ground ubiquity score)								
	JS399-19			Azoxystrobin			Kresoxim-methyl		
	DT50/day	KOC	GUS	DT50/day	KOC	GUS	DT50/day	KOC	GUS
Jiangxi red soil	330	902	2.63	407	633	3.13	0.56	1001	−0.25
Taihu paddy soil	107	4023	0.80	277	2737	1.37	0.67	4898	−0.05
Northeast China black soil	96.3	4716	0.65	223	3600	1.04	0.63	4675	−0.07

equilibrium speed and its adsorption is irreversible (Gao et al. 2014). When it is chemical adsorption, the adsorption easily passivates and becomes inactive (Porfiri et al. 2015). $\triangle G$ for the strobilurin fungicides in different soils showed negative values (Table 4), indicating that their adsorption belonged to the exothermic reaction and physical adsorption. The lower temperature was beneficial to the adsorption.

Influence of three strobilurin fungicides on ground water

In rural areas, the quality of drinking water is an important indicator of social and economic development. In many rural areas of China, drinking water is still directly taken from ground water without any treatment (Ding et al. 2015). As pesticides have been widely used, more

Table 6 Desorption of three strobilurin fungicides in different soils

Pesticide	Soil type	M_0 (μg)	M_{ad} (μg)	M_{de} (μg)	Desorption rate (%)	Average (%)
JS399-19	Jiangxi red soil	7.75	4.25	2.04	47.9	45.6
		19.5	8.00	3.81	47.6	
		36.25	14.8	7.12	48.1	
		75.75	26.8	10.37	38.7	
	Taihu paddy soil	7.75	6.25	1.86	29.8	30.2
		19.5	14.00	4.05	28.9	
		36.25	29.25	8.22	28.1	
		75.75	58.25	19.81	34.0	
	Northeast China black soil	7.75	6.75	1.56	23.1	27.0
		19.5	17.00	4.05	23.8	
		36.25	29.75	8.60	28.9	
		75.75	65.25	21.14	32.4	
Azoxystrobin	Jiangxi red soil	7.0	2.5	1.00	40.0	36.7
		21.5	5.5	2.27	41.2	
		37.0	10	3.83	38.3	
		76.0	22.5	7.13	31.7	
	Taihu paddy soil	7.0	4.5	0.78	17.3	16.2
		21.5	12.5	1.93	15.4	
		37.0	24	4.34	18.1	
		76.0	52	7.28	14.0	
	Northeast China black soil	7.0	5.5	0.62	11.3	10.1
		21.5	17.5	1.37	7.8	
		37.0	30.5	2.71	8.9	
		76.0	58	7.19	12.4	
Kresoxim-methyl	Jiangxi red soil	1.65	0.35	0.19	54.0	46.1
		3.30	0.60	0.27	44.2	
		5.10	1.20	0.54	45.4	
		6.85	1.90	0.78	40.8	
	Taihu paddy soil	1.65	0.90	0.15	16.8	17.0
		3.30	1.90	0.34	18.0	
		5.10	2.90	0.50	17.4	
		6.85	4.45	0.70	15.7	
	Northeast China black soil	1.65	1.05	0.14	13.2	12.8
		3.30	2.40	0.31	13.0	
		5.10	3.75	0.49	13.0	
		6.85	4.70	0.56	12.0	

Table 7 The linear correlation (R^2) of desorption rate and soil properties

Chemical	JS39-199	Azoxystrobin	Kresoxim-methyl
pH	0.7567	0.8055	0.7166
Organic matter	0.8746	0.9110	0.8429
CEC	0.9121	0.9426	0.8846

attention has been paid to pesticide pollution to ground water in rural areas. The mobility and durability of pesticide are some principal factors of pesticide pollution for the ground water (Arias-Estévez et al. 2008). The ground ubiquity score (GUS) was chosen to evaluate the possibility of pesticide leaching, as presented by the following equation: $GUS = \lg T_{1/2}\ (4 - \lg K_{OC})$. According to the method (Michael 1995), pesticides are easy to leach when GUS is more than 2.8; pesticides have medium leaching property when GUS is 1.8~2.8, whereas pesticides is not easy to leach when GUS is less than 1.8.

In our research, the GUS values of three strobilurin fungicides were less than 1.8 in Taihu Paddy Soil and Northeast China black soil (Table 5), suggesting that they were not easy to leach in the two soils. In Jiangxi red soil, the GUS values of JS399-19 and azoxystrobin were 2.63 and 3.13, respectively, indicating that JS399-19 had medium leaching property in the soil and some risk of pollution to the ground water. Azoxystrobin was easy to leach in the soil, which was likely to have a high risk of pollution to the ground water. As kresoxim-methyl had a very short half-life period in the three soils, it could be less likely to pollute the ground water.

Desorption of JS399-19, azoxystrobin, and kresoxim-methyl

Desorption of three strobilurin fungicides in different soils

To further investigate the soil environmental behavior of three fungicides, desorption of JS399-19, azoxystrobin, and kresoxim-methyl was tested after their adsorption in soils. The average desorption rates of JS399-19, azoxystrobin, and kresoxim-methyl were 45.6, 36.7, and 46.1 % in Jiangxi red soil; 30.2, 16.2, and 17.0 % in Taihu paddy soil; and 27.0, 10.1, and 12.8 % in Northeast China black soil, respectively (Table 6). These results indicated that three strobilurin fungicides were hard to be desorbed in Northeast China black soil and Taihu paddy soil but desorbed relatively easy in Jiangxi red soil. In Jiangxi red soil, the three fungicides show strong desorption performance.

Influence of soil property on desorption of three strobilurin fungicides

Analysis of the linear correlation between desorption of three strobilurin fungicides in the soils, along with their soil physicochemical properties, was conducted. The soil pH, SOM, and CEC were close to the desorption rate (Table 7), consistent with the correlation between the adsorption and soil properties. SOM was an important factor in the desorption of three fungicides. However, when SOM content was lower, the other soil properties such as soil types, pH, clay particle, and CEC also affected the adsorption/desorption of

Table 8 Distribution of three strobilurin fungicides in different soil thin layers ($n = 3$)

Soil layer (cm)	JS399-19 (mg/kg)			Azoxystrobin (mg/kg)			Kresoxim-methyl (mg/kg)		
	Jiangxi red soil	Taihu paddy soil	Northeast China black soil	Jiangxi red soil	Taihu paddy soil	Northeast China black soil	Jiangxi red soil	Taihu paddy soil	Northeast China black soil
0~2	1.46	1.84	1.9	1.85	1.75	1.87	0.75	0.59	1.64
2~4	0.49	0.6	0.56	0.58	0.54	0.32	0.99	1.19	0.78
4~6	0.42	0.26	0.07	0.05	0.06	<0.05	0.78	0.49	<0.05
6~8	0.23	<0.05	<0.05	<0.05	<0.05	<0.05	0.18	0.08	<0.05
8~10	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.06	<0.05	<0.05
10~12	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
12~14	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
14~18	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

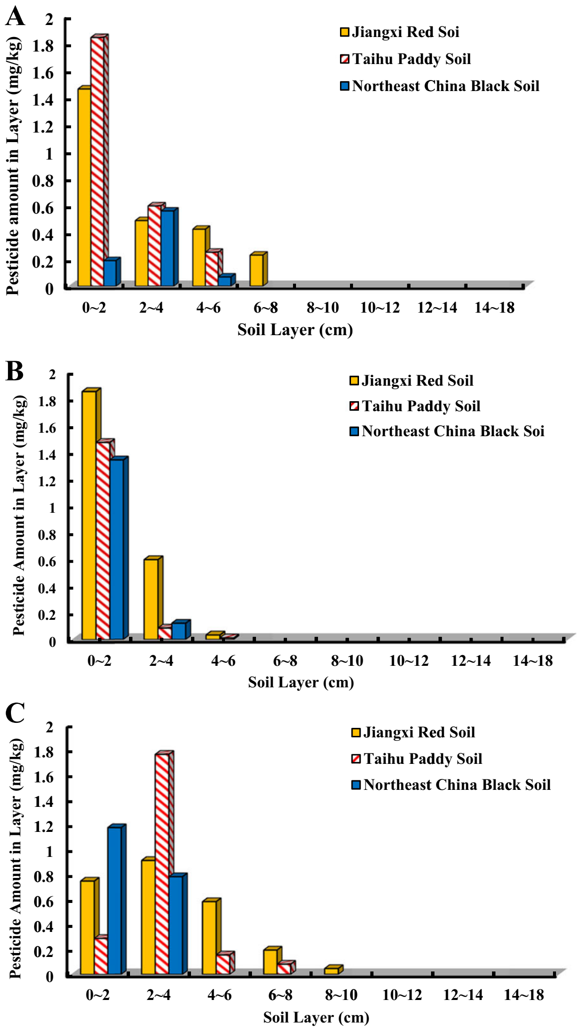

Fig. 2 Distribution of JS399-19 (**a**), azoxystrobin (**b**), and kresoxim-methyl (**c**) in different soil thin layers

pesticides (Bresnahan et al. 2002; Singh 2002). Soil CEC was closely correlated with the desorption of three fungicides, with the correlation coefficient (R^2) being 0. 9163–0.9323 (Table 7).

Mobility of three strobilurin fungicides in different soils

To assess the pesticide pollution to soil and ground water, soil thin-layer chromatography was employed to dissect the mobility and distribution of three fungicides in soil. The profiling of three fungicides in the different soils was shown in Table 8 and Fig. 2. JS399-19 in Jiangxi red soil, Taihu paddy soil, and Northeast China black soil moved a distance of 6–8, 4–6, and 4–6 cm in soil thin layer, respectively, indicating that the mobility of JS399-19 was faster in Jiangxi red soil than in other two soils. Azoxystrobin in Jiangxi red soil, Taihu paddy soil, and Northeast China black soil moved forward 4–6, 4–6, and 2–4 cm in soil thin layer, respectively. The maximum concentration of JS399-19 and azoxystrobin in three soils was all found in 0–2 cm. These results suggested that JS399-19 and azoxystrobin had weaker mobility in Northeast China black soil than in other two soils. Kresoxim-methyl in Jiangxi red soil, Taihu paddy soil, and Northeast China black soil moved for 8–10, 6–8, and 2–4 cm in soil thin layer, respectively, indicating that its mobility was slowest in Northeast China black soil and fastest in Jiangxi red soil.

The calculated mobility distribution coefficients (R_{fs}) of three fungicides were shown in Table 9. The R_f values of JS399-19 in Jiangxi red soil, Taihu paddy soil, and Northeast China black soil were 0.08, 0.06, and 0.06, respectively. The R_f values of azoxystrobin were 0.06 in three soils. The R_f values of kresoxim-methyl in Jiangxi red soil, Taihu paddy soil, and Northeast China black soil were 0.17, 0.17, and 0.08, respectively. These results indicated that kresoxim-methyl in Jiangxi red soil and Taihu paddy soil was not easy to move, and JS399-19 and azoxystrobin in three soils and kresoxim-methyl in Northeast China black soil did not move at all.

Table 9 R_f of three strobilurin fungicides in soil layers

Parameter	JS399-19			Azoxystrobin			Kresoxim-methyl		
	Jiangxi red soil	Taihu paddy soil	Northeast China black soil	Jiangxi red soil	Taihu paddy soil	Northeast China black soil	Jiangxi red soil	Taihu paddy soil	Northeast China black soil
L (mm)	15	10	10	10	10	10	30	30	15
L_{max} (mm)	180	180	180	180	180	180	180	180	180
R_f (R_1)	0.08	0.06	0.06	0.06	0.06	0.06	0.17	0.17	0.08

Conclusions

Under the experimental condition, three fungicides JS399-19, azoxystrobin, and kresoxim-methyl were uneasy to be adsorbed in Jiangxi red soil. But they had a medium adsorption capability in Tanhu paddy soil and Northeast China black soil. Soil pH, SOM, and CEC were positively correlated with the adsorption and desorption of three fungicides. The strobilurin fungicides had weak mobility in soil. As azoxystrobin and JS399-19 had good stability in soil, they might cause pollution to soil. Further studies are required to track and monitor residues of the fungicides in soils and underground water.

Acknowledgments The authors acknowledge the financial support of the Special Fund for Agro-scientific Research in the Public Interest (No. 201203022) from the Ministry of Agriculture of China.

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