Adsorption and degradation of neonicotinoid insecticides in agricultural soils

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Abstract

The adsorption and degradation of seven commercially available neonicotinoid insecticides in four types of agricultural soils from three states (Mississippi, Arkansas, and Tennessee) in the United States were studied. The adsorptions of all the neonicotinoids fit a linear isotherm. The adsorption distribution coefficients (K_d) were found to be below 2.0 L/kg for all the neonicotinoids in all the soils in Mississippi and Arkansas. Only in the Tennessee soil, the K_d ranged from 0.96 to 4.21 L/kg. These low values indicate a low affinity and high mobility of these insecticides in the soils. The soil organic carbon-water partitioning coefficient K_{oc} ranged from 349 to 2569 L/kg. These K_d values showed strong positive correlations with organic carbon content of the soils. The calculated Gibbs energy change (ΔG) of these insecticides in all the soils ranged from − 14.6 to -19.5 kJ/mol, indicating that physical process was dominant in the adsorptions. The degradations of all these neonicotinoids in the soils followed a first-order kinetics with half-lives ranging from 33 to 305 d. The order of the insecticides with decreasing degradation rate is: clothianidin > thiamethoxam > imidacloprid > acetamiprid > dinotefuran > thiacloprid > nitenpyram. The moisture content, clay content, and cation exchange capacity showed positive effects on the degradation rate of all the neonicotinoids. The Groundwater Ubiquity Score (GUS) calculated from the adsorption distribution coefficient, organic content, and half-life indicates that, except for thiacloprid, all the neonicotinoids in all the soils are possible leachers, having potentials to permeate into and through groundwater zones.

1. Introduction

The neonicotinoid insecticides play a vital role in the control of different types of insects in the process of crop production and management. The use of neonicotinoids has been increasing in the last two decades since the first neonicotinoid imidacloprid was commercialized in 1991 (Mörtl et al. 2016). Neonicotinoids are registered for use on over 290 crops in more than 120 countries (Jeschke et al. 2011; Main et al. 2015). In developed countries, neonicotinoids are mainly used as seed dressing agents for many crops such as canola, sunflower, grains, beets and potatoes (Tomizawa and Casida 2005; Goulson 2013). The amounts of neonicotinoids applied in the United Kingdom, one of few countries from which detailed records are available, rose from 3,000 kg in 1994 to 120 tons in 2016 (Goulson 2013; FERA 2017). Given the massive scale of use of neonicotinoids in both rural and urban areas, their impacts on environmental health and other non-target organisms have become a global concern.

There are seven neonicotinoids commercially available on today's insecticide market: imidacloprid, thiamethoxam, clothianidin, dinotefuran, acetamiprid, thiacloprid, and nitenpyram (Li et al 2018). It is estimated that, once applied through soil or seed dressing, only about 2–20% of the neonicotinoids are taken up by the crop and the rest will typically enter the soil (Goulson 2013; Sur and Stork 2003; Wood and Goulson 2017). The possible accumulation of the neonicotinoids in the environment has been found and reported. A study on 48 streams in the U.S. found that more than 50% of them had more than one neonicotinoid (Hladik and Kolpin 2015). In the Pearl River of Guangzhou, China, the insecticides of acetamiprid, thiamethoxam, imidacloprid and clothianidin were detected in all 14 sampling sites with a concentration of 93–321 ng/L (Yi et al. 2019). In Sydney, Australia, more than 90% of 14 selected rivers were found to contain two or more neonicotinoids with concentrations of 0.06 to 4.5 µg/L (Sánchez-Bayo and Hyne 2014). Data on degradation and adsorption of the neonicotinoids in soils are critical for evaluating the fate and transport of these insecticides in soils and groundwater. Previous studies to obtain these data have been reported in many countries including Austria (Kah et al. 2018), India (Gupta et al. 2002 and Gupta et al. 2008), China (Wu et al. 2012; Han et al. 2019), Spain (Rodríguez-Liébana et al. 2018), Canada (Morrissey et al. 2015), and US (Papiernik et al. 2006; Li et al. 2018). They concluded that a low soil adsorption (log K_{oc}) is found, which suggests a transport of these insecticides through irrigation and runoff. Meanwhile, Rodríguez-Liébana et al. (2018) and Papiernik et al. (2006) reported the adsorption of thiacloprid and imidacloprid could relate to the organic matters or pH in soils. A comprehensive study on the effects of soil properties including clay content, silt content, cation exchange capacity, organic carbon content, and pH on the adsorption of all seven insecticides is still missing.

In this study, four different agricultural soils with different physicochemical properties were collected in Mississippi, Arkansas, and Tennessee in the U.S. The adsorption and degradation of all seven commercially used neonicotinoids were investigated. The effects of soil properties and conditions on adsorption and degradation of the neonicotinoids were scrutinized. The data are important for evaluating the environmental impacts of the use of these insecticides in the world.

2. Materials And Methods

The neonicotinoids used in this study were obtained from Chem Service, Inc. and had a purity of 99.9%. The stock solutions (1000 mg/L) of each insecticides were prepared in methanol (HPLC grade). The physical-chemical properties of these neonicotinoids are summarized in Table 1.

The soils used in this study were collected from different agricultural sites in Mississippi, Arkansas, and Tennessee. Two were from Mississippi State University's Truck Crops Branch Experiment Station located in Crystal Springs (TCB) and Beaumont Horticulture Unit in Beaumont (BHU), Mississippi, respectively; one from Lon Mann Cotton Research Station of Arkansas Agricultural Experiment Station (CRS), Arkansas; and another from Tennessee State University's Agricultural Farm (TSU) in Nashville, Tennessee.

Soils samples were collected from three depths: top 30 cm, 30–60 cm, and 60–90 cm. The collected soils were air-dried in the laboratory with a room temperature 21 ± 2 °C for at least 5 d, then crushed and passed through a U.S. standard No. 10 sieve (2 mm openings). The moisture contents of all air-dried soil samples were measured to be less than 1%. The characteristics of the selected soils at different depths were summarized in Table 2.

2.2. Adsorption Tests

The batch adsorption tests of the neonicotinoids in four different soils were carried out. Aliquots of 10 mL of 0.01 M $CaCl_2$ solution with insecticides' concentrations from 0.05 to 10 mg/L were mixed with 2.0 g of air-dried soil of each type in 50 mL centrifuge tubes. The centrifuge tubes were agitated on a shaker at 200 rpm in the laboratory for 48 h. The samples were then centrifuged at 4500 rpm for 20 mins and supernatants were taken and filtered through a 0.45 μm filter. The samples will be analyzed using high performance liquid chromatography (HPLC).

2.3. Degradation Test

Degradation tests were conducted in soils sampled from three different depths (0–30, 30–60, 60–90 cm) at four different sites (BHU, CRS, TCB, TSU) and at different moisture contents (air-dried, 20%, 40% w/w). For each moisture content, 30 degradation test samples were prepared for the soil sample from each depth and each site. In each test sample, 20 g soil was weighed into an aluminum tin, and mixed with 1 mL of 200 mg/L neonicotinoid stock solution so that the initial insecticide content in each soil sample was 10 mg/kg. The sealed tins were cultured in a dark incubator at room temperature (21 ± 2 °C) for different degradation periods. Upon the completion of the degradation periods, triplicate tins were taken and the content of the insecticide in the soil in each tin was determined by extraction and analysis using HPLC as described in Sections 2.4 and 2.5.

Table 2
Physicochemical properties of soils used in this study

Soil site	Soil texture	Soil depth (cm)	Clay Content (%)	Silt Content (%)	Cation exchange capacity (cmol(+)/kg)	pH	Organic carbon content (%)
BHU	Sandy loam	0–30	3	29	4.2	6.0	0.279
		30–60	3	48	7.2	5.0	0.149
		60–90	3	45	6.1	4.8	0.065
CRS	Silt	0–30	1	96	13.3	7.2	0.323
		30–60	1	96	11.9	5.3	0.166
		60–90	1	96	14.5	4.6	0.101
TCB	Silt	0–30	19	32	10.8	5.7	0.279
		30–60	20	33	11.9	5.1	0.138
		60–90	20	33	11.0	5.0	0.184
TSU	Silt loam	0–30	1	78	9.8	5.6	0.731
		30–60	3	82	10.0	5.6	0.505
		60–90	3	82	9.9	5.4	0.275

2.4. Extraction of Soil Samples for Analysis

For the degradation test samples, the soil in each tin was transferred to a centrifuge tube and 30 mL of water and acetonitrile (20: 80 v/v) was added to extract the neonicotinoid. This extraction solution was also used in the studies by Gupta et al. (2008), Wu et al. (2012)d rtl et al. (2016). The mixture was agitated on the shaker for 30 min, then centrifuged at 4500 rpm for 20 min. Each soil sample will be extracted three times following the same method to ensure a complete extraction. The extractants were then combined and transferred into a separatory funnel, and 5 mL of saturated saline and 20 mL of dichloromethane were added into the funnel to mix with the extractant. The organic fraction was separated in a round bottom flask and concentrated using a rotary evaporator (Heidolph G1, Germany). The evaporation residue was dissolved in methanol and transfer to a 2 mL amber vial for HPLC analysis. Extraction recovery test was conducted on all neonicotinoids in this study to ensure the reliability of the extraction method. The average recoveries were 88.2 ± 4.5% for imidacloprid, 92.3 ± 2.8% for thiamethoxam, 94.1 ± 1.3% for thiacloprid, 91.3 ± 2.1% for clothianidin, 89.3 ± 3.5% for acetamiprid, 93.3 ± 1.8% for nitenpyram, and 87.9 ± 4.8% for dinotefuran.

2.5 HPLC Analysis

The analysis of all the samples from the adsorption tests and the degradation tests was performed using a HPLC (LC virtual Advisor, Shimadzu). The Diamonsil C_{18} column (5 μm, 250 × 4.6 mm) is equipped. The separation conditions in the HPLC test were: flow rate 0.6 mL/min, column thermostat 25°C, injection volume 10 μL, detection wavelength of UV absorption 254 nm, mobile phase of 65% methanol and 35% water with 0.1% formic acid. The retention times under these separation conditions was 6.1 min for imidacloprid, 5.3 min for thiamethoxam, 8.0 min for thiacloprid, 5.6 for clothianidin, 6.7 min for acetamiprid, 4.2 for nitenpyram, and 4.5 for dinotefuran.

3. Results And Discussion

3.1 Adsorption

The linear isotherm ($S = K_d C$) was found to be well-fit the adsorption results of all the neonicotinoids in this study. This model presents the amount of neonicotinoids adsorbed by the soil (S) versus equilibrium concentration in the solution (C), and the slope of the model represents the adsorption distribution coefficients (K_d). Since the adsorptions of all the seven neonicotinoids in all the soil samples had the sample isotherm pattern, only the graph for the adsorption equilibrium concentrations of imidacloprid is given (Fig. 1). The results based on the graphs for all the neonicotinoids can be found in Table 3. The coefficients of determination (R^2) and another sol adsorption coefficient (K_{oc}) are also provided in Table 3. The standard deviations for all the K_d results in Table 3 are less than 3% of the mean values except clothianidin in TCB soil for which the standard deviations of K_d range are 5–10% of the mean values.

Table 3 summarizes the adsorption coefficients of all neonicotinoids from slopes of the fitting equation at different depth and soil sites. The K_d values are below 2.0 L/kg for all the neonicotinoids in all the soils in Mississippi and Arkansas. Only in the Tennessee soil, the K_d values range above 2.0 to 4.21 L/kg. In all the soils nitenpyram has the lowest K_d and thiacloprid has the highest. In the meantime, the K_d values in the top layers of all the soils are the highest. The K_d values for nitenpyram in the top layers of soils range from 1.02 to 2.58, while those for thiacloprid 2.08 to 4.21. The K_d values appear to be closely related to the OC in the soil – the higher the OC, the greater the K_d value. It can be seen in Table 2 that the OC values in the soils decrease as the depth increases, so do the K_d values as shown in Table 3. The highest and lowest K_d values are found in the top layer soil at TSU and bottom layer at BHU respectively; the highest OC and the lowest OC are also found in these layers. Zhang et al. (2020) and Wang et al. (2020) reported same phenomena on the adsorption of herbicide pyraclonil and pesticide exianliumi in soils. Meanwhile, the K_{oc} value, which is obtained by normalizing the adsorption coefficient to the OC of the soil tends to be steady in TSU soil but varies significantly in BHU, CRS, and TCB soils. Papienik et al. (2006), Morrissey et al. (2015) and Mortl et al. (2016) reported the K_{oc} values for imidacloprid, clothianidin, and thiamethoxam to be 82 to 43,000, 84 to 350, and 33 to 237 L kg -1 respectively. The K_{oc} of clothianidin and thiamethoxam found in this study were higher than the reported values. This could be due to the low OC in the soils. Papiernik et al. (2006) and Li et al. (2018) reported that the value of K_{oc} could vary by an order of magnitude, especially when OC is low.

The relations between soil adsorption and the soil properties were analyzed using Kendall’s Tau-b correlation coefficients, which are calculated using the IBM SPSS statistics 27. The detailed description of this software can be found in our previous work (Li et al. 2018). Table 4 summarized the Kendall’s Tau-b correlation coefficients calculated for K_d and K_{oc} for all neonicotinoids as they relate to the soil parameters. The results in Table 4 indicate that K_d has a strong positive correlation with OC ($p < 0.01$), while the K_{oc} has a strong negative correlation with OC ($p < 0.01$). Except for nitenpyram, all other neonicotinoids’ K_d values also have significant positive correlations with CEC of the soils ($p < 0.05$), and their K_{oc} values have negative correlations with CEC ($p < 0.05$). However, neither K_d nor K_{oc} has significant correlation with clay content, silt content, or pH. Flores-Céspedes et al. (2002) and Aseperi et al. (2020) reported the adsorption of imidacloprid and also found that the $K_d$is closely related to OC in the soils. However, Aseperi et al. (2002) reported that the adsorption of thiacloprid and thiamethoxam were not related to OC in the soils, which is opposite to the results from this study.

Table 3
Adsorption coefficients of neonicotinoids in four different agricultural soils

Neonicotinoid	Soil depth (cm)	BHU soil			CRS soil			TCB soil			TSU soil		
		K_d (L/kg)	R^2	K_{oc} (L/kg)	K_d (L/kg)	R^2	K_{oc} (L/kg)	K_d (L/kg)	R^2	K_{oc} (L/kg)	K_d (L/kg)	R^2	K_{oc} (L/kg)
Imidacloprid	0–30	1.39	0.99	498	1.66	0.99	514	1.53	0.99	548	2.96	0.99	404
	30–60	0.93	0.99	624	1.42	0.99	855	1.28	0.99	927	2.24	0.99	444
	60–90	0.70	0.99	1076	0.89	0.99	881	1.52	0.99	826	1.32	0.99	480
Clothianidin	0–30	1.51	0.98	541	1.75	0.96	542	1.64	0.99	588	3.18	0.99	435
	30–60	1.02	0.99	685	1.59	0.95	958	1.43	0.99	1036	2.48	0.99	491
	60–90	0.79	0.99	1215	1.02	0.94	1010	1.66	0.99	902	1.54	0.99	560
Thiacloprid	0–30	2.08	0.90	746	2.13	0.99	659	2.02	0.99	724	4.21	0.99	576
	30–60	1.42	0.99	953	1.97	0.95	1187	1.89	0.99	1370	3.17	0.99	628
	60–90	1.67	0.99	2569	1.43	0.97	1416	2.03	0.99	1103	2.03	0.99	702
Thiamethoxam	0–30	1.34	0.99	480	1.54	0.99	477	1.48	0.99	530	2.91	0.99	398
	30–60	0.87	0.99	584	1.41	0.99	849	1.32	0.99	957	2.11	0.99	418
	60–90	0.67	0.99	1031	0.82	0.99	812	1.43	0.99	777	1.38	0.99	502
Dinotefuran	0–30	1.26	0.96	452	1.50	0.99	464	1.39	0.99	498	2.86	0.99	391
	30–60	0.79	0.92	530	1.37	0.99	825	1.20	0.99	870	2.03	0.99	402
	60–90	0.61	0.99	938	0.81	0.99	802	1.37	0.99	745	1.21	0.99	440
Acetamiprid	0–30	1.44	0.99	516	1.69	0.98	523	1.53	0.99	548	3.02	0.99	413
	30–60	0.93	0.99	624	1.44	0.99	867	1.31	0.97	949	2.24	0.99	444
	60–90	0.71	0.99	1092	0.89	0.99	881	1.52	0.99	826	1.47	0.98	535
Nitenpyram	0–30	1.02	0.91	366	1.29	0.98	399	1.29	0.94	462	2.58	0.99	353
	30–60	0.63	0.90	423	1.10	0.91	663	1.07	0.91	775	1.78	0.99	352
	60–90	0.48	0.91	738	0.98	0.91	970	1.17	0.90	636	0.96	0.95	349

R^2 is the coefficient of determination for each regression line from which the K_d value is obtained.

To further investigate the mechanisms in the adsorption of the neonicotinoids in the soils, the Gibbs energy change (ΔG) were calculated using the equation $\Delta G = -RT\ln K_{oc}$, where R (J/K·mol) is the gas constant, and T (K) is the absolute temperature (27, 28). The Gibbs energy change (ΔG) indicates the degree of spontaneity of an adsorption process. The ΔG values can be used to describe the driving force of the adsorption. The more advantageous adsorption process is, the higher the negative value of ΔG will be (Zhang et al. 2007). If the absolute value of ΔG is less than 40 kJ/mol, physical adsorption is dominant (Carter et al. 1995).

The calculated ΔG values of all the seven neonicotinoids in all four agricultural soils range from − 14.6 to -19.5 kJ/mol, indicating that the adsorption of all insecticides is mainly physical process. The low ΔG values also indicates that the adsorption between the insecticides and soils is dominated by van der Waals force. Thus, the adsorption is relatively weak and reversible. This weak adsorption also indicates a high mobility of the insecticides in the soils.

The adsorption distribution coefficients (K_d) are relatively low for all the insecticides in al soils, indicating a low affinity of these insecticides in these soils. This result suggests that the insecticides will be easily transported through irrigation or runoff. Meanwhile, the calculated Gibbs energy change demonstrated the adsorption between insecticides and soils is mainly van der Waals force, i.e., a weak and reversible adsorption process. Han et al. (2019) also reported the part of the adsorption of insecticide thiamethoxam is reversible. From Tables 3 and 4, it can be found the organic carbon content dominants the adsorption process. In agricultural use, organic carbon content suggests increasing to prevent the transport of insecticides through irrigation and runoff to groundwater and surface water.

Table 4
Kendall’s Tau-b correlation coefficients between adsorption distribution coefficients and soil parameters

Neonicotinoid		**Clay content**	**Silt content**	**pH**	**CEC**	**OC**
Imidacloprid	K_d	-0.01	0.01	0.01	**0.55**[*]	**0.84**[**]
	K_{oc}	0.19	0.02	0.26	**-0.49**[*]	NA[***]
Clothianidin	K_d	-0.09	0.08	0.09	**0.48**[*]	**0.77**[**]
	K_{oc}	0.23	0.02	0.26	**-0.55**[*]	NA
Thiacloprid	K_d	-0.01	0.01	0.14	0.43	**0.72**[**]
	K_{oc}	-0.09	0.08	0.10	**-0.54**[*]	NA
Thiamethoxam	K_d	-0.07	0.00	0.00	**0.57**[*]	**0.86**[**]
	K_{oc}	0.23	0.02	0.26	**-0.55**[*]	NA
Dinotefuran	K_d	-0.18	0.06	0.06	**0.54**[*]	**0.80**[**]
	K_{oc}	0.20	0.02	0.23	**-0.46**[*]	NA
Acetamiprid	K_d	-0.12	0.05	0.05	**0.52**[*]	**0.81**[**]
	K_{oc}	0.26	-0.02	0.19	**-0.55**[*]	NA
Nitenpyram	K_d	-0.11	0.06	0.12	0.42	**0.71**[**]
	K_{oc}	0.12	-0.05	0.35	0.43	NA

[*] Significant at $p < 0.05$

[**] Significant at $p < 0.01$

[***] Not applicable because K_{oc} is already a parameter that is normalized with OC content of soil

3.2 Degradation

The degradation kinetics of all seven neonicotinoids in all four soils were well-fitted to the first order reaction model $C_s = C_i e^{-kt}$, where C_t and C_0 represent the concentration of neonicotinoids in the soil and the initial concentration of the neonicotinoids respectively, and k is the degradation rate constant. The Root-mean-square deviations (RMSE) are used to indicate the quality of the fitting curves, and these values ranged from 0.2 to 0.26. Figure 2 presents the degradation data of imidacloprid in the four soils at three different depths in air-dried soils and the regression curves according to the first order reaction model. The degradation data of all other six neonicotinoids in the four soils and at three moisture contents (air dried, 20, and 40%) followed the same trend. The half-lives of each neonicotinoid at different soil conditions can be calculated using the equation of $T_{1/2} = 0.693/k$. The standard deviations for all the results in Table 5 are less than 5% of the mean values except thiamethoxam in BHU and TSU soils for which the standard deviations are 5–10%.

Table 5 summarizes the half-lives of all neonicotinoids in soils from four sampling sites and at three different depths and three moisture contents. It can be seen in the table that the half-lives of the neonicotinoids range from 33–305 d in all these soil samples. In general, the ranking of the half-lives is clothianidin > thiamethoxam > imidacloprid > acetamiprid > dinotefuran > thiacloprid > nitenpyram. The effects of the soil type on the half-lives are noticeable, but not as significant as the neonicotinoid type. Under the same moisture condition, the same neonicotinoid has the highest half-life in BHU soil and the lowest in TCB soil. Their half-lives in CRS and TSU soils have no significant differences. Considering the physicochemical parameters of the soils (Table 2), the significant differences between BHU soil and TCB soil exist in clay content (3% for BHU and 20% for TCB) and CEC (4–7 cmol/kg for BHU and 11–12 cmol/kg for TCB). According to Das and Adhya (2015), clay content associated with iron oxides can increase the surface area and induce surface catalyzed hydrolysis. This could be a cause for the significant differences in half-lives of the neonicotinoids in BHU and TCB soils, the latter had higher clay content and in which the neonicotinoids had shorter half-lives.

The half-lives of all the neonicotinoids also increase with the soil depth as shown in Table 5. The soil properties in Table 2 show that OC the only parameter that decreases significantly with soil depth. Therefore, it is very likely that the OC in the soil facilitates the degradation of the neonicotinoids. Anhalt et al. (2008) reported a similar result that the degradation rate of imidacloprid in subsurface was much slower than that in the surface soil. Tao and Yang (2011) and Ou et al. (2020) studied the degradation of insecticides fluroxypyr and phenazine-1-carboxamide respectively and they both concluded that higher organic matter content could increase the amount of microorganisms, thus enhance the degradation of the insecticides.

The data in Table 5 also reveal that the half-lives of all neonicotinoids decrease with the increase of soil moisture content, indicating that hydrolysis could play a key role in the degradation process. Similar results for clothianidin and thiamethoxam were also reported by Li et al. (2018) and Gupta et al. (2008). The microbial degradation could be another route of the degradation of all insecticides. The microbial activity seems to be negligible in dry condition. With moisture conditions (20% water content), the microbial is expected to be aerobic and start to be active and thus the degradation process will be faster than in dry condition. This is also confirmed by the study of Morrissey et al. (2015). After the moisture content increased to 40% (almost submerged moisture condition), the microbial is mainly anaerobic. The effect of anaerobic microbial and aerobic microbial is almost the same since the degradation half-lives under 20% and 40% moisture content are almost the same.

Table 5
Degradation half-lives (d) of neonicotinoids in different soils at different depths and different moisture contents

Neonicotinoid	Soil depth (cm)	BHU Soil			CRS Soil			TCB Soil			TSU Soil		
		Air dried [a]	20%[b]	40%	Air dried	20%	40%	Air dried	20%	40%	Air dried	20%	40%
Imidacloprid	0–30	163	144	142	105	89	82	96	78	76	105	89	81
	30–60	174	163	158	119	103	96	101	91	90	113	103	100
	60–90	271	248	230	136	123	106	130	113	104	156	139	135
Clothianidin	0–30	159	142	136	118	102	98	102	86	81	127	108	102
	30–60	176	163	157	128	108	104	119	105	96	137	115	102
	60–90	304	286	271	149	136	125	139	116	114	158	136	125
Thiacloprid	0–30	76	55	58	58	46	42	53	47	39	49	42	39
	30–60	89	71	66	63	49	48	59	49	43	51	45	42
	60–90	103	80	69	68	51	51	72	61	53	58	52	46
Thiamethoxam	0–30	172	155	152	132	118	110	112	101	95	147	135	126
	30–60	188	156	143	138	120	116	116	103	96	152	142	141
	60–90	305	266	253	152	134	126	152	126	125	179	168	159
Dinotefuran	0–30	79	53	52	65	53	50	55	46	42	72	63	59
	30–60	84	69	62	73	64	62	60	57	53	83	70	64
	60–90	101	85	81	81	72	70	73	65	61	89	76	71
Acetamiprid	0–30	119	102	96	102	86	82	86	69	66	98	87	82
	30–60	140	119	115	127	102	96	97	89	85	112	101	100
	60–90	184	169	163	139	124	118	104	91	86	137	110	102
Nitenpyram	0–30	62	43	38	55	46	44	42	35	33	53	40	36
	30–60	74	62	56	63	53	50	48	40	36	69	52	49
	60–90	84	80	72	78	68	67	57	48	44	84	68	61

a. Moisture contents of the soil samples (w/w) is lower than 2%

b. Moisture contents of the soil samples (w/w)

The Groundwater Ubiquity Score (GUS) was used in this study to predict the leachability of a chemical into groundwater (Gustafson et al. 1989). The GUS can be calculated by the following equation: GUS = log 10 ($T_{1/2}$) * [4 – log $_{10}$ (K_{oc})]. According to this study, when the GUS value is great than 2.8, the chemical is defined as a leacher; when it is less than 1.8, a non-leacher; and when it is between 1.8 and 2.8, a possible leacher. The calculated GUS values of all the neonicotinoids in different soils at different depths and different moisture contents are presented in Table 6 and Figure 3. In this study, the GUS values for imidacloprid was calculated to be between 2.0- 2.9 in all the tested soils, clothianidin 2.0- 2.9, thiacloprid 1.5- 2.1, thiamethoxam 2.1- 3.0, dinotefuran 1.8- 2.7, acetamiprid 2.0- 2.8, and nitenpyram 1.7-2.8. If an insecticide has low GUS value and short half-life in a soil, it's transport in the soil will be limited because it is slow to leach and fast to degrade. This is the case for the neonicotinoids in TCB soil where they have the lowest GUS values and the shortest half-lives as compared to ither soils tested. All neonicotinoids in the tested soils except thiacloprid in BHU, CRS, and TCB soils and nitenpyram in TCB soil with 40% moisture content are possible leacher, having potentials to permeate through groundwater. TSU soil provides the most leachable environment for the neonicotinoids.

Table 6
GUS values of neonicotinoids in different soils at different depths and different moisture contents

Neonicotinoid	Soil depth (cm)	BHU soil			CRS soil			TCB soil			TSU soil		
		Air dried	20%	40%	Air dried	20%	40%	Air dried	20%	40%	Air dried	20%	40%
Imidacloprid	0–30	2.9	2.8	2.8	2.6	2.5	2.5	2.5	2.4	2.4	2.8	2.7	2.7
	30–60	2.7	2.7	2.6	2.2	2.1	2.1	2.1	2.0	2.0	2.8	2.7	2.7
	60–90	2.4	2.3	2.3	2.3	2.2	2.2	2.3	2.2	2.2	2.9	2.8	2.8
Clothianidin	0–30	2.8	2.7	2.7	2.6	2.5	2.5	2.5	2.4	2.3	2.9	2.8	2.7
	30–60	2.6	2.6	2.6	2.1	2.1	2.1	2.0	2.0	2.0	2.8	2.7	2.6
	60–90	2.3	2.2	2.2	2.2	2.1	2.1	2.2	2.2	2.1	2.8	2.7	2.6
Thiacloprid	0–30	2.3	2.2	2.2	2.2	2.1	2.1	2.1	2.0	1.9	2.3	2.2	2.1
	30–60	2.2	2.1	2.0	1.8	1.7	1.7	1.7	1.6	1.5	2.2	2.2	2.1
	60–90	1.8	1.7	1.6	1.7	1.6	1.6	1.9	1.8	1.8	2.2	2.1	2.0
Thiamethoxam	0–30	2.9	2.8	2.8	2.7	2.7	2.7	2.6	2.5	2.5	3.0	2.9	2.9
	30–60	2.7	2.6	2.6	2.3	2.2	2.2	2.1	2.1	2.0	3.0	2.9	2.9
	60–90	2.4	2.3	2.3	2.3	2.2	2.2	2.4	2.3	2.3	2.9	2.8	2.8
Dinotefuran	0–30	2.6	2.3	2.3	2.4	2.3	2.3	2.3	2.2	2.1	2.6	2.5	2.5
	30–60	2.5	2.3	2.3	2.0	2.0	2.0	1.9	1.9	1.8	2.7	2.6	2.5
	60–90	2.1	2.0	2.0	2.1	2.0	2.0	2.1	2.0	2.0	2.6	2.6	2.5
Acetamiprid	0–30	2.7	2.6	2.6	2.7	2.6	2.6	2.5	2.3	2.3	2.8	2.7	2.7
	30–60	2.6	2.6	2.5	2.3	2.2	2.2	2.0	2.0	2.0	2.8	2.8	2.8
	60–90	2.2	2.2	2.2	2.3	2.3	2.3	2.2	*2.2*	2.1	2.8	2.7	2.6
Nitenpyram	0–30	2.6	2.3	2.3	2.4	2.3	2.3	2.2	2.1	2.0	2.5	2.3	2.3
	30–60	2.6	2.5	2.4	2.1	2.0	2.0	1.9	1.8	1.7	2.7	2.5	2.5
	60–90	2.2	2.2	2.1	1.9	1.9	1.9	2.1	2.0	2.0	2.8	2.7	2.6

4. Conclusions

The adsorption of all the seven neonicotinoids in the four agricultural soils from three states (Mississippi, Arkansas, and Tennessee) in the United States followed a linear isotherm. The K_d values were found to be below 2.0 L/kg for all the neonicotinoids in all the soils in Mississippi and Arkansas. Only in the Tennessee soil, the K_d values range from 0.96 to 4.21 L/kg. In all the soils nitenpyram has the lowest K_d and thiacloprid has the highest. The K_d values for all insecticides are closely related to the OC in the soils – the higher the OC, the greater the K_d value. The calculated ΔG values of all neonicotinoids in all soils ranged from – 14.6 to -19.5 kJ/mol, indicating that the adsorption between insecticides and soils is mainly van der Waals force, which result in a weak and reversible adsorption process. The degradations of all insecticides in all tested soils followed the exponential decay model, and half-lives of the neonicotinoids ranged from 33 to 305 d. The correlation between half-life and soil property parameters indicates a positive effect of clay content and/or CEC on the degradation rates of the neonicotinoids. The Groundwater Ubiquity Scores calculated from the leachability index model indicates that all neonicotinoids, except for thiacloprid, in the tested soils are possible leacher, having the potential to permeate into or through groundwater zones.

Declarations

Data availability

All data from this study can be obtained from the corresponding author.

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Contributions

Yang Li was responsible for designing the research and write the manuscript. Yadong Li was responsible for performing the analysis of this research and revising the manuscript. Guihong Bi was responsible for testing the soil properties and revising the manuscript. Timothy Ward and Lin Li were providing technical support for analysis the samples and revising the manuscript.

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Ethics declarations

Ethics approval

The authors in the study have read and approved the work and have given their consent to the submission and publication of the manuscript.

Consent to participate

Not applicable.

Consent for publication

Applicable.

Competing interests

The authors declare no competing interests.

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Table 1

Table 1 is available in the Supplementary Files section.

Figures

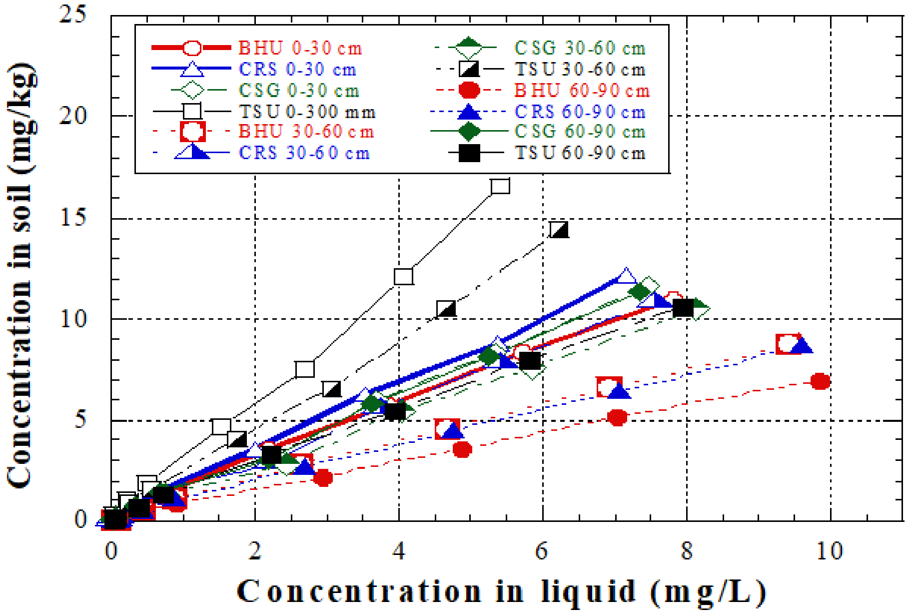

Figure 1

Adsorption equilibrium concentrations of imidacloprid in soil samples from BHU, CRS, TCB, and TSU at different sampling depths

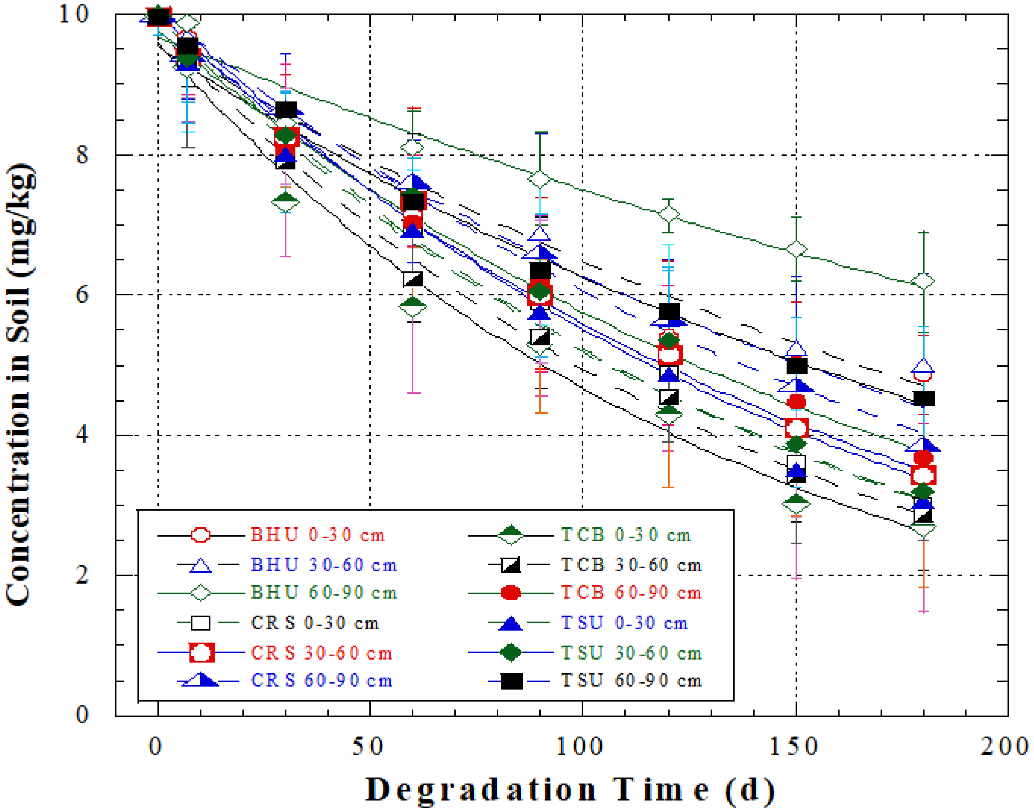

Figure 2

Degradation of imidacloprid in BHU, CRS, TCB, and TSU soils at three depths in air-dried soils

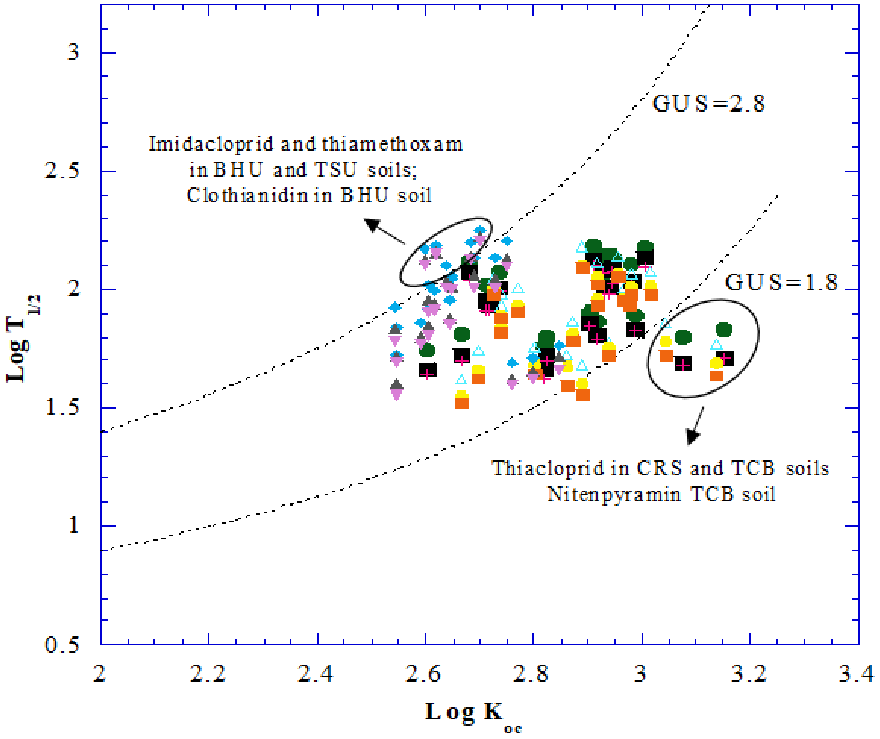

Figure 3

The calculated GUS values of all insecticides in different agricultural soils.

Supplementary Files

- Table1.docx