

Research Article

Dissipation Dynamics of Imidacloprid Residue in Different Saline Soils

¹Qingming Zhang and ²Caixia Wang

¹College of Chemistry and Pharmaceutical Sciences,

²College of Agronomy and Plant Protection, Qingdao Agricultural University, Qingdao 266109, China

Abstract: A method was developed for determining imidacloprid in soil using high performance liquid chromatography with UV-vis detector. The dissipation of imidacloprid in saline soil was also investigated under field and laboratory controlled conditions. The average recoveries ranged from 84.4 to 88.1% with relative standard deviations of 2.0 to 3.2% at three spiking levels (0.05, 0.5 and 5.0 mg/kg) in soil matrix. Under the field conditions, the half-life of imidacloprid in soil ranged from 8.6 to 11.4 days in Dongying and from 9.3 to 12.1 days in Binzhou. The dissipation rates of imidacloprid were almost same in the two locations. Under the laboratory conditions, the half-life of imidacloprid in soil with 0.3% NaCl was slightly longer than that in the soil without NaCl, which indicated that the dissipation of imidacloprid could be retarded in soil under salinity stress. These results could provide guidance for risk assessment and proper use of imidacloprid in relative saline regions.

Keywords: Dissipation, HPLC, imidacloprid, pesticide, salinity

INTRODUCTION

The Yellow River Delta (YRD) is one of China's three major river deltas and mainly includes Dongying and Binzhou cities of Shandong Province, which is located to the east longitude 117°51'40"-118° 24'29" and north latitude 37°56'58"-38°15'51". This area is an important agricultural production base especially for grain and cotton (Jiang *et al.*, 2011). As an estuarine delta, soil salinization is a primary character of this region. In addition, secondary salinization has also become increasingly severe in recent years due to human activities, such as the application of fertilizers and pesticides to enhance crop yields (Fang *et al.*, 2005; Zhang *et al.*, 2011). Previous studies have reported that the degradation behaviors of pesticides were different in different soils. The dissipation rates of pesticides mainly depend on soil type, soil moisture and soil organic matter content, etc (Thorstensen and Lode, 2001; Alam *et al.*, 2013). Since the soil characteristics of YRD is different from other areas, it is highly necessary to investigate the degradation behaviors of pesticides in soil for reducing soil contamination and salinization.

Imidacloprid (1-((6-chloro-3-pyridinyl)methyl)-N-nitro-2-imidazolidinimine), a neonicotinoid insecticide, is widely used to control sucking insects, termites, soil insects and some chewing insects in agriculture worldwide (Bajeer *et al.*, 2012). In YRD, imidacloprid is now extensively applied to cotton, grain and vegetables. Since the special action mechanism and

slathered utilization, many studies have been conducted on imidacloprid with main respects to control efficacy, resistance, environmental behavior, ecological effect, etc (Bonmatin *et al.*, 2005; Larsen *et al.*, 2005; Sánchez-Bayo and Goka, 2006). For the degradation of imidacloprid in soil, many studies reported that the dissipation rate of imidacloprid depended on soil type, pH, organic matter content and presence or absence of ground cover. Consequently, the half-life of imidacloprid in soil varies and the time ranges from several days to several months (Rouchaud *et al.*, 1994; Sarkar *et al.*, 2001; Sharma and Singh, 2014). However, to our knowledge, little is known about the dissipation of imidacloprid in saline soil. Hence, the present study was carried out to investigate the persistence and dissipation kinetics of imidacloprid residues in saline soil under field and laboratory conditions, with the aim to providing a reference for safe and reasonable use of imidacloprid.

MATERIALS AND METHODS

Reagents and equipment: Standard imidacloprid (CAS No. 138261-41-3, purity 98.5%) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). Methanol, hydrochloric acid, dichloromethane, sodium chloride and anhydrous sodium sulfate (all analytical grade), were purchased from Beijing Chemical Reagents Company (Beijing, China). Imidacloprid stock standard solution of 1000 µg/mL was prepared in methanol (HPLC grade, Hengxing, Tianjin, China) and

Corresponding Author: Caixia Wang, College of Agronomy and Plant Protection, Qingdao Agricultural University, Qingdao 266109, China, Tel.: +86 532 88030480; Fax: +86 532 88030480

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stored at 4°C. Working standard solutions were prepared by gradient dilution of the above-mentioned solution with methanol and stored at 4°C until use.

The SHA-B water bath shaker was purchased from Ronghua Instrument Company (Shanghai, China). The RE-52A vacuum rotary evaporator was from Yarong Instrument Company (Shanghai, China). The SHP-250 biochemical incubator was obtained from Sanfa Instrument Company (Shanghai, China). Agilent 1100 HPLC system (Agilent Technologies, USA) equipped with ultraviolet detector was used to analyze samples.

Experiment design: The supervised field trials were conducted in cotton fields of Dongying and Binzhou City in Shandong Province, China in 2012 and 2013. The dissipation experiments in supervised field trials were designed according to the Guideline for Pesticide Residue Trials (NY/T 788-2004) issued by the Ministry of Agriculture of the People’s Republic of China. The area of each experiment plot was 10 m² (2×5 m) and each treatment was designed with three replicated plots. Each plot was separated by a buffer area. In July when cotton reached flowering stage, imidacloprid (10% WP) was applied by one time spray to soil at the dosage of 70 g a.i. ha⁻² (twice the recommended dosage for the control of cotton aphid). From each plot 1-2 kg non-rhizosphere soil was collected with a soil auger (15 cm long, 2.5 cm diameter) by using a five-point method at 2 h, 1, 3, 7, 14, 21, 30 and 45 days after spraying. Then

the collect soil from each plot were pooled together and mixed thoroughly, air dried, screened through 20-mesh sieves and stored at -20°C for further analysis.

The soil collected in Dongying was used as the experimental sample in laboratory testing. For simulating the situation of moderate salinity stress, four treatments were set: 5 mg/kg imidacloprid, 5 mg/kg imidacloprid+0.3%NaCl, 10 mg/kg imidacloprid and 10 mg/kg imidacloprid+0.3%NaCl in dry soil. Each treatment was in triplicate. The treated soil samples were placed in brown glasses (250 mL) and sealed with cotton plugs to minimize water loss. All samples were incubated in the dark at 25°C for 60 days. The soil moisture contents were monitored every two days by weighing and deionized water was added to maintain the water holding capacity at 60%. Soil samples were collected from each treatment in 2 h and 1, 3, 7, 14, 21, 28, 35 and 60 days for imidacloprid residue determination.

Soil characterization: The soils collected in two locations were classified as Fluvo-aquic soil according to the USDA Soil Taxonomy System. The other physico-chemical properties including pH, organic matter, available N, available P, available K and water holding capacity of the soil were determined with the method of Qiao (2012). The soil salinity was measured following the method of Rhoades (1990). The soil properties were listed in Table 1.

Table 1: Physical and chemical properties of the experimental soil

Soil spots	pH (H ₂ O)	Salt content (g/kg)	Organic matter (mg/kg)	Organic nitrogen (mg/kg)	Available phosphorus (mg/kg)	Available potassium (mg/kg)
Dongying	7.8	1.4	11.3	86.3	11.2	123.4
Binzhou	7.6	0.9	14.2	97.6	13.6	112.7

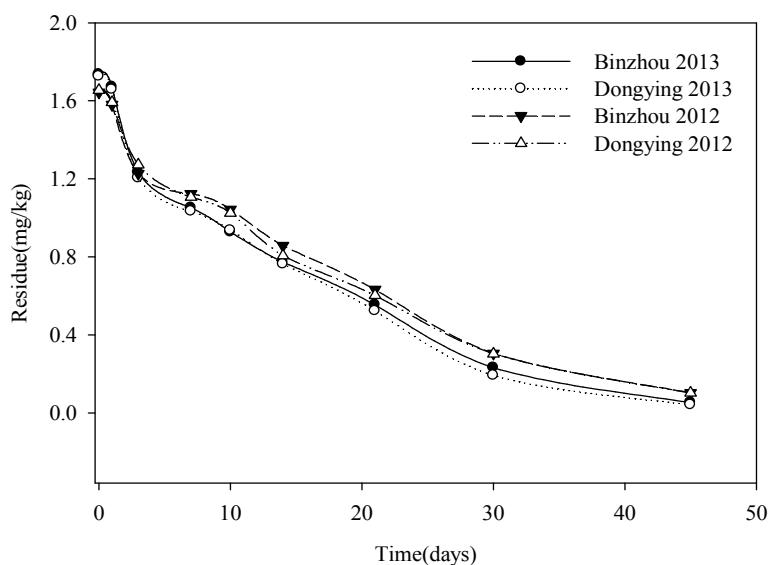


Fig. 1: The dissipation of imidacloprid in soils both in Dongying and Binzhou

Sample preparation: Twenty five grams of soil sample was weighed and placed into a conical flask (250 mL) and shaken for 30 min at 250 rpm on a mechanical shaker with 60 mL methanol and 20 mL hydrochloric acid solution (pH = 3). The extracts were filtered through a buchner funnel using 50 mL methanol: distilled water (3:1, v/v) as washing solvent. Filtrates were pooled and transferred to a 500 mL separatory funnel and 100 mL 5% saturated NaCl solution was added. The solution was then extracted with dichloromethane (3×40) and the extracts were dehydrated using 10 g anhydrous sodium sulfate. The combined dichloromethane layer was concentrated to near dryness on a vacuum rotary evaporator with a water bath at 40°C. The residue was dissolved with 5 mL methanol and filtered through a 0.22 µm pore membrane filter for High-Performance Liquid Chromatography (HPLC) analysis.

HPLC determination and calculation: Imidacloprid was determined using Agilent 1100 and separated with an agilent HC-C18 (2) reversed-phase column (4.6×250 mm, 5 µm) maintained at 25°C. The mobile phase used was methanol:water (4:6, v/v) with a flow rate of 0.8 mL/min. The detection wavelength was 270 nm and the injection volume was 10 µL. With these operating parameters, the approximate retention time of imidacloprid was 7.9 min (Fig. 1). The residues were calculated by comparing the peak areas of the samples with that of standards that was run under the same HPLC conditions. The degradation rate constant and half-life of imidacloprid were calculated using first-order kinetics equations $C_t = C_0 e^{-kt}$ and $t_{1/2} = \ln 2/k$, where C_t denotes the concentration of the pesticide residue at time of t, C_0 denotes the initial concentration, k is the dissipation degradation rate constant and $t_{1/2}$ is the half-life (Wang *et al.*, 2013).

RESULTS AND DISCUSSION

Method validation: Several procedures to determine imidacloprid in different matrices have been reported, in which HPLC was most commonly utilized (Vilchez *et al.*, 1996; Baskaran *et al.*, 1997; Bonmatin *et al.*, 2003; Sharma and Singh, 2014). To determine the imidacloprid residues in soil, this current study developed a reliable HPLC method. Linearity of this

procedure was evaluated with matrix-matched standard calibration method to eliminate the matrix effects. Good linearity of the response was obtained within a concentration ranging from 0.1 to 10 mg/L of imidacloprid and the squared correlation coefficient (R^2) reached 0.9997. Accuracy was evaluated by the recovery efficiency, as determined at three concentration levels of spiking (0.05, 0.5 and 5.0 mg/kg) with three replicates for each level. The average recovery of imidacloprid soil ranged from 84.4 to 88.1%, with Relative Standard Deviation (RSD) of 2.8 to 3.2% (Table 2). The Limit of Detection (LOD) for imidacloprid was 0.03 ng at a Signal-to-Noise (S/N) ratio of 3. The Limit of quantitation (LOQ) was 0.01 mg/kg at a S/N ratio of 10. The above results indicated that the established method met the requirement and was suitable for pesticide residue analysis.

Dissipation of imidacloprid in soils: The dissipation dynamic of imidacloprid in soil under field conditions was shown in Fig. 1 and the regression equations, correlation coefficients and half-life were listed in Table 3. The initial concentrations of imidacloprid in soil from Dongying and Binzhou were 1.65 to 1.72 mg/kg and 1.64 to 1.74 mg/kg in both years, respectively. As time went on, a gradual decline in residue content was observed in samples from both locations and the dissipation processes followed the first order reaction kinetics, which was further supported by the significant correlation coefficient ($R^2 = 0.9911-0.9993$) of the dissipation data. The calculated half-life of imidacloprid in soil from Dongying and Binzhou were 8.6 to 11.4 days and 9.3 to 12.1 days, respectively, which was no obvious difference in the half-life of imidacloprid in both experiment sites. These results indicated that the soil characters were basically the same in both experiment sites, as confirmed by the result of soil properties (Table 1). Another line of evidence was that the dissipation of imidacloprid was closely related to soil characters such as soil type, pH,

Table 2: Recovery of imidacloprid in soil (n = 3)

Fortified level (mg/kg)	Recovery (%)			Average recovery (%)	RSD (%)
0.05	83.6	87.9	81.7	84.4	3.2
0.50	90.8	86.8	85.5	87.7	2.8
5.00	87.3	85.4	91.6	88.1	3.1

Table 3: The regression equation, correlation coefficient and the half-lives of imidacloprid in soil

Experimental design	Treatments	Regression equation	Correlation coefficient	Half-life (days)
Field	Dongying 2012 (75 g a.i/ ha)	$C = 1.7862e^{-0.0607t}$	0.9993	11.4
	Binzhou 2012 (75 g a.i/ ha)	$C = 1.8372e^{-0.0574t}$	0.9935	12.1
	Dongying 2013 (75 g a.i/ ha)	$C = 2.1118e^{-0.081t}$	0.9903	8.6
	Binzhou 2013 (75 g a.i/ ha)	$C = 2.017e^{-0.075t}$	0.9911	9.3
Laboratory	5 mg/kg imidacloprid	$C = 4.7121e^{-0.0423t}$	0.9811	16.4
	5 mg/kg imidacloprid+3%NaCl	$C = 5.089e^{-0.0413t}$	0.9896	16.8
	10 mg/kg imidacloprid	$C = 8.7531e^{-0.0563t}$	0.9749	12.3
	10mg/kg imidacloprid+3%NaCl	$C = 8.9591e^{-0.0537t}$	0.9790	12.9

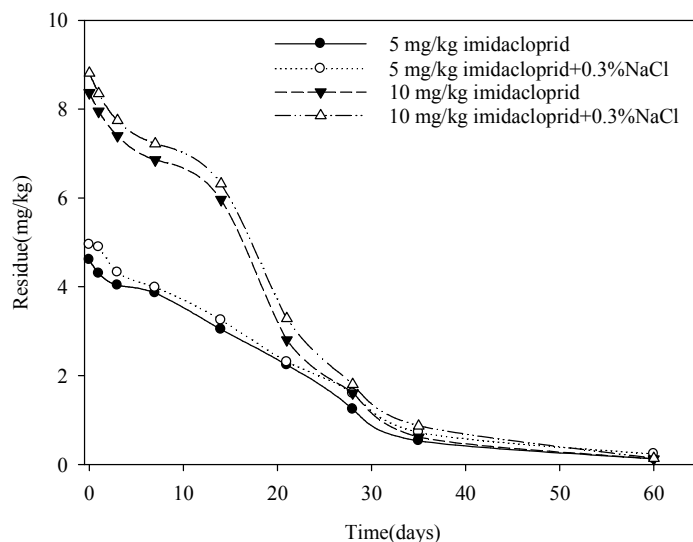


Fig. 2: The dissipation of imidacloprid in soils under laboratory conditions

organic matter content, etc. Our results were consistent with previous studies which reported that soil characters played a significant role during the degradation of pesticides (Kumar *et al.*, 2005; Sun *et al.*, 2013; Zhang *et al.*, 2013). However, in these two locations, the half-life of imidacloprid in 2012 was longer than that in 2013. According to the information provided by Binzhou weather bureau, the average precipitation and temperature of 2013 were higher than those in 2012 during the period of experiment. These climate factors may accelerate the dissipation of imidacloprid in the soil. This conjecture has been reported by Wang *et al.* (2013) who found that climate factors such as high precipitation and temperature could accelerate the dissipation of fungicide azoxystrobin in soil.

For eliminating the interference of externally variable factors under field condition, laboratory test was conducted. The dissipation dynamic of imidacloprid and other relevant parameters were presented in Fig. 2 and Table 3, respectively. The dissipation processes of two concentrations of imidacloprid followed the first order reaction kinetics. The half-lives of 5 and 10 mg/kg imidacloprid were 16.4-16.6 days and 12.3-12.9 days, respectively. The half-life of imidacloprid in laboratory soil is longer than that in field soil. This indicated that the dissipation rate of imidacloprid in field is faster than that in laboratory. Interestingly, for each concentration of imidacloprid, its half-life in soil with 0.3% NaCl was longer than that in soil without NaCl, which suggested that salinity stress could mitigate the dissipation of imidacloprid in soils. The possible reason is that soil microbial activity was inhibited under the salinity stress (Rietz and Haynes, 2003) and thus dissipation rate becomes slower since soil microorganism plays an important role in the degradation of imidacloprid (Anhalt *et al.*, 2007). Therefore, based on the collected data, we suggest that it is necessary to prolong the

interval time of imidacloprid application in relatively saline fields for reducing the soil contamination.

CONCLUSION

In this study, a HPLC method was developed to determine imidacloprid in soil. Dissipation of imidacloprid in soils under field and laboratory condition was also investigated. Results showed that the half-life of imidacloprid in soils from Dongying and Binzhou was basically same under field conditions. However, in laboratory conditions, the half-life of imidacloprid in soil with 0.3% NaCl was slightly longer than that in soil without plus NaCl. In conclusion, the results presented in this study could provide reference for the environmental risk assessment and reasonable use of imidacloprid in salinized farmland.

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