Dissipation of propisochlor and residue analysis in rice, soil and water under field conditions

Su-li Wang [a,b], Feng-mao Liu [a,*], Shu-hui Jin [a], Shu-ren Jiang [a]

[a] *College of Science, China Agricultural University, Beijing 100094, China*
[b] *HeBei North University, HeBei 075131, China*

Abstract

The analytical method for the residues of a new herbicide propisochlor and its dissipation and residual amounts in soil, water and rice plants in field conditions (rice cropping system) were studied. The chloroacetanilide herbicide, propisochlor (72% w/w EC) was applied at two dosages, $108 \, g \, a.i. \, ha^{-1}$ (recommended) and $162 \, g \, a.i. \, ha^{-1}$ (1.5 times of the recommended dosage) seven days after transplanting rice seedlings in the experimental fields in both Beijing and Fujian provinces (experimental localities). Soil, water and rice plant samples were collected at intervals and analyzed for propisochlor residues. The detection limit (LOD) of propisochlor is $0.2 \, \mu g \, kg^{-1}$ and the limit of quantification (LOQ) was established as $1 \, \mu g \, kg^{-1}$. At three different spiking levels, mean recoveries and relative standard deviation (RSD) from fortified samples in three replicated experiments for each matrix were in the range 81–109% and 1.3–13.1%, respectively. The results showed that the half-lives of propisochlor in water, soil and rice plant from Beijing were 0.56, 5.25 and 1.46 days respectively, and the half-lives of propisochlor in water, soil and rice plant from Fujian were 0.62, 5.12 and 0.81 days. At harvest, soil, straw, rice hull and husked rice samples were found to contain propisochlor well below the limit of detection (LOD) following the recommended dosage and 1.5 times dosage.
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1. Introduction

Rice is an important alimentary source throughout the world and the quality of the grain can be compromised by the presence of pesticide residues.

Pesticides are routinely used in integrated farm management programs to reduce possible losses due to pests. Pesticides when applied to crops undergo transformation under the influence of the environment. The persistent agrochemicals often cause health hazards to non-target organisms including animals and human beings. The fate of herbicides applied to soil is governed by various processes such as adsorption, herbicide transformation and transportation in addition to the influence of factors such as herbicide application rate, crop type, agricultural practices and climatic conditions (Arnold & Briggs, 1990; Cheng, 1990). Propisochlor is used for weed control in soybean, corn, peanut, jowar and rice crop field. When absorbed through the roots and shoots just above the seed of the target weeds, it acts as a growth inhibitor by suppressing synthesis of protein (Wang & Guan, 2000; Xu, Wu, & Zhang, 1998).

The herbicide propisochlor has been studied for its fate in the environment by different researchers. Wang, Zhao, and Zhu (2003) in their studies revealed that the half-life of propisochlor photolysis in four different kinds of simulated natural water was within 0.12–0.59 h. Lengyel and Foldenyi (2001) studied adsorption on different soil types of acetochlor and propisochlor, revealed that the amount of the compound adsorbed on a unit mass of the soils is higher in the case of propisochlor than in the case of acetochlor.

Czinkota, Foldenyi, and Lengyel (2002) studied adsorption of propisochlor on three different kinds of soils and adsorption curves fitting well to the experimentally obtained two-step isotherms. Konda and Pasztor (2001) studies in environmental distribution of acetochlor, atrazine, chlorpyrifos and propisochlor under field conditions showed that there was a consistent decrease in pesticide in the 0–5 cm soil layer with time after spraying, at 140th day after treatment only atrazine and chlopyrifos were present; acetochlor and propisochlor were not detected. Atrazine and chlopyrifos in the soil at a depth of 5–20 cm were detectable during the whole experiment, whereas acetochlor and propisochlor concentrations were below the limit of detection.

Propisochlor (2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-[(1-methylethoxy) methyl] acetamide) is a pre-emergent herbicide that is used to control some broad leaf and annual grass weeds. Propisochlor with the commercial name of *pulebao*, is a new chloroacetanilide herbicide that is produced in Hungary.

Usually, propisochlor mixed with other herbicides, can reduce necessary dosage and enhance the efficiency. In China, it was only registered and permitted to control the weeds in soybean and corn with the usage rates of 90–108 g a.i. ha^{-1} and 125–150 g a.i. ha^{-1} of 72% propisochlor EC, it was not registered for use on rice. The objective of this work was to establish the analytical methods for the residues of propisochlor in rice, and to evaluate its dissipation rate and residue levels under field conditions.

2. Materials and methods

2.1. Chemical materials

Reference standard of propisochlor (>95% purity) and propisochlor (72% EC) was supplied by WuXi RuiZe Pesticide Ltd., Jiangsu Province. Dichloromethane, petroleum ether, acetone and ethyl acetate were of analytical reagent grades redistilled doublely. Analytical sodium chloride and anhydrous sodium sulfate were analytical grade reagents. Florisil was purchased from Beijing Chemistry Reagent Company and heated at 130 °C for 12 h. Activated charcoal was cleaned with HCl and washed free of HCl residue with water.

2.2. Field study

Field experiments were conducted in Beijing and Fujian province during 2003 and 2004 according to "The guideline for Pesticide Residue Field Experiment" issued by the Institute of the Control of Agrochemicals, Ministry and Agriculture, The People's Republic of China. Nine different trial plots each with a dimension of 5×6 m (30 m^2) were prepared. A 1 m distance was maintained between the plots. All four sides of the plots were protected by soil boundaries raised to a level of 30 cm height and 30 cm width. Seven days after transplanting rice seedlings, propisochlor emulsifiable concentrate (propisochlor 72%, w/w) was applied at

108 g a.i. ha^{-1} (low concentration, recommended dosage) and 162 g a.i. ha^{-1} (high concentration, 1.5 times recommended dosage). For low concentration, 6.7 ml of the propisochlor 72% EC formulation was mixed with sand and sprinkled on 30 m^2 plot. For high concentration, 10.1 ml of the propisochlor, 72% EC formulation was mixed with sand and sprinkled on 30 m^2 plot. Three different plots (triplicates) were sprinkled for each dose. A further three different triplicate plots were maintained as a control with no herbicide.

2.3. Sampling and storage

Samples were collected at random from each plot at different time intervals i.e, 0 day (2 h after application), 1, 3, 5, 7, 10, 14, 21, 28, 45 days after the herbicide application. Soil samples were collected randomly from each plot using a soil auger to a depth of 15 cm from the surface. Little stones and other unwanted materials were removed. Water samples were collected in the plastic bottles randomly from each plot and filtered through a 12-cm Buchner funnel. Plant samples with roots were collected and washed. At harvest, soil, straw and rice samples were collected for terminal residue analyses. Rice was air-dried at room temperature and shelled into rice hull and husked rice. Husked rice was ground to powder. All samples were stored at −20 °C except for water samples at 4 °C until analysed.

2.4. Analytical procedure

2.4.1. Extraction and clean-up of water sample

To 250 ml of water was added 200 ml 2% Na$_2$SO$_4$ (w/v) solution and 40 ml of dichloromethane. The contents were shaken vigorously for 2 min. The organic layer was collected and the aqueous layer was re-extracted using the same procedure. The dichloromethane layers were collected and dried over 10 g anhydrous sodium sulfate, evaporated with rotary evaporator at <40 °C near to dryness and then dried under a nitrogen stream. The residue was dissolved in 2 ml of *n*-hexane for GC-ECD analysis.

2.4.2. Extraction and clean-up of soil sample

Soil samples were collected from a trial field in Beijing and Fujian. Characteristic properties of these soils used in the fields were the following: Beijing, clay loam; organic matter—2.28%; pH—7.32, Fujian, sandy clay loam; organic matter—3.28%; pH—6.56.

Soil samples were dried at room temperature and screened through 40-mesh sieves. A portion (20 g) of homogenized soil sample was weighed into a flask, 60 ml of mixture of petroleum ether/acetone = 1:1 (v/v) was added, and shaken for half an hour vigorously. The over layer was filtered through a Buchner funnel. The solid soil mud sample and the flask were washed twice with 2×20 ml a mixture of petroleum ether/acetone = 1:1 (v/v) and the solid soil sample was discarded; the mixtures were combined and transferred into a 500 ml separating funnel, 100 ml 2% Na$_2$SO$_4$ (w/v) solution was added and shaken for 1 min.

The aqueous layer was transferred into another separating funnel, another 30 ml petroleum ether was added and reextracted. The organic portions were combined and filtered through 10 g anhydrous sodium sulfate and evaporated to approximately 5 ml using a vacuum rotatory evaporator (40 °C) for further clean-up.

A glass column was packed with 3 g of mixture florisil/activated charcoal = 20:1 (m/m) between two layers of 1 g of anhydrous sodium sulfate. The concentrated extract of different substrates was poured on the top of the column and eluted with a 40 ml mixture of petroleum ether/ethyl acetate = 8:2 (v/v). The first 5 ml of eluate was discarded. The remaining eluate was concentrated to dryness in a rotary evaporator under vacuum at 40 °C and made up to 1 ml in *n*-hexane for GC-ECD analysis.

2.4.3. Extraction and clean-up of rice plant, straw, rice hull and husked rice samples

Rice plant samples were collected from the trial field for dissipation studies of propisochlor. Straw and rice samples were collected for the terminal residue of propisochlor.

Rice plant and straw samples were cut into small pieces using a mechanical slicer. Rice plant portion (20 g) or 10 g of the straw, rice hull and husked rice samples respectively were weighed and 80 ml of the mixture of petroleum ether/acetone = 1:1 (v/v) added. The further process was then the same as the soil samples described above.

2.5. Instrument

Rotary Evaporator (N-1) (TOKYO RIKAKIKAI CD, Ltd.), Glass column (10 mm i.d. × 30 cm) was purchased from BeiJing CaoLun (China), Air bath vibrator (HZQ-C, Haerbing Donglian Electron exploiture CO. Ltd., Heilunjiang Province, China), Agilent 4890 GC, equipped with electron capture detector (ECD), HP-35MS capillary column (30 m length × 0.25 mm i.d and 0.25 μm film thickness), injector temperature 280 °C, detector temperature 280 °C, programmed oven temperature from 120 °C to 260 °C, injection volume 1 μl, carrier nitrogen 1 ml min^{-1}.

For the complete separation of propisochlor and impurities in different samples, different temperature programs were used.

2.6. Statistical analysis

The degradation kinetics of the propisochlor in water, soil and rice plant were determined by plotting residue concentration against time and the maximum squares of correlation coefficients found were used to determine the equations of best fit curves. For all the samples studied, exponential relationships were found to apply, corresponding to first order rate equation. Confirmation of the first order kinetics was further made graphically from the linearity of the plots of Ln C against time. The rate equation was calculated from the first order rate equation: $C_t = C_0 e^{-kt}$, where C_t represents the concentration of the pesticide residue at time t, C_0 represents the initial concentration and k is the rate constant in days^{-1}. The half-life ($t_{1/2}$) was determined from the k value for each experiment, being $t_{1/2} = \ln 2/k$.

3. Results and discussion

3.1. Recovery and detection limits

Different known concentrations of propisochlor (0.1, 0.5, 2.5, 5.0, 10.0 mg l^{-1}) were prepared in *n*-hexane by diluting the stock solution. One microliter of each standard solution was injected into the injector of GC-ECD and the peak area measured. A standard calibration curve of propisochlor was constructed by plotting analyte concentrations against peak areas. Good linearity was achieved between the range 0.1–10 mg l^{-1} with a correlation coefficient of $r = 0.9998$. The standard curve equation was $y = 15374x + 1884.8$. Validation of the method was performed in terms of recovery studies before analysis of unknown samples. The recovery study was conducted for different substrates. At three different fortified levels (0.05, 0.1, 1, 0.01 (for water sample) mg kg^{-1}) the mean recoveries from fortified samples in three replicated experiments for each matrix were in the range 81–109%. The relative standard deviation (RSD) ranged from 1.3% to 13.1% and suggested that extraction and clean-up procedure could be considered fit for purpose for routine analysis of propisochlor in experimental matrices. The recovery and relative standard deviation (RSD) are shown in Table 1. The LOD of propisochlor is 0.2 μg kg^{-1}, and the signal-to-noise (S/N) ratios is 3:1. The

Table 1
Average recovery and relative standard deviation (±RSD) of fortified samples[a]

Fortified level (mg kg^{-1})	Water (%)	Soil (%)	Rice plant (%)	Straw (%)	Ricehull (%)	Husked rice (%)
0.01	96 ±3.7	–	–	–	–	–
0.05	103 ±5.5	86 ±4.3	87 ±8.8	87 ±7.9	97 ±7.5	99 ±4.7
0.1	100 ±1.3	102 ±6.6	85 ±5.5	88 ±2.2	101 ±2.5	107 ±3.1
1	–	100 ±1.7	91 ±2.3	97 ±5.9	97 ±13.1	97 ±5.1

[a] Values are average of triplicate analysis at each fortification level.

LOQ was established as $1 \mu g \, kg^{-1}$ that yielded a signal-to-noise (S/N) ratio of 10. No substrate interference was observed at this quantification level as evidenced by the control sample analysis.

3.2. Dissipation of propisochlor in the rice field conditions

3.2.1. Dissipation of propisochlor in water

The initial concentration of propisochlor in water was 0.14 and $0.11 \, mg \, l^{-1}$ in Beijing and Fujian at high concentration, respectively. There was a steady decrease in the residue content and by the 10th day the residues were at $3.5 \, \mu g \, kg^{-1}$ and $1.3 \, \mu g \, kg^{-1}$ levels from Beijing and Fujian water. Thereafter no residue was found in soils in Beijing and Fujian. Fig. 1 shows the dissipation curve of propisochlor in water under rice field conditions. The half-lives and other statistical parameters of the propisochlor residue dissipation were calculated from the experimental data and are summarized in Table 2. The half-lives were 0.56 and 0.62 days in Beijing and Fujian. Propisochlor degraded a little more rapidly in water matrix in Beijing than in Fujian.

3.2.2. Dissipation of propisochlor in soil under field conditions

The initial concentration of propisochlor in soil was 0.020 and $0.024 \, mg \, kg^{-1}$ in Beijing and Fujian at high concentration, respectively. There was a steady decrease in the residue content and by the 14th day the residues were at $6.1 \, \mu g \, kg^{-1}$ and $2.2 \, \mu g \, kg^{-1}$ levels from Beijing and Fujian soil. Thereafter no residue was found in soils in Beijing and Fujian. Fig. 2 shows the dissipation curve of propisochlor in soil under natural field conditions. The half-lives and other statistical parameters of the propisochlor residue dis-
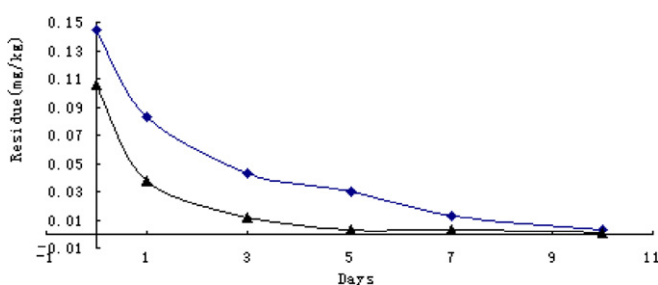

Fig. 1. Dissipation of residues of propisochlor under natural field conditions in water in Beijing and Fujian: top line, Beijing; bottom line, Fujian.
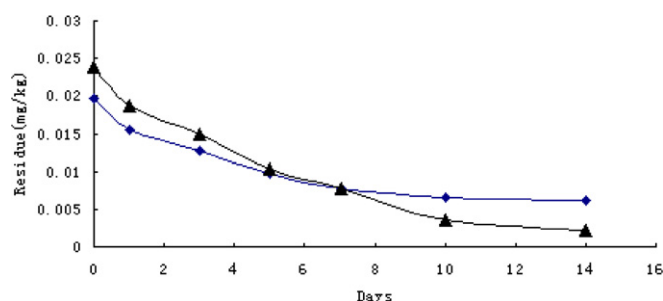

Fig. 2. Dissipation of residues of propisochlor under natural field conditions in soil in Beijing and Fujian: bottom line, Beijing; top line, Fujian.
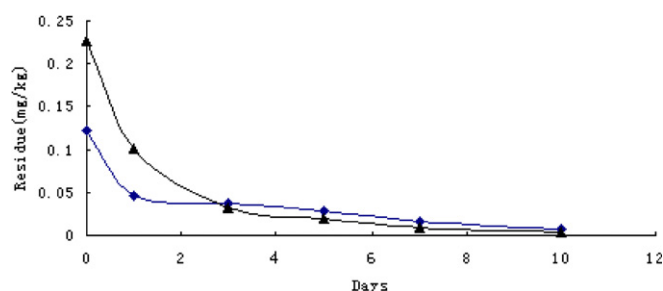

Fig. 3. Dissipation of residues of propisochlor under natural field conditions in rice plants in Beijing and Fujian: bottom line, Beijing; top line, Fujian.

sipation were calculated from the experimental data and are summarized in Table 2. The half-lives were 5.25 and 5.12 days in Beijing and Fujian. Propisochlor degraded a little more rapidly in soil in Fujian than in Beijing.

3.2.3. Dissipation of propisochlor in rice plant under field conditions

The initial concentration of propisochlor in rice plant was 0.12 and $0.23 \, mg \, kg^{-1}$ in Beijing and Fujian at high concentration, respectively. There was a steady decrease in the residue content and by the 10th day the residues were at $6.9 \, \mu g \, kg^{-1}$ and $3.9 \, \mu g \, kg^{-1}$ levels from Beijing and Fujian rice plants, Thereafter the residual content went below the LOD. Fig. 3 shows the dissipation curve of propisochlor in rice plant under natural field conditions. The half-lives and other statistical parameters of the propisochlor residue dissipation were calculated from the experimental data and are summarized in Table 2. The half-lives were 1.46 and 0.81 days in Beijing and Fujian. Propisochlor degraded more rapidly in rice plants in Fujian than in Beijing.

Table 2
Half-life and other statistical parameters for propisochlor dissipation in the rice field conditions

Matrix	Locality	Regression equation	Determination coefficient (R^2)	Degradation rate constant k (days^{-1})	Half-life (days)
Water	Beijing	$Ln \, C_t = -0.3529t + 0.1375$	0.9865	1.23	0.56
	Fujian	$Ln \, C_t = -0.5323t + 0.0733$	0.9487	1.12	0.62
Soil	Beijing	$Ln \, C_t = -0.1727t + 0.0244$	0.9697	0.13	5.25
	Fujian	$Ln \, C_t = -0.1919t + 0.0290$	0.9067	0.14	5.12
Rice plant	Beijing	$Ln \, C_t = -0.2492t + 0.0881$	0.9362	0.47	1.46
	Fujian	$Ln \, C_t = -0.3968t + 0.1563$	0.9624	0.86	0.81

3.3. Terminal residue levels

When propisochlor was used following the recommended dosage and 1.5 times of dosage with only one application, terminal residue levels of propisochlor in soils, straw, rice hull and husked rice were detected in Beijing and Fujian in 2003 and 2004, respectively. The residue content of propisochlor in soils, straw, rice hull and husked rice at these harvests were well below the LOD.

3.4. Discussion

From the results it is clearly evident that propisochlor degraded rapidly in rice field under natural conditions. Wang (2003, 2004) reported that the degradation of propisochlor in water was effected by light, heat, pH and dissolved oxygen concentrations. Usually, the degradation of propisochlor in soil was relevant to soil type, pH and organic matter content. In the degradation of pesticides in the plant. besides the effect of some physical and chemical factors like light, heat, pH and moisture, growth dilution factor might have played a significant role (Dhananjay, Vipin, Ravindranath, & Adarsh, 2005). In this study, besides the physical and chemical factors, the growth dilution factor played a significant role in the degradation of propisochlor in rice plant. Furthermore, the other influences of the cropping system might have influenced the dissipation. The kinetics of the dissipation is found to be first order in both sites. No residue was detectable in the final harvest products like rice hull, husked rice and straw.

4. Conclusions

The LOD of propisochlor is $0.2 \, \mu g \, kg^{-1}$ and the LOQ was established as $1.0 \, \mu g \, kg^{-1}$. The ranges of fortified recoveries and relative standard deviation (RSD) of the method were 81–109% and 1.3–13.1%, respectively. The method satisfied the requirements of propisochlor residue analysis. A decline study showed the half-lives obtained for propisochlor in water, in soil, in rice plant of Beijing and Fujian were 0.56 and 0.62 days, 5.25 and 5.12 days, 1.46 and 0.81 days respectively under the field conditions. The residue of propisochlor in soils, straw, rice hull and husked rice at harvest were not detected under the conditions of this field, following the recommended dosage and 1.5 times dosage. As there was no available MRL value in rice set up in China and any other countries, according to the same basic structure of propisochlor as metolachlor and pretilachlor, and MRL $(0.1 \, mg \, kg^{-1})$ of metolachlor and pretilachlor in rice, it should be safe to apply 72% propisochlor EC at the recommend dosage in the rice field.

Acknowledgements

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