

Abiotic partitioning of clothianidin under simulated rice field conditions

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Abstract

BACKGROUND: Clothianidin is registered for pre- and post-flood application in Californian rice fields for control of the rice seed midge, *Cricotopus sylvestris*, and the rice water weevil, *Lissorhoptrus oryzophilus*. The objective was to characterize air–water and soil–water partitioning of clothianidin under simulated Californian rice field conditions.

RESULTS: Clothianidin was confirmed to be non-volatile (from water) via the gas purge method, as no loss from the aqueous phase was observed at 22 and 37 °C; an upper-limit K_H value was calculated at 2.9×10^{-11} Pa m³ mol⁻¹ (20 °C). Soil–water partitioning was determined by the batch equilibrium method using four soils collected from rice fields in the Sacramento Valley, and sorption affinity (K_d), sorbent capacity, desorption and organic-carbon-normalized distribution (K_{oc}) were determined. Values for pH, cation exchange capacity and organic matter content ranged from 4.5 to 6.6, from 5.9 to 37.9 and from 1.25 to 1.97% respectively. The log K_{oc} values (22 and 37 °C) ranged from 2.6 to 2.7, while sorption capacity was low at 22 °C and decreased further at 37 °C. Hysteresis was observed in soils at both temperatures, suggesting that bound residues do not readily desorb.

CONCLUSIONS: Soil–water and air–water partitioning will not significantly reduce offsite transport of clothianidin from flooded rice fields via drainage.

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Keywords: neonicotinoid insecticides; clothianidin; soil–water partitioning; air–water partitioning; abiotic pesticide dissipation

1 INTRODUCTION

Clothianidin, a synthetic neonicotinoid insecticide, acts as an agonist at post-synaptic nicotinic acetylcholine receptors within the central nervous system of a variety of insects, including Hemiptera, Thysanoptera, Coleoptera, Lepidoptera and Diptera.^{1–3} Laboratory studies have demonstrated that neonicotinoids (in general) and clothianidin (in particular) are highly toxic towards pollinators, and some investigators and regulators are concerned that neonicotinoid exposure in field conditions may be a compounding factor in colony collapse disorder.^{4,5} Overall, its use in agricultural areas of California is low, with less than 7000 lbs of active ingredient applied in 2012.⁶ However, its use has increased significantly since 2011, as a number of products containing the active ingredient have recently been registered for cotton, cucumber, grapes and tomatoes.⁶ It was recently registered for pre-flood (to paddy soil) and post-flood (to paddy water) aerial application to protect Californian rice fields against the rice seed midge, *Cricotopus sylvestris*, and the rice water weevil, *Lissorhoptrus oryzophilus*.

In California, rice fields are flooded prior to planting, and water levels are maintained throughout the growing season, although fields may be drained for up to 3 weeks soon after planting in order to apply pesticides.⁷ Discharged field water flows directly into the Sacramento River Basin (SRB), a system of lakes, streams and rivers supporting a variety of aquatic species that are crucial to the economic and environmental health of the state. Clothianidin has been classified as highly toxic to sediment-dwelling organisms such as *Mysidopsis bahia*, *Chironomus riparius* and *Leptocherius plumulosus*.^{8,9} The California Department of Pesticide Regulation

(DPR) requires that treated water be held for 14 days before the draining of fields, based on the assumption that, when applied in shallow, aqueous conditions, the compound will break down rapidly. This is further based on the assumption that dissipation is dominated, or controlled, by aqueous-phase processes.¹⁰ The degree to which this is true depends on the compound's partitioning behavior – particularly between soil and water, which we address. In order comprehensively to quantify the risk to the SRB watershed, abiotic partitioning should be assessed with respect to conditions and soils specific to Californian rice fields.¹¹ To our knowledge, no peer-reviewed environmental fate studies concerning the abiotic dissipation of clothianidin under flooded rice field conditions are available.

Clothianidin (pK_a 11.0) is a neutral species within environmentally relevant pH ranges, has a low vapor pressure (3.8×10^{-11} Pa at 20 °C) and a low octanol–water partitioning coefficient (0.7 at 20 °C) and is moderately soluble (327 mg L⁻¹ at 20 °C). On the basis of these properties and reports generated by the registrant,

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volatilization from the water is not likely to occur, and soil sorption may allow for decreased risk of offsite transport.^{8,9,12} However, the physical properties of the compound are not sufficient to predict the fate of a pesticide in an environment as chemically complex as a flooded rice field. In order to understand the fate, and therefore to characterize the potential exposure routes, for non-target organisms, partitioning parameters should be tested with site-specific environmental conditions and management factors taken into account.^{11,13}

The primary objective was to characterize equilibrium-phase partitioning of clothianidin under representative Californian rice field conditions. In California, field water is subject to daily temperature fluctuations (20–36 °C). Both air–water and soil–water partitioning processes are temperature dependent, and the effects of these temperature fluctuations can be significant.^{11,14,15} The gas purge method was used to determine Henry's law constant (K_H).¹⁶ The batch equilibrium method, based on OECD guideline 106, was used to determine the soil sorption (K_d) and organic-carbon-normalized (K_{oc}) distribution coefficients.¹⁷

2 MATERIALS AND METHODS

2.1 Chemicals

Analytical clothianidin (99.9% purity) was purchased from Sigma Aldrich (St Louis, MO). All solvents (acetonitrile, methanol, water) were HPLC grade and purchased from Sigma Aldrich. Calcium chloride and ammonium acetate were purchased from Fisher Scientific (Hampton, NH). A 100 µg mL⁻¹ stock solution of clothianidin was prepared and stored in amber glass bottles at 4 °C. Dilutions were prepared with a 0.01 M calcium chloride solution to achieve final concentrations.

2.2 Soil collection and characterization

The soil sorption and desorption potential was evaluated for four soils taken from rice fields in the Sacramento Valley. Rice field soil samples were collected near Davis (DfT) and Biggs (BfB) and from two different fields in Richvale (RvT, RvB). The Davis soil, a Sacramento silty clay loam, is taxonomically classified as a fine, smectic, thermic cumulic Vertic Endoaquolls; the Biggs and Richvale soils, both of the Esquon Neerdobe clay series, are taxonomically classified as fine, smectic, thermic Xeric Epiaquerts.¹⁸ Several kilograms of each soil was randomly collected from the 0–10 cm layer, air dried and ground with a porcelain mortar and pestle to pass through a 2 mm sieve. In order to inhibit microbial activity, soils were autoclaved at 120 °C for 1 h. Although studies have shown that autoclaving can produce physical changes in soil, von Oepen *et al.* (1989) and Lotrario (1995) demonstrated that the overall effect on soil sorption is negligible.^{19–22}

The physicochemical properties and organic carbon content of the soils were determined by the UCD Analytical Laboratory (Table 1); the analytical methods can be found via the website (<http://anlab.ucdavis.edu/>).

2.3 Air–water partitioning

Henry's law constant K_H was calculated by dividing the vapor pressure VP by the water solubility S (25 °C). Additionally, the gas purge method was used to determine K_H at both 20 and 37 °C.¹⁶ In the method, aqueous insecticide was saturated with ultrapure N₂ gas passed through at a controlled flow rate, and the aqueous concentration was monitored over time. The rate of

analyte transfer to air in a well-mixed aqueous phase follows the first-order decline of its aqueous concentration:

$$\ln\left(\frac{C_t}{C_i}\right) = -\left(\frac{K_H * g}{V * R * T}\right)t \quad (1)$$

where V is the volume of the solution (m³), C_i and C_t are the analyte concentrations (µg mL⁻¹), t is the sampling time point (h), K_H is Henry's law constant (Pa m³ mol⁻¹), g is the gas flow rate (m³ h⁻¹), R is the universal gas constant (Pa m³ mol⁻¹ K⁻¹) and T is the temperature of the system (K).¹⁶ Accordingly, Henry's law constants can be calculated from the slope of linear plots of $\ln(C_t/C_i)$ versus time.

Gas-stripping experiments (at both 20 and 37 °C) were performed in duplicate using two jacketed Pyrex cylinders (1 m × 51 mm i.d.) with 1.5 L of a 5 µg mL⁻¹ solution of clothianidin in 0.01 M CaCl₂, and temperature was maintained with a recirculating water bath. Columns were foil wrapped to prevent photodegradation. Preliminary studies showed no evidence for loss of clothianidin by adsorption to tubes or by chemical degradation. High-purity N₂ gas was filtered through a hydrocarbon trap and streamed through the bottom of each column at a flow rate of approximately 0.05 m³ h⁻¹ for 48 h. Water samples (approximately 2 mL) were collected from the column at various time intervals over the course of the experiment to measure the decrease in aqueous concentration over time. Aqueous clothianidin concentrations were determined on a high-performance liquid chromatograph coupled to a diode array detector (HPLC-DAD).

2.4 Soil–water partitioning

Isotherms were constructed using the batch equilibration method.^{17,23} Experiments were constructed using triplicate samples and blanks to calculate standard deviation, and sorbed concentration was calculated from mass balance. Isotherms were obtained using 50 mL amber polytetrafluoroethylene (PTFE) screw-top centrifuge tubes. CaCl₂ was used as a background solution to control the ionic strength of the soil solution. Preliminary kinetic experiments demonstrated that a soil-to-solution ratio of 1:2 allowed for 20–85% sorption; apparent sorption equilibrium was reached after 72 h. For each experiment, 5 g was suspended in 9 mL of 0.01 M CaCl₂ and mixed on a rotary shaker (200 rpm, 12 h) before the addition of clothianidin. An aliquot of 1 mL of clothianidin stock solution in 0.01 M CaCl₂ was added to each experiment to achieve initial concentrations of 0.05, 0.1, 0.15, 0.2, 0.5, 0.8, 1, 2, 5 and 10 µg mL⁻¹. Isotherms were run at 22 ± 2 °C for each of the four soils, as well as at 37 ± 2 °C for the RvT and RvB soils.

Suspensions were agitated on a rotary shaker (200 rpm, 72 h) at either 22 ± 2 °C or 37 ± 2 °C. Equilibrium phases were separated by centrifugation (2000 × RCF) for 30 min, and 7 mL of supernatant was decanted from each experiment. A 1 mL aliquot of supernatant was passed through a 13 mm Acrodisc syringe tip filter with a 0.45 µm polypropylene hydrophilic filter (PTFE; Pall, Port Washington, NY). Clothianidin concentrations were determined by liquid chromatography–tandem mass spectrometry (LC-MS/MS). Controls prepared either without soil or without pesticide stock solution were run in triplicate for each set of experiments to show that 1 no interfering compounds were detected in the soil, and 2 clothianidin was stable and did not sorb to the surface of the centrifuge tube or PTFE filter (less than 3.3% loss).

Table 1. Properties of four rice field soils

Soil	Texture	Collection site	Post-harvest straw disposal	OC (%)	Silt (%)	Clay (%)	Sand (%)	pH	CEC(mequiv 100 g ⁻¹)
DfT	Silty clay loam	Davis, 38° 33' 22" N, 121° 38' 48" W	Till	2.3	32	44	24	6.6	37.9
BfB	Clay	Biggs, 39° 27' 39" N, 121° 43' 57" W	Burn	1.7	32	48	9	4.69	20
RvB	Clay	Richvale, 39° 29' 22" N, 121° 44' 12" W	Burn	2.1	40	24	35	4.56	5.88
RvT	Clay	Richvale, 39° 29' 22" N, 121° 44' 12" W	Till	1.4	36	26	40	4.46	5.97

The amount of clothianidin sorbed to soil after equilibration was calculated as the difference between the initial and equilibrium solution concentration using the equation

$$q_{\text{eq}}^s = (C_i - C_{\text{eq}}^s) \frac{V_i}{m} \quad (2)$$

where q_{eq}^s is the amount of pesticide sorbed by soil at equilibrium ($\mu\text{g g}^{-1}$), C_i and C_{eq}^s are the initial and equilibrium concentrations ($\mu\text{g mL}^{-1}$), V_i is the soil solution volume (mL), and m is the soil mass (g).

Desorption experiments were conducted as a continuation of the sorption experiments by the conventional single-step decant-refill technique. For each sample, 7 mL of fresh 0.01 M CaCl_2 was added to replace the discarded supernatant. Samples were placed back onto the rotary shaker and agitated for an additional 72 h and processed as described above. Mass balance calculations established the amount of pesticide desorbed from the soil.

The amount of clothianidin desorbed from soil was calculated as the difference between the initial amount sorbed and the aqueous-phase concentration of clothianidin corrected for incomplete decant according to the equation

$$q_{\text{eq}}^d = q_{\text{eq}}^s - \left(\frac{C_{\text{eq}}^d - (C_{\text{eq}}^s * \frac{V_i - V_r}{V_i})}{m} V_i \right) \quad (3)$$

where q_{eq}^d is the amount of pesticide remaining sorbed by the soil ($\mu\text{g g}^{-1}$), C_{eq}^d and C_{eq}^s are the concentrations in solution at desorption and sorption equilibrium respectively, V_i and V_r are the initial and replacement solution volumes (mL) and m is the soil sample mass (g).

All sorption–desorption data were fitted to the logarithmic form of the Freundlich equation:

$$\log q_{\text{eq}} = N \log C_{\text{eq}} + \log K_f \quad (4)$$

where K_f is the Freundlich coefficient, N is the Freundlich exponent, q_{eq} represents q_{eq}^s and q_{eq}^d in the sorption and desorption case respectively and C_{eq} represents C_{eq}^s and C_{eq}^d in the sorption and desorption case respectively.

Sorption data were used to calculate soil–water distribution coefficients, K_d , and the experimental organic-carbon-normalized sorption coefficients, K_{oc} , for aqueous equilibrium concentration with initial aqueous loading $C_i = 0.1 \mu\text{g mL}^{-1}$. The recommended application rate of 34 g Al acre⁻¹ will yield field water concentrations below this value. The K_d and K_{oc} values were calculated according to the equations

$$K_d = \frac{q_{\text{eq}}^s}{C_{\text{eq}}^s} \quad (5)$$

$$K_{\text{oc}} = \frac{K_d}{f_{\text{oc}}} \quad (6)$$

where K_d and K_{oc} have units of L kg^{-1} , and f_{oc} is the fraction of organic carbon in the sediment.

2.5 Sample analysis

Air–water partitioning samples were analyzed using an Agilent 1100 HPLC (Santa Clara, CA) with an Agilent 1100 autosampler coupled to a DAD and controlled by an Agilent Chem Station interface. An Xterra C18 column (3.5 μm particle size, 4.6 \times 250 mm i.d.; Waters, Milford, MA) and isocratic mobile phase of 85% 2 mM ammonium acetate with 0.1% formic acid in acetonitrile (0.5 mL min⁻¹, ambient temperature) were used. Clothianidin was detected at 265 nm. An external calibration curve was constructed from the peak area of triplicate injections of clothianidin standards prepared in 0.01 M CaCl_2 . The calibration curve was linear from 0.015 to 10 $\mu\text{g mL}^{-1}$, with a regression coefficient $R^2 = 0.9999$ and residuals less than 10%.

Soil–water partitioning samples were analyzed using an Agilent 1100 HPLC with an 1100 series autosampler coupled to a model AP2000 PE SCIEX triple quadrupole mass spectrometer (Foster City, CA) equipped with an atmospheric pressure chemical ionization source (APCI) and controlled by Analyst interface software (v.1.4.2). The HPLC was equipped with a 3.5 μm particle size, 4.6 \times 250 mm i.d. Xterra C18 column using an isocratic mobile phase of 70% methanol with 0.1% formic acid and 30% water with 0.1% formic acid at 400 $\mu\text{L min}^{-1}$ flow rate at ambient temperature with a 50 μL injection volume. Detection used multiple reaction monitoring (MRM) in the positive ion mode using the protonated molecular ions $(\text{M} - \text{H})^+$ of 250 m/z as the precursor ion. The retention time, product ion, dwell time, collision energy and collision cell

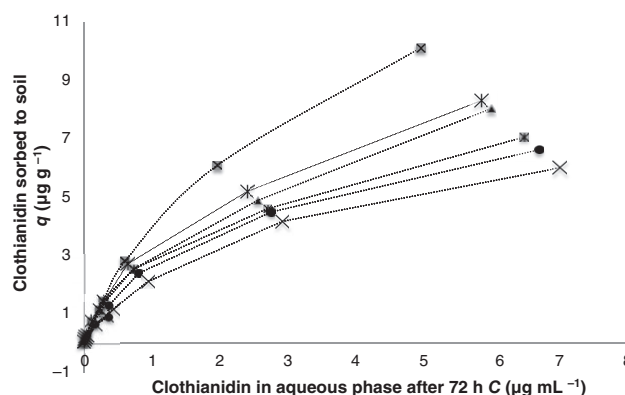


Figure 1. Sorption of clothianidin on four representative rice field soils at 22 and 37 °C: ○DfT (22 °C); △RvB (22 °C); □RvB (37 °C); ◇BfB (22 °C); ▽RvT (22 °C); ×RvT (37 °C). Points represent mean \pm SE ($n = 3$).

Table 2. Freundlich sorption (K_f) and desorption (K_f^d) coefficients, slope values (N), correlation coefficients (R^2), soil–water partitioning coefficients (K_d) and organic-carbon-normalized partitioning coefficients (K_{oc}) for initial concentrations of $0.1 \mu\text{g mL}^{-1}$

Soil	$T(^{\circ}\text{C})$	$K_d(\text{L kg}^{-1})$	$\log K_{oc}(\text{L kg}^{-1})$	Sorption			Desorption		
				$\log K_f$	N	R^2	$\log K_f^d$	N	R^2
RvT	37	5.1	2.6	0.29 ± 0.01	0.71 ± 0.01	0.992	1.14 ± 0.08	0.92 ± 0.05	0.932
	22	6.1	2.7	0.34 ± 0.02	0.72 ± 0.02	0.982	0.92 ± 0.07	0.79 ± 0.05	0.917
RvB	37	9.8	2.7	0.43 ± 0.02	0.66 ± 0.02	0.984	1.45 ± 0.09	0.92 ± 0.05	0.932
	22	10.3	2.7	0.44 ± 0.01	0.68 ± 0.01	0.994	0.92 ± 0.07	0.79 ± 0.05	0.917
BfB	22	10.8	2.8	0.47 ± 0.02	0.69 ± 0.01	0.989	1.08 ± 0.04	0.77 ± 0.03	0.967
DfT	22	7.9	2.8	0.55 ± 0.01	0.78 ± 0.01	0.994	0.61 ± 0.01	0.73 ± 0.01	0.995

exit potential used for clothianidin quantification were 8.49 min, 169 m/z , 150 ms, 19 V and 6 V respectively. Other MS parameters were as follows: heated drying gas temperature 425°C ; curtain gas pressure 50 psi; collision gas pressure 4 psi; ion source gas (N_2) GS_1/GS_2 75 psi/15 psi; focusing potential 370 V; entrance potential 8 V; declustering potential 16 V. External matrix-matched calibration curves were weighted as $1/x$ and linear from 0.005 to $10 \mu\text{g mL}^{-1}$, with a regression coefficient $R^2 = 0.9998$ and residuals less than 10%.

2.6 Statistical analysis

Data were analyzed using JMP software package v.10.0 (SAS Institute Inc., Cary, NC). The Freundlich parameter values K_f and N , standard errors and coefficient of determination R^2 were obtained from a linear regression analysis of the log-transformed sorption and desorption data [equation 3]. Standard errors were used to distinguish differences between the Freundlich isotherm parameters K_f and N . Discrete differences among sorption and desorption isotherms (hysteresis), soils and temperature treatments were determined by calculating the P -values associated with the one-way ANOVA test and *post hoc* comparison (Tukey's HSD test, $\alpha = 0.05$). Significance was determined at $\alpha = 0.05$ confidence.

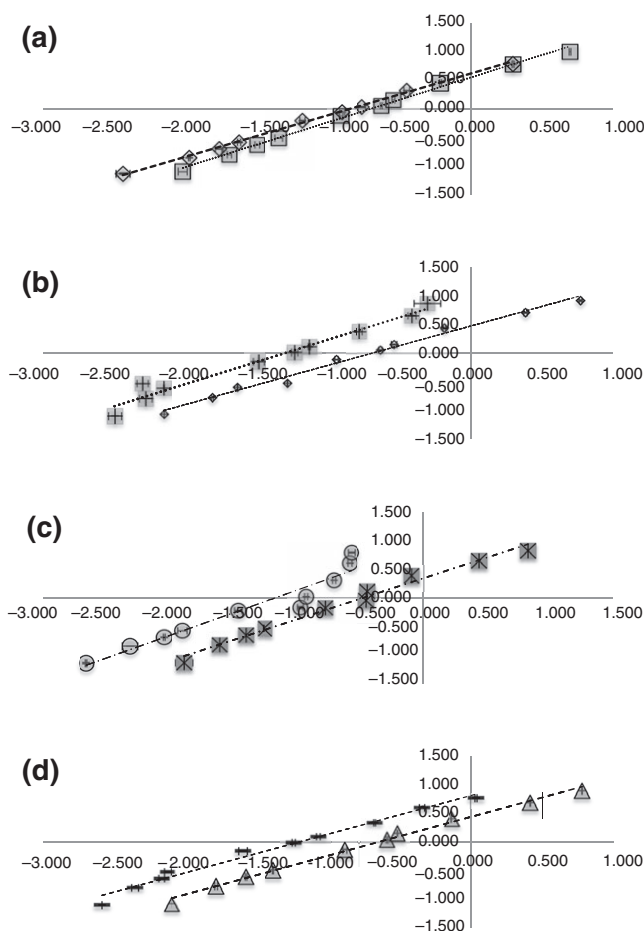
3 RESULTS AND DISCUSSION

3.1 Experimental determination of Henry's law constant

The tendency of a pesticide to volatilize from water is described by its K_H , which relates vapor pressure (Pa) to water solubility (M); K_H may also be determined experimentally using the gas purge method.^{14,16} Clothianidin is moderately water soluble (327 mg L^{-1} at 20°C), but has a low VP ($3.8 \times 10^{-11} \text{ Pa}$ at 20°C), suggesting that it has negligible potential to volatilize from flooded rice fields.⁵ A K_H value of $2.9 \times 10^{-11} \text{ Pa m}^3 \text{ mol}^{-1}$ (20°C) was calculated for clothianidin; pesticides with K_H values less than $3 \times 10^{-7} \text{ Pa m}^3 \text{ mol}^{-1}$ are considered to be non-volatile and will remain in field water.²⁴ It was not possible accurately to calculate K_H at 37°C because experimentally determined S and VP values were limited to 20°C in the literature. However, clothianidin was confirmed to be non-volatile via the gas purge method, as no loss from the aqueous phase was observed at either 22 or 37°C . Therefore, even under conditions favorable to volatilization, clothianidin will remain in the aqueous phase.

3.2 Soil–water partitioning

Adsorption isotherms for clothianidin in four soils representative of the Sacramento Valley are shown in Fig. 1. The convex curvature

**Figure 2.** Sorption and desorption isotherms for the 22°C experiments: (a) \square DfT sorption, \diamond DfT desorption; (b) \diamond BfB sorption, \square BfB desorption; (c), \times RvT sorption, \circ RvT desorption; (d) \times RvB sorption, \triangle RvB desorption. Points represent mean \pm SE ($n = 3$).

of the sorption data shown in Fig. 1 may be described as L-type, indicating that sorption affinity of the agent decreased as aqueous concentrations increased for both 22 and 37°C temperature treatments.^{25,26} Isotherm data were log transformed to fit the Freundlich model using equation 4; corresponding Freundlich parameters $\log K_f$ and N , their SE values and R^2 values are listed in Table 2.

The log-transformed Freundlich adsorption and desorption data for clothianidin are shown in Figs 2 and 3 for 22 and 37°C respectively. In all cases, sorption isotherms were non-linear ($0.67 \leq N \leq 0.78$), indicating that sorption capacity for the pesticide

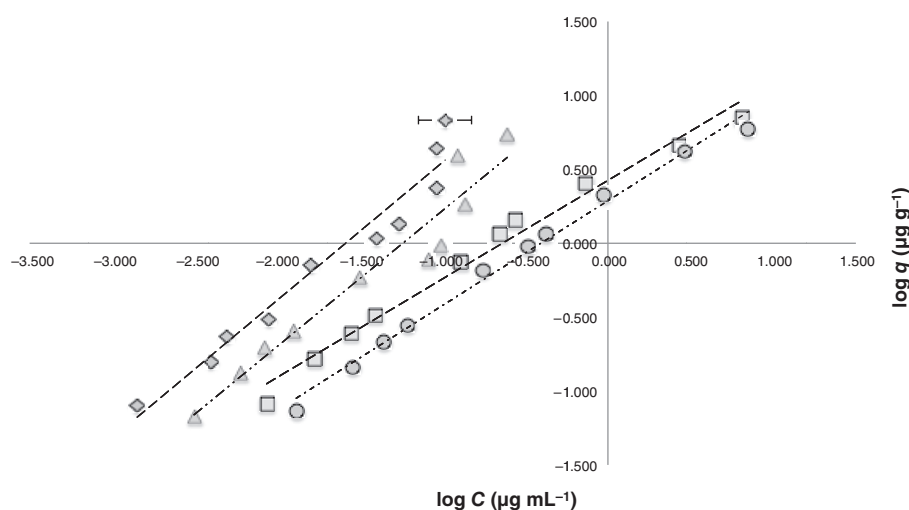


Figure 3. Sorption and desorption isotherm for the 37 °C experiments: □RvB sorption, ○RvT-sorption, ◇RvB desorption, △RvT desorption. Points represent mean \pm SE ($n = 3$).

decreases as the aqueous concentration increases (Table 2). The leaching potential of clothianidin on rice soils will therefore be dependent upon the amount applied to fields. The K_f is an empirical value, and is a measure of the sorption capacity of a soil for a pesticide; low K_f values indicate decreased sorption capacity and increased leaching potential.^{14,26} Sorption isotherms exhibited low $\log K_f$ values ranging from 0.34 to 0.55 and from 0.29 to 0.43 at 22 and 37 °C respectively (Table 2). Furthermore, significant decreases in $\log K_f$ values and a greater degree of non-linearity were observed on the 37 °C isotherms ($P < 0.05$). These results indicate that the overall sorption capacity of rice field soil for clothianidin is low and will decrease at elevated temperatures (potentially because of elevated S).

In order to compare sorption capacities between the four soils, K_d and K_{oc} values were calculated for an initial concentration, C_i , of $0.1 \mu\text{g mL}^{-1}$, using equations 5 and 6, and are presented in Table 2. The K_d values demonstrate a relationship between sorption and soil organic carbon content. The $\log K_{oc}$ values ranged from 2.6 to 2.8 at 22 and 37 °C (Table 2), and no significant relationship between soil pH or cation exchange capacity (CEC) and K_d was observed. This lack of dependency is consistent with the fact that clothianidin (pK_a 11.0) is a neutral species within environmentally relevant pH ranges.⁹ The $\log K_{oc}$ values for clothianidin on rice field soils are low compared with more hydrophobic rice pesticides like etofenprox ($S = 405 \mu\text{g L}^{-1}$), which has $\log K_{oc}$ values ranging from 6.0 to 6.4 and 6.1 L kg^{-1} at 22 and 35 °C, respectively, for similar rice field soils.²⁷

3.3 Desorption

Desorption processes affect pesticide mobility and hysteresis; sorption and desorption are important factors in assessing pesticide fate and transport.^{26,28,29} Desorption isotherms for clothianidin describe the amount remaining sorbed to soil at desorption equilibrium (Figs 2 and 3). Data from the isotherm experiments for the four soils were log transformed to fit the Freundlich model using equation 4, and the corresponding Freundlich parameters K_f^d and N^d , their SE and n values and R^2 values are listed in Table 2. Hysteresis is characterized by significant differences between the slopes of adsorption and desorption isotherms.^{29–31} One-way ANOVA tests and *post hoc* comparisons (Tukey's HSD test,

$\alpha = 0.05$) confirmed that hysteresis was observed in all four soils at 22 °C and for the two soils run at 37 °C.

The desorption experiments and the observed hysteric behavior demonstrate that sorbed clothianidin is not easily desorbed from the studied soils. There was a significant relationship between the initial concentration of clothianidin and the percentage of desorption observed ($P < 0.05$). Increased desorption was observed for higher initial isotherm concentrations for all sorbents. The mean percentage of clothianidin desorbed from soil was $11.5 \pm 1.2\%$ and $7.8 \pm 1.2\%$ for the 22 and 37 °C treatments respectively. This indicates that, even under a range of temperature conditions (e.g. elevated temperatures of a hot summer day), sorbed clothianidin residues will remain bound to soil.

4 CONCLUSIONS

These data suggest that soil sorption is primarily controlled by soil organic matter content, and that mineral-phase properties are less important. The sorption capacity of the soils for clothianidin is low and will decrease as temperature increases, potentially owing to increased water solubility. Sorbed clothianidin residues are not easily desorbed from the studied rice field soils. Overall, clothianidin has the potential to be mobile in soil and may pose a risk to both ground and surface waters.⁸ Further investigation should focus on biological and photochemical degradation, processes known to be important in rice paddies, and the potential for offsite transport in field tail water.^{32–34}

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REFERENCES

- Jeschke P, Clothianidin (TI-435) – the third member of the chloronicotinyl insecticide family. *Pflanzenschutz-Nachr Bayer* **56**:5–25 (2003).
- Tomizawa M and Casida JE, Neonicotinoid insecticide toxicology: mechanisms of selective action. *Annu Rev Pharmacol Toxicol* **45**:247–268 (2005).

- 3 Umene H, Konobe M, Akayama A, Yokota T and Mizuta K, Discovery and development of a novel insecticide clothianidin. *Sumitomo Kagaku* **2**:1–14 (2006).
- 4 Fairbrother A, Purdy J, Anderson T and Fell R, Risks of neonicotinoid insecticides to honeybees. *Environ Toxicol Chem* **33**(4):719–731 (2014).
- 5 Blacquiere T, Smagghe G, van Gestel CAM and Mommaerts V, Neonicotinoids in bees: a review on concentrations, side-effects and risk assessment. *Ecotoxicology* **21**:973–992 (2012).
- 6 Summary of pesticide use report data 2011, indexed by commodity. *California Department of Pesticide Regulation*, California Environmental Protection Agency, Sacramento, CA, p. 86 (2013).
- 7 Linquist BA, Koffler K, Hill JE and van Kessel C, Rice field drainage affects nitrogen dynamics and management. *Calif Agric* **65**(2):80–84 (2011).
- 8 *Registration review: problem formulation for the environmental fate and ecological risk, endangered species, and drinking water exposure assessment of clothianidin*. USEPA, Washington, DC (2011).
- 9 Clothianidin registration of Prosper T400 seed treatment on mustard seed (oil seed and condiment) and Poncho/Votivo seed treatment on cotton. Environmental risk assessment. *Memorandum from Joseph DeCant and Michael Barret to Kable Davis, Risk Management Reviewer*. Environmental Fate and Effects Division, USEPA, Washington, DC (2010).
- 10 Notice of proposed and final decisions and public reports. *Pesticide Registration Branch*, California Department of Pesticide Regulation, Sacramento, CA, pp. 14–16 (2013).
- 11 Wauchope RD, Yeh S, Linders JBHJ, Kloskowski R, Tanaka K, Rubin B *et al.*, Review. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. *Pest Manag Sci* **58**:419–445 (2002).
- 12 Stupp H-P and Fahl U, Environmental fate of clothianidin (TI-435; Poncho). *Pflanzenschutz-Nachr Bayer* **56**:59–74 (2003).
- 13 Jury WA, Focht DD and Farmer WJ, Evaluation of pesticide groundwater pollution potential from standard indices of soil – chemical adsorption and biodegradation. *J Environ Qual* **16**(4):422–428 (1987).
- 14 Schwarzenbach RP, Gschwend PM and Imboden DM, *Environmental Organic Chemistry*, 2nd edition. John Wiley & Sons, Inc., Hoboken, NJ (2002).
- 15 Ngim KK, *The fate and kinetics of pesticides in California flooded rice fields*. Dissertation, University of California, Davis, Ann Arbor, MI (1999).
- 16 Mackay D, Shiu WY and Sutherland RP, Determination of air–water Henry's law constants for hydrophobic pollutants. *Environ Sci Technol* **13**(3):333–337 (1979).
- 17 OECD 106: Adsorption–desorption using a batch equilibrium method. OECD Guidelines for the Testing of Chemicals (2000).
- 18 Web soil survey. *Natural Resources Conservation Services*, United States Department of Agriculture, Washington, DC (2013).
- 19 Berns AE, Philipp H, Narres HD, Burauel P, Vereecken H and Tappe W, Effect of gamma-sterilization and autoclaving on soil organic matter structure as studied by solid state NMR, UV and fluorescence spectroscopy. *Eur J Soil Sci* **59**:540–550 (2008).
- 20 Burke V, Treumann S, Duennbier U, Greskowiak J and Massmann G, Sorption behavior of 20 wastewater originated micropollutants in groundwater – column experiments with pharmaceutical residues and industrial agents. *J Contam Hydrol* **154**:29–41 (2013).
- 21 Lotrario JB, Stuart BJ, Lam T, Arands RR and O'Connor OA, Effects of sterilization methods on the physical characteristics of soil: implications for sorption isotherm analyses. *Environ Contam Toxicol* **54**:668–675 (1995).
- 22 von Oepen B and Klein W and Kordel W, Soil preparation for the estimation of adsorption coefficients (K_{oc}) of organic chemicals. *Chemosphere* **18**(7–8):1495–1511 (1989).
- 23 OPPTS 835.1220: Sediment and soil adsorption/desorption isotherm. *EPA Fate, transport and transformation test guidelines*. USEPA, Washington, DC (1998).
- 24 Mabury SA, Cox JS and Crosby DG, Environmental fate of rice pesticides in California. *Rev Environ Contam Toxicol: Continuation Residue Rev* **147**:71–117 (1996).
- 25 Calvet R, Adsorption of organic chemicals in soils. *Environ Hlth Perspect* **83**:145–177 (1989).
- 26 Sparks DL, *Environmental Soil Chemistry*. Academic Press, San Diego, CA (2003).
- 27 Vasquez ME, Gunasekara AS, Cahill TMM and Tjeerdema RS, Partitioning of etofenprox under simulated California rice-growing conditions. *Pest Manag Sci* **66**:28–34 (2010).
- 28 Boivin A, Cherrier R and Schiavon M, A comparison of five pesticides adsorption and desorption processes in thirteen contrasting field soils. *Chemosphere* **61**(5):668–676 (2005).
- 29 Huang WL and Weber WJ, A distributed reactivity model for sorption by soils and sediments. 10. Relationships between desorption, hysteresis, and the chemical characteristics of organic domains. *Environ. Sci. Technol.*, **33**(6):2562–2569 (1999).
- 30 Bronzic D and Milin C, Effects of temperature on sorption–desorption processes of imidacloprid in soils of Croatian coastal regions. *J Environ Sci Hlth B* **47**:779–794 (2012).
- 31 Lima DLD, Schneider RJ, Scherer HW, Duarte AC, Santos EBH and Esteves VI, Sorption–desorption behavior of atrazine on soils subjected to different organic long-term amendments. *J Agric Food Chem* **58**(5):3101–3106 (2010).
- 32 Jabusch TW and Tjeerdema RS, Photodegradation of penoxsulam. *J Agric Food Chem* **54**:5958–5961 (2006).
- 33 Tomco PL and Tjeerdema RS, Photolytic versus microbial degradation of clomazone in a flooded rice field. *Pest Manag Sci* **68**:1141–1147 (2011).
- 34 Vasquez ME, Cahill T and Tjeerdema RS, Soil and glass surface photodegradation of etofenprox under simulated California rice growing conditions. *J Agric Food Chem* **59**:7874–7881 (2011).