ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE
January 1, 2019 – December 31, 2019

PROJECT TITLE: The Environmental Fate of Pesticides Important to Rice Culture

PROJECT LEADER: Ronald S. Tjeerdema, Department of Environmental Toxicology, College of Agricultural and Environmental Sciences, University of California, One Shields Avenue, Davis, CA 95616-8588

PRINCIPAL UC INVESTIGATOR: Ronald S. Tjeerdema, Department of Environmental Toxicology, College of Agricultural and Environmental Sciences, UCD

COOPERATORS: Zachary Redman (UCD) and David Ball (CSU Chico)

LEVEL OF 2019 FUNDING: $49,091

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

Objective I. To investigate the factors governing pesticide dissipation in California rice fields. Emphasis for 2019 will be to focus on the insecticide Coragen (chlorantraniliprole) by characterization of its degradation via sunlight (photolysis) under California rice field conditions.

Objective I. Photolysis of Coragen in Rice Field Soils

The photochemical degradation of chlorantraniliprole (3-Bromo-N-[4-chloro-2-methyl-6 (methylcarbamoyl)phenyl]-1-(3-chloro-2-pyridine-2-yl)-1H-pyrazole-5-carboxamide; CAP, Figure 1) was characterized under simulated solar light with 2-nitrobenzaldehyde (2NB) actinometry. Overall CAP degraded quickly via direct photolysis processes with no significant difference observed between high purity water and filtered rice field water. The 24 h average half life normalized to summer sunlight using 2NB actinometry was 34.45 ± 3.97 h ($j_{CAP,env.}$ = 0.0203 ± 0.0023 h^{-1}, n = 3) and the calculated quantum yield was 0.00985 ± 0.000592.

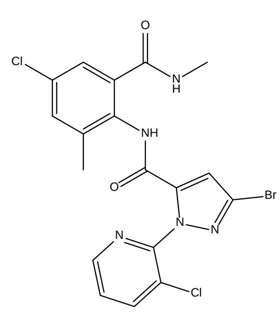

Figure 1. Chlorantraniliprole, the active ingredient of Coragen.

This work marks the completion of our goal to elucidate the environmental fate of chlorantraniliprole under California rice field conditions (Figure 2). Air-water and soil-water partitioning were previously characterized mathematically and via a batch equilibrium method. Air-water partitioning was characterized through calculation of Henry's law constant (K_H) between 15 – 35 °C while soil-water partitioning was investigated in three soils, collected from rice fields in the Sacramento Valley, at 15, 25 and 35 °C under varied aqueous salinities. K_H and organic carbon normalized soil water partitioning coefficient (Log(K_{OC})) determined for CAP were 1.69×10^{-16} – 2.81×10^{-15} atm·m^3·mol^{-1} and 2.59 – 2.93; indicating that volatilization will not contribute to its dissipation and its sorption to soils is moderately weak. Furthermore, sorption to CAP to soil was reversible resulting in an estimated 12 – 22% and 77 – 88 % of the applied mass to partition into water and soil, respectively, by the Pesticides in Flooded Applications Model (PFAM).

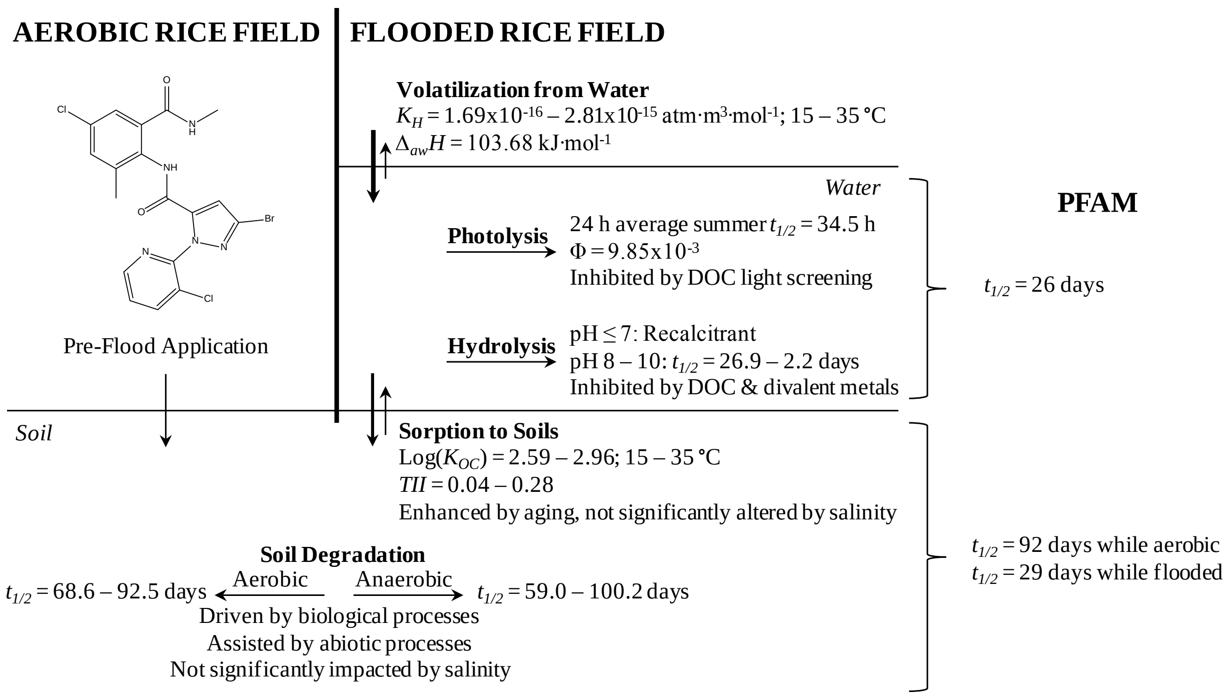

Figure 2. Summary of the environmental fate of CAP under simulated California rice field conditions.

As CAP would be applied pre-flooding directly to the soil surface and the majority of the applied mass is anticipated to remain in the soil its degradation in both unflooded and flooded rice field soils was investigated via microcosm experiments employing varied aqueous salt concentrations. The half-life ($t_{1/2}$) of CAP in two soils ranged from 59 – 100.2 days and was not significantly impacted by aqueous salinity; therefore, enhanced ionic strength due to evapoconcentration of salts in rice fields will not have a large impact on the dissipation of CAP from soils. However, degradation in sterilized microcosms ($t_{1/2}$ = 78.5 – 171.7 days) indicates that dissipation, while primarily biologically driven, was assisted by abiotic processes such as oxidation by manganese oxides and the formation of non-extractible residues. Overall degradation in soil was slow with 98% dissipation expected to occur within 471 – 601.2 days.

Due to its anticipated recalcitrance in soil, the hydrolysis of CAP was investigated within the pH range 6 – 10. Further experiments were conducted using buffered rice field water and the addition of divalent metals (Cu^{2+}, Zn^{2+}, Ni^{2+} and Mn^{2+}) in order to determine the impact dissolved species common to California rice fields might have on the persistence of the insecticide. CAP was stable to hydrolysis under acidic and neutral conditions with addition of divalent metals having no observable catalytic effect; however, degradation occurred rapidly under alkaline conditions with half-lives ranging from 26.9 – 2.2 days between pH 8 – 10. Furthermore, the reaction was observed to proceed slower in buffered rice field water than lab grade water and the addition of Ni^{2+} and Mn^{2+} at elevated pH were observed to inhibit the reaction; indicating that the persistence of CAP, while dominated by pH, may be significantly altered between rice fields as a result of varied concentrations of dissolved organic carbon and metal species.

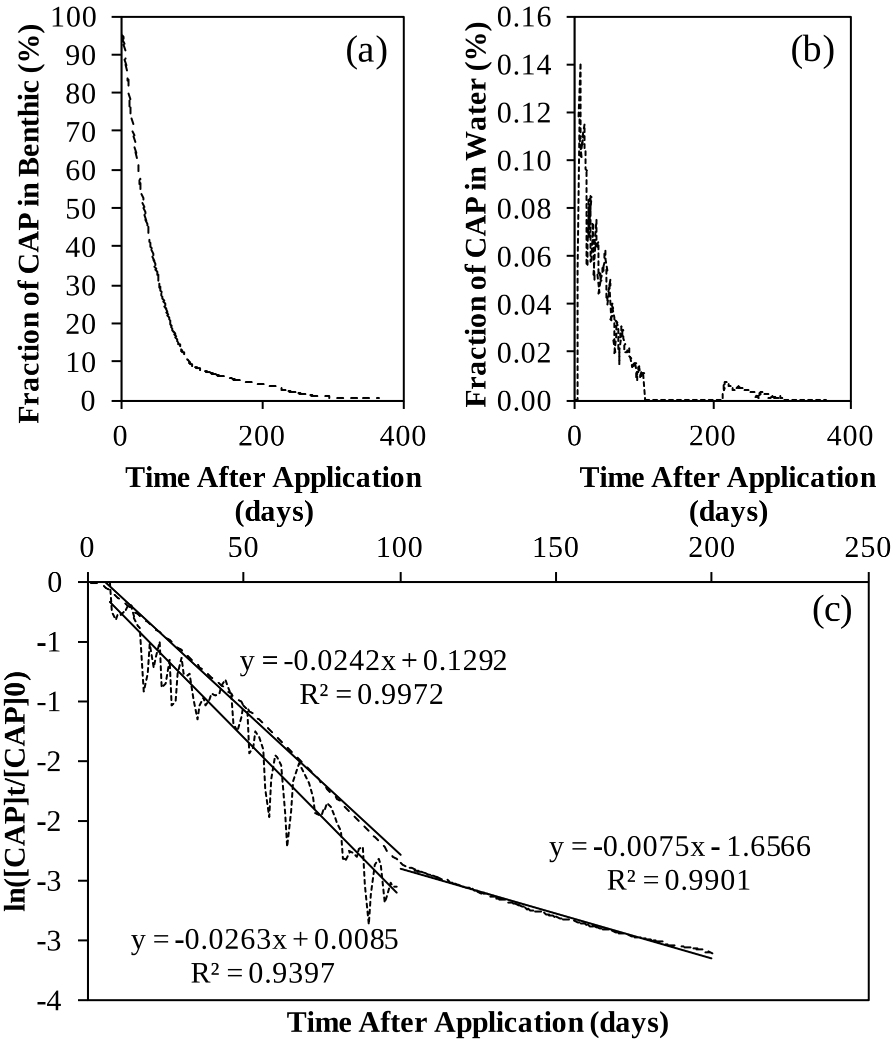

Figure 3. PFAM predicted dissipation of CAP from (a) benthic and (b) water compartments of a simulated California rice field with (c) natural-log linearized plot assuming first order degradation of CAP for the determination of estimated environmental half-lives.

Newly generated parameters for the photochemical degradation of CAP, reflective of California rice field conditions, were used alongside its previously characterized partitioning, degradation in soil and hydrolysis parameters in the Pesticides in Flooded Applications Model (PFAM) to simulate its dissipation in a model California rice field (Figure 3). The resulting simulation predicted that the majority of the insecticide will remain in the soil where it will degrade slowly ($t_{1/2}$ = 29 and 92 days under flooded and non-flooded conditions) while the percentage of initially applied CAP in the water will remain below 0.2% as a result of its combined rapid photolysis and hydrolysis ($t_{1/2}$ = 26 days). However, while the concentration of CAP in the aqueous phase is expected to remain low (< 1 $\mu g \cdot L^{-1}$), approximately 9% is expected to remain in the soil upon draining the field after a 100 day flooding period at which point its dissipation is expected to slow precipitously. As a result, CAP may accumulate over time in the soil leading to unintended chronic exposure to wildlife upon desorption during overwinter flooding or development of pest resistance particularly when considering that 67% remains in the soil after a more typical hold time of only 20 d.

Sample analysis via liquid chromatography-tandem mass spectrometry (LC-MS/MS) will continue into 2020 to confirm identification of the major degradation products resulting from both microbial and photochemical processes.

SUMMARY OF 2019 RESEARCH (major accomplishments) BY OBJECTIVE:

Objective I. The photolysis of chlorantraniliprole was investigated under California rice field conditions. CAP was degraded quickly via direct photolysis ($t_{1/2}$ = 34.5 h) processes with no significant catalysis or inhibition by secondary processes in rice field water. The quantum yield was also determined using 2-nitrobenzaldehyde actinometry as 0.00985. These parameters were used along with partitioning, soil degradation and hydrolysis parameters previously determined in the Pesticides in Flooded Applications Model (PFAM). Simulation of the insecticide's overall fate in a California rice field resulted in an estimated environmental half-life of 26 days in the aqueous phase due to its rapid photolysis and hydrolysis; however, the majority of applied CAP is anticipated to persist in soils.

PUBLICATIONS OR REPORTS (to date):

1. Palumbo, A. J., P. L. TenBrook, A. Phipps and R. S. Tjeerdema, 2004. Comparative toxicity of thiobencarb and deschlorothiobencarb to rice (*Oryza sativa*). *Bull. Environ. Contam. Toxicol.* 73, 213–218.
2. Schmelzer, K. R., C. S. Johnson, P. L. TenBrook, M. R. Viant, J. F. Williams and R. S. Tjeerdema, 2005. Influence of organic carbon on the reductive dechlorination of thiobencarb (Bolero) in California rice field soils. *Pest Manage. Sci.* 61, 68–74.
3. TenBrook, P. L. and R. S. Tjeerdema, 2005. Comparative actions of clomazone on β-carotene and growth in rice and watergrasses (*Echinochloa* spp.). *Pest Manage. Sci.* 61, 567–571.
4. Gunasekara, A. S., A. J. Palumbo, P. L. TenBrook and R. S. Tjeerdema, 2005. Influence of phosphate and copper on reductive dechlorination of thiobencarb in California rice field soils. *J. Agric. Food. Chem.* 53, 10113–10119.

5. Jabusch, T. W. and R. S. Tjeerdema, 2005. Partitioning of penoxsulam: A new sulfonamide herbicide. *J. Agric. Food Chem.* 53, 7179–7183.
6. Jabusch, T. W. and R. S. Tjeerdema, 2006. Microbial degradation of penoxsulam in flooded rice field soils. *J. Agric. Food Chem.* 54, 5962–5967.
7. Jabusch, T. W. and R. S. Tjeerdema, 2006. Photochemical degradation of penoxsulam. *J. Agric. Food Chem.* 54, 5958–5961.
8. TenBrook, P. L. and R. S. Tjeerdema, 2006. Biotransformation of clomazone in rice (*Oryza sativa*) and early watergrass (*Echinochloa oryzoides*). *Pestic. Biochem. Physiol.* 85, 38–45.
9. Gunasekara, A. S., J. Troiano, K. Goh and R. S. Tjeerdema, 2007. Chemistry and fate of simazine. *Rev. Environ. Contam. Toxicol*. 189, 1–24 (invited).
10. Gunasekara, A. S., K. Goh and R. S. Tjeerdema, 2007. Chemistry and fate of fipronil. *J. Pestic. Sci.* 32, 189–199 (invited).
11. Jabusch, T. W. and R. S. Tjeerdema, 2008. Chemistry and fate of triazolopyrimidine sulfonamide herbicides. *Rev. Environ. Contam. Toxicol.* 193, 31–52 (invited).
12. Yasuor, H., P. L. TenBrook, R. S. Tjeerdema and A. J. Fischer, 2008. Responses to clomazone and 5-ketoclomazone by *Echinochloa phyllopogon* resistant to multiple herbicides in Californian rice fields. *Pest Manage. Sci.* 64, 1031–1039.
13. Gunasekara, A. S., K. Goh, F. Spurlock, A. L. Rubin and R. S. Tjeerdema, 2008. Environmental fate and toxicology of carbaryl. *Rev. Environ. Contam. Toxicol.* 196, 95–121 (invited).
14. Gunasekara, A. S., I. D. P. de la Cruz, M. J. Curtis, V. P. Claassen and R. S. Tjeerdema, 2009. The behavior of clomazone in the soil environment. *Pest. Manage. Sci.* 65, 711–716.
15. Vasquez, M. E., A. S. Gunasekara, T. M. Cahill and R. S. Tjeerdema, 2010. Partitioning of etofenprox under simulated California rice growing conditions. *Pest Manage. Sci.* 66, 28–34.
16. Tomco, P., D. M. Holstege, W. Zhou and R. S. Tjeerdema, 2010. Microbial degradation of clomazone in California rice fields. *J. Agric. Food. Chem.* 58, 3674–3680.
17. Yasuor, H., W. Zou, V. V. Tolstikov, R. S. Tjeerdema and A. J. Fischer, 2010. Differential oxidative metabolism and 5-ketoclomazone accumulation are involved in *Echinochloa phyllopogon* resistance to clomazone. *Plant Physiol.* 153, 319–326.
18. Vasquez, M. E., D. M. Holstege and R. S. Tjeerdema, 2011. Aerobic versus anaerobic microbial degradation of etofenprox in a California rice field soil. *J. Agric. Food Chem.* 59, 2486–2492.
19. Vasquez, M. E., T. Cahill and R. S. Tjeerdema, 2011. Soil and glass surface photodegradation of etofenprox under simulated California rice growing conditions. *J. Agric. Food Chem.* 59, 7874–7881.
20. Tomco, P. and R. S. Tjeerdema, 2012. Photolytic versus microbial degradation of clomazone in a flooded California rice field soil. *Pest. Manage. Sci.* 68, 1141–1147.
21. Tomco, P., W. Holmes and R. S. Tjeerdema, 2013. Biodegradation of clomazone in a California rice field soil: Carbon allocation and microbial community effects. *J. Agric. Food Chem.* 61, 2618–2624.
22. Mulligan, R. A., S. J. Parikh and Ronald S. Tjeerdema, 2015. Abiotic partitioning of clothianidin under simulated rice field conditions. *Pest. Manage. Sci.* 71, 1419–1424.
23. Rering, C. C., M. Gonzales, M. Keener, D. Ball and R. S. Tjeerdema, 2015. Photochemical degradation of imazosulfuron under simulated California rice field conditions. *Pest. Manage. Sci.* 72, 1117–1123.
24. Mulligan, R. A., Z. Redman, M. Keener, D. Ball and R. S. Tjeerdema, 2016. Photodegradation of clothianidin under simulated California rice field conditions. *Pest. Manage. Sci.* 72, 1322–1327.

25. Mulligan, R. A., P. L. Tomco, M. Howard, T. Howard, D. Stewart, S. Phillip, D. Ball and R. S. Tjeerdema, 2016. Aerobic versus anaerobic microbial degradation of clothianidin under simulated California rice field conditions. *J. Agric. Food Chem.* 64, 7059–7067.
26. Kanawi, E., Van Scoy, A., Budd, R. and R. S. Tjeerdema, 2016. Environmental fate and ecotoxicology of propanil: A review. *Toxicol. Environ. Chem.* 7, 689–704.
27. Williams, K. and R. S. Tjeerdema, 2016. Hydrolytic activation kinetics of the herbicide benzobicyclon in simulated aquatic systems. *J. Agric. Food Chem.* 64, 4838-4844.
28. Rering, C. C., M. J. Hengel and R. S. Tjeerdema, 2017. The role of indirect photolysis in imazosulfuron photodegradation. *J. Agric. Food Chem.* 65, 3103-3108.
29. Williams, K., J. J. Gladfelder, L. L. Quigley, D. B. Ball, and R. S. Tjeerdema, 2017. Dissipation of the herbicide benzobicyclon hydrolysate in a model California rice field soil. *J. Agric. Food Chem.* 65, 9200-9207.
30. Williams, K. L., R. Kaur, A. S. McFall, C. Anastasio, J. Kalbfleisch, J. J. Gladfelder, D. B. Ball and R. S. Tjeerdema, 2018. Aqueous photolysis of benzobicyclon hydrolysate. *J. Agric. Food Chem*. 66, 5462–5472.
31. Redman, Z. C. and R. S. Tjeerdema, 2018. Impact of simulated California rice-growing conditions on chlorantraniliprole partitioning. *J. Agric. Food Chem*. 66, 1765–1772.
32. Redman, Z. C.; Parikh, S. J.; Hengel, M. J.; Tjeerdema, R. S., 2019. Influence of flooding, salinization and soil properties on degradation of chlorantraniliprole in California rice field soils. *J. Agric. Food Chem.* 67, 8130–8137.
33. Redman, Z. C., K. H. Tran, S. J. Parikh and R. S. Tjeerdema, 2019b. Influence of pH and divalent metals relevant to California rice fields on the hydroxide mediated hydrolysis of the insecticide chlorantraniliprole. *J. Agric. Food Chem*. (in press).
34. Redman, Z. C., C. Anastasio and R. S. Tjeerdema. Determination of quantum yield for the aqueous photochemical degradation of chlorantraniliprole and reassessment of p-nitroanisole/pyridine and p-nitroacetophenone/pyridine actinometers. *J. Agric. Food Chem*. (submitted).

CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:

1. The overall goal of our ongoing research program is to characterize the dissipation of pesticides under California rice field conditions. There are generally four contributing processes are investigated: volatilization to air, sorption (bonding) to soils, and degradation by either sunlight or soil microbes.

2. For Coragen, experiments conducted using simulated sunlight show that the active ingredient chlorantraniliprole (CAP) is expected to rapidly degrade via direct photolysis. Degradation in experiments using rice field water was not significantly different than those with high purity water, indicating that secondary photolysis will not be a major contributor to its dissipation. Chemical actinometry allowed for the derivation of environmentally relevant photochemical half-lives reflective of California rice field summer time growing conditions such that the Pesticides in Flooded Applications Model could be used to estimate its overall fate. Simulations estimate that CAP will degrade moderately fast once desorbed; however it is anticipated to persist in the soil for much longer periods.