

ANNUAL REPORT  
COMPREHENSIVE RESEARCH ON RICE  
January 1, 2008 – December 31, 2008

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: Jim Hill (UC Cooperative Extension), Albert Fischer (UCD), Martice Vasquez (UCD), Patrick Tomco (UCD), Shinobu Hagio (UCD), Donald Crosby (UCD)

LEVEL OF 2008 FUNDING: \$54,102

OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:

**Objective I.** To investigate the natural factors governing the dissipation of pesticides in California rice fields. Emphasis for 2008 was to characterize the anaerobic microbial degradation of the insecticide etofenprox under California rice field conditions.

**Objective II.** To investigate the natural factors governing the dissipation of pesticides in California rice fields. Emphasis for 2008 was to characterize the anaerobic microbial degradation of the herbicide Cerano (clomazone) under California rice field conditions.

**Objective III.** To investigate the natural factors governing the dissipation of pesticides in California rice fields. Emphasis for 2008 was to characterize the potential for volatilization of the insecticide clothianidin under California rice field conditions.

SUMMARY OF 2008 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

**OBJECTIVE I**

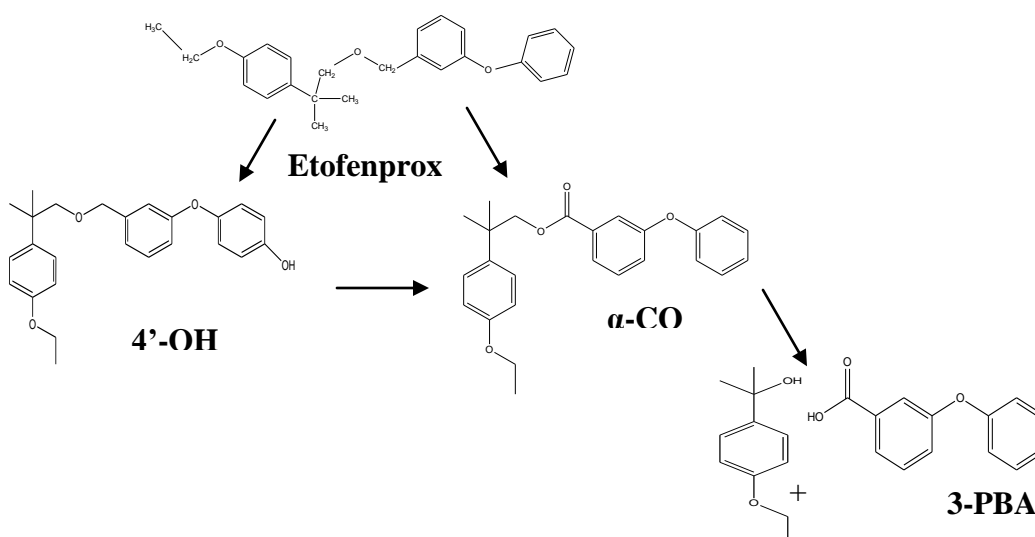
*Introduction*

The partitioning of etofenprox between air, water and soil under representative California rice field conditions has been characterized in previous work. In summary, volatilization was shown to be an insignificant dissipation pathway compared to sorption of etofenprox. The Henry's law constant was calculated at  $1.8 \times 10^{-5} \text{ Pa} \cdot \text{m}^3/\text{mol}$  over a temperature range of 5-40°C. Sorption to the experimental apparatus not only invalidated the experimental approach but also gave insight to the magnitude of the affinity to partition from water to soil and glass. Two representative rice field soils (Princeton and Richvale) showed a similar magnitude of soil sorption overall, with  $\log K_{oc}$

values measured at 6.0 and 6.4 (25°C), respectively. An increase in temperature during soil-water partitioning experiments resulted in a small increase in sorption but overall a similar magnitude  $\log K_{oc}$  for etofenprox, 6.1 at 35°C compared to 6.0 at 25°C for the same soil.

Movement of etofenprox to soil after aqueous application requires the investigation of the ability of soil microbes to metabolize residues. Soil microbial decomposition is one of the most important degradation pathways for pesticides and can greatly reduce a compound's persistence in a soil-water matrix. Management practices in rice production generally create two soil types: anaerobic when the field is flooded and aerobic when it is not. As a result of the presence of both aerobic and anaerobic conditions, it is necessary to probe the soil communities for function under both conditions to measure degradation rates and products of etofenprox.

Previously studied and characterized pyrethroid degrading bacteria have been isolated from aerobic sites and conditions and assessed for esterase presence and activity. Although etofenprox is an ether pyrethroid, it is hypothesized the microbial community in California rice fields will be able to degrade it. The temporal change in the oxic level with in the rice field system has been shown to alter the community structure (Liesack, 2000). As a result, it is necessary to investigate the function of these communities under anaerobic, as well as aerobic, conditions. Esterases are expected to function under both aerobic and anaerobic conditions, and activity has been shown for an anaerobic soil bacterium, *Azoarcus* sp. Strain EbN1 (Rabus, 2005). Because both esterases and etherases belong to the broader class of hydrolases, it is likely they will both be present in the functional community. It is also hypothesized that degradation rates of etofenprox will be greater under aerobic conditions than anaerobic conditions, and etofenprox would likely follow the pathways in Figure 1. Thus, this study aimed to characterize the microbial degradation of etofenprox under simulated rice field conditions by determining its dissipation rate constant ( $k$ ), half-life ( $t_{1/2}$ ) and degradation pathways under both anaerobic and aerobic conditions.



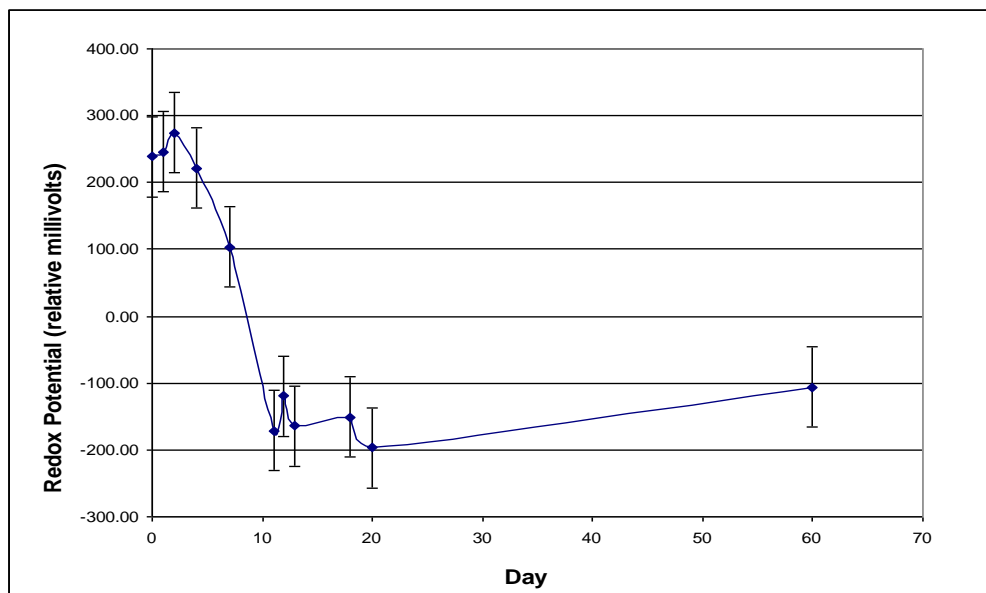
**Figure 1.** Potential degradation of etofenprox based on chemical structure and known microbial metabolic processes.

## Materials and Methods

**Chemicals, soil and irrigation water.** Etofenprox,  $\alpha$ -carbonyletofenprox ( $\alpha$ -CO) and 4-hydroxyetofenprox (4'OH) were supplied *gratis* by Mitsui Chemical Co. (Japan). Sodium azide and 3-phenoxybenzoic acid (PBA) were purchased from Sigma Chemical Co. (St. Louis, MO). Stock solutions of etofenprox were prepared in methanol and used to prepare microcosm samples. Rice field soil was collected from the Rice Experiment Station (Biggs, CA) in May 2008; it was air-dried and ground to pass through a 2-mm sieve, then stored at 4°C until used. Water (pH 7.5) used for “flooding” the microcosms was collected from an irrigation outfall (Berryessa Irrigation District) located at UCD in July 2008.

**Soil characterization.** The soil is currently undergoing complete characterization by the Division of Agriculture and Natural Resources (ANR) Analytical Laboratory at UCD. Complete description of the methods is in Schmelzer *et al.*, 2005, or the ANR website (<http://danranlab.ucdavis.edu>).

**Anaerobic microbial degradation of etofenprox.** Microcosms were constructed with a 2.5 cm soil layer (50 g) and flooded to a depth yielding a 1.5 cm water layer (60 mL) in a 300 mL amber screw cap bottle. All microcosms were prepared in triplicate and incubated at room temperature in the dark. Control soils (triplicate) were autoclaved before flooding and application of etofenprox. Control “flood” water contained 200 mg/L sodium azide for microbial inhibition. The oxidation-reduction (redox) potential of the flooded soil (Figure 2) was monitored to determine when anaerobic conditions were achieved, which were generally within 14 days of flooding, thus this time interval was adequate for establishment of anaerobic conditions prior to introduction of etofenprox. Periodic soil sampling (t=0, 1, 3, 7, 14, 21, 28, 35, 42, 56, 70 days) after etofenprox addition (150  $\mu$ g) was used to determine degradation rates and metabolite formation. Microcosm samples were solvent extracted and are currently awaiting analysis by LC/MS/MS.



**Figure 2:** Redox profile of flooded soil at various times. Anaerobic conditions (-100 to -200 mV) achieved within 14 days of soil flooding.

## Results

**Extraction and analysis.** To each microcosm 60 mL of acetone was added; they were then placed on a platform shaker at 135 rpm for 24 h. Samples were then vacuum filtered and the filter cake was washed with acetone, which was then removed by evaporation under N<sub>2</sub> gas. The remaining aqueous phase was liquid-liquid extracted using hexane(20 mL) three times; the extracts were then dried with sodium sulfate, brought to dryness under N<sub>2</sub> gas then dissolved in 2 mL of 40:60 acetonitrile-water (0.1% ammonium acetate) for analysis by LC/MS/MS.

The analytical method development for etofenprox and its known and unknown metabolites has proven challenging yet progressive. Although the manufacturer provided many means of analysis (GC/MS, LC/DAD) for various matrices, LC/MS/MS is not included. LC/MS/MS is advantageous because chemicals become more water soluble (polar) as transformation occurs, thus not amenable to analysis by GC/MS, although it can be done after chemical modification. Comparison of the LC/MS/MS to the LC/DAD reveals differences in levels of sensitivity and selectivity, with the former instrument far more sensitive and capable of generating structural information about an unknown compound. For these reasons, both microbial and photolytic transformation experiments will be analyzed by the LC/MS/MS method currently being developed.

LC/MS/MS analysis was performed on an Applied Biosystems Sciex 2000 LC/MS/MS using electrospray ionization (ESI) in positive mode. Chromatographic and MS/MS parameters are summarized in Tables 1A and 1B. To determine if the instrument was sensitive enough for the

**Table 1:** Table A.) Selected ion transitions for etofenprox and known metabolites using positive mode ESI LC/MS/MS. Sum of ions used for analyte quantification. Table B.) Chromatographic conditions using Titan C18 column (5  $\mu$ m, 2.1 mm ID x 100 mm), 0.25 mL/min flow rate, and 40  $\mu$ L injection.

**Table A:**

Transition Monitored (mass/charge)	Analyte, MW	Q1 and Q2 parameters DP/FP/EP/CE/CXP	Retention Time
394.4 to 359	Etofenprox 376	40/400/10/20/3	12.59
394.4 to 177.1	Etofenprox 376	40/400/10/20/3	12.59
359 to 183	Etofenprox 376	40/400/10/20/3	12.59
407.8 to 177.4	$\alpha$ -CO 390	30/400/10/19/3	12.13
407.8 to 134.9	$\alpha$ -CO 390	30/400/10/19/3	12.13
407.8 to 149.3	$\alpha$ -CO 390	30/400/10/19/3	12.13
409.8 to 177.1	4'-OH 392	40/400/10/55/3	10.34
409.8 to 134.9	4'-OH 392	40/400/10/55/3	10.34
375.1 to 177.1	4'-OH 392	40/400/10/55/3	10.34
To be determined (TBD)	3-PBA	TBD	TBD
TBD	3-PBA	TBD	TBD
TBD	3-PBA	TBD	TBD
Same as 4'-OH	6'-OH 392	40/400/10/55/3	unknown
TBD	Unknown	Unknown	Unknown
TBD	Unknown	Unknown	Unknown

Declustering Potential (DP), focusing potential (FP), entrance potential (EP), collision energy (CE), collision exit potential (CXP), multiple reaction monitoring (MRM)

**Table B:**

Time (min)	Water (%) +0.1% ammonium acetate	ACN (%) +0.1% ammonium acetate
0	60	40
4.5	5	95
10	5	95
11	60	40
20	60	40

**Table 2:** Instrument detection limits for etofenprox,  $\alpha$ -CO and 4'OH using LC/MS/MS (%R-percent recovery; STD-standard deviation; IDL-instrument detection limit; IQL-instrument quantitation limit).

Sample #	Etofenprox		alpha-CO		4'-OH	
	0.01 mg/L	0.05 mg/L	0.01 mg/L	0.05 mg/L	0.01 mg/L	0.05 mg/L
1	0.00518	0.0611	0.0254	0.0552	0.00336	0.052
2	0.00673	0.0974	0.0195	0.0683	0.0029	0.0399
3	0.0119	0.0783	0.0222	0.0609	0.00198	0.0488
4	0.00423	0.0648	0.0232	0.0534	0.00429	0.0635
5	0.00155	0.041	0.0233	0.0504	0.00553	0.0533
6	0.00573		0.0237		0.00661	
7	0.00509		0.0209		0.00487	
Average	0.00577	0.06852	0.0226	0.05764	0.00422	0.0515
Ave %R	57.7	137	226	115	42.2	103
STD	0.003	0.021	0.002	0.007	0.002	0.009
T factor	3.143	3.747	3.143	3.747	3.143	3.747
IDL	0.010	0.079	0.006	0.027	0.005	0.032
IQL	0.03	0.24	0.02	0.08	0.02	0.10
7 replicate t test at 98% confidence interval = 6 degrees of freedom; t factor = 3.143						
5 replicate t test at 98% confidence interval = 4 degrees of freedom; t factor = 3.747						

designed experiment, a target detection limit of 0.75 mg/L for etofenprox and its metabolites (or 1% of the initial amount of etofenprox) was set. Replicates of low level standards of etofenprox,  $\alpha$ -CO and 4'OH were quantified against a second order calibration curve generated in Analyst Software version 1.2.4. The standard deviation of the replicate measurements is used to calculate the precision of the instrument whereas the percent recovery of the analyte describes the accuracy of the instrument. The results are summarized in Table 2. All analytes had an IDL (instrument detection limit) of less than 0.75mg/L. Thus, the instrument proved sensitive enough to utilize for quantification of etofenprox and its metabolites.

With the near completion of the instrument and method validation, the processed anaerobic samples will be quantified within the next few months. This data will yield the anaerobic microbial dissipation rate of etofenprox and half-life under California rice conditions. Aerobic degradation will be characterized following completion of the anaerobic samples. This analytical procedure will also be used in subsequent photodegradation of etofenprox experiments.

Etofenprox was selected for this investigation due to growing interest by the rice industry; because of its usefulness, it is under consideration for emergency registration (Section 18) in Louisiana (R. Firoved and L. Godfrey, pers. comm., 2005). Mitsui (Japan), through Landis International, has provided the analytical standards *gratis* necessary to perform the above studies.

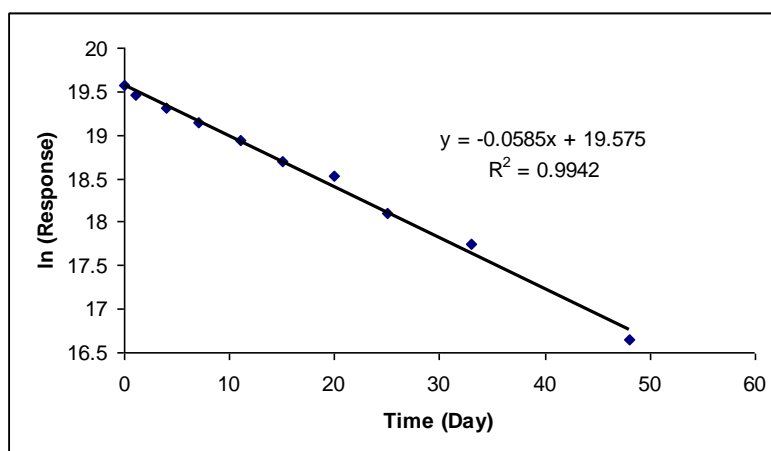
Understanding the degradation of etofenprox in rice fields is critical to characterizing dissipation. Results will provide half-lives and rates, providing a better understanding of the dissipation processes active in rice fields and guidance for the safe and effective use of the insecticide.

## OBJECTIVE II

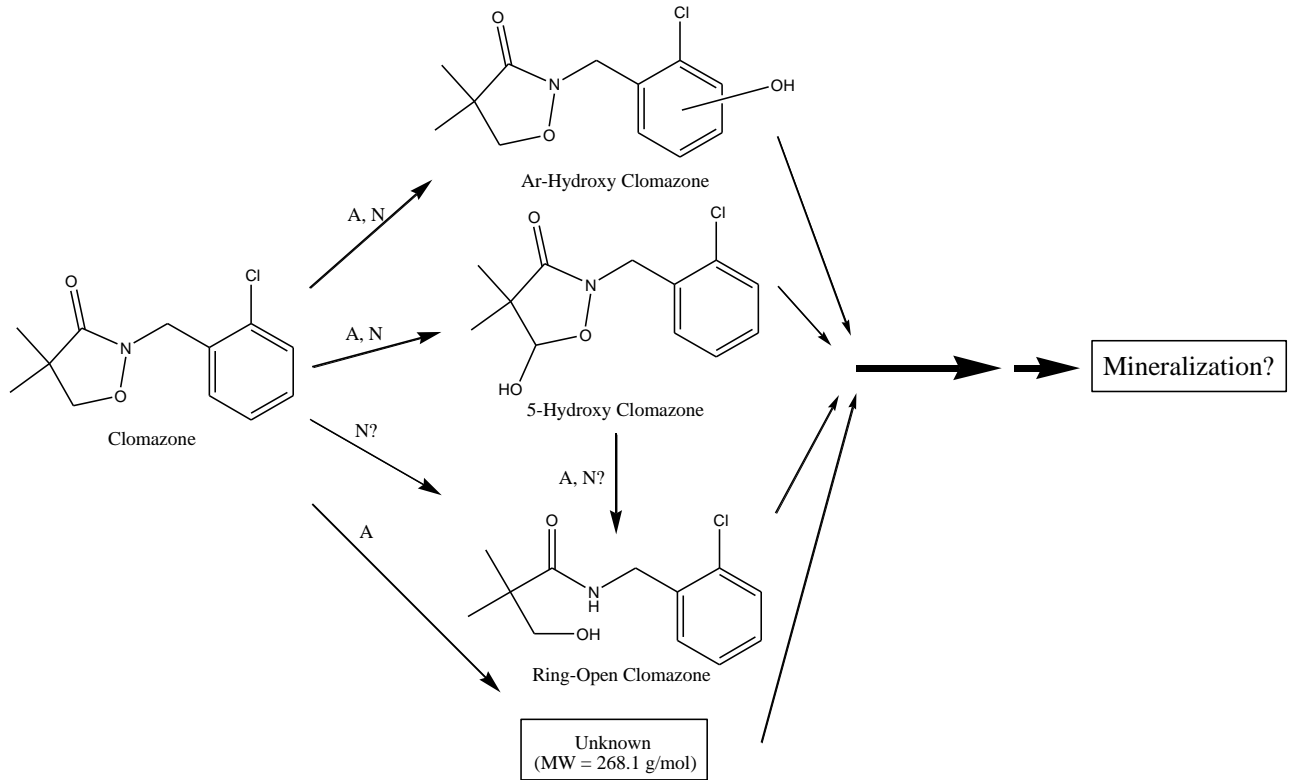
Cerano (clomazone) is an herbicide used in California rice fields, the application of which has increased from 500 lbs applied in 2002 to 61,000 lbs in 2006 (WSSA, 2006). It has received continued attention from the rice industry as a potential replacement for herbicides such as Ordram and/or Bolero. Previous environmental fate data from our laboratory have indicated Cerano does not appreciably sorb to soil (Gunasekara *et al.*, *in press*), and with the development of new formulations to prevent volatilization and drift, Cerano will persist primarily in the water column.

Cerano is utilized as a carbon source by soil microbes, and is transformed into various phase I metabolites. The community uses different pathways to degrade the pesticide, which, among others, depend on soil redox potential ( $E_h$ ), which is linked to field flooding. Since flooded rice field  $E_h$  varies widely, metabolism data from highly anaerobic/aerobic microcosms is best suited to simulate degradation in flooded and non-flooded fields. Microcosms consisting of distilled water and soil sampled from Biggs Rice Research Station were extracted over a 48-day (anaerobic) or 72-day (aerobic) period. At defined time intervals, samples were shaken, centrifuged and cleaned with solid-phase extraction. Analysis was performed via LC/MS/MS. Before analysis, aliquots of each replicate were pooled, and analyte abundance is reported as a function of machine response.

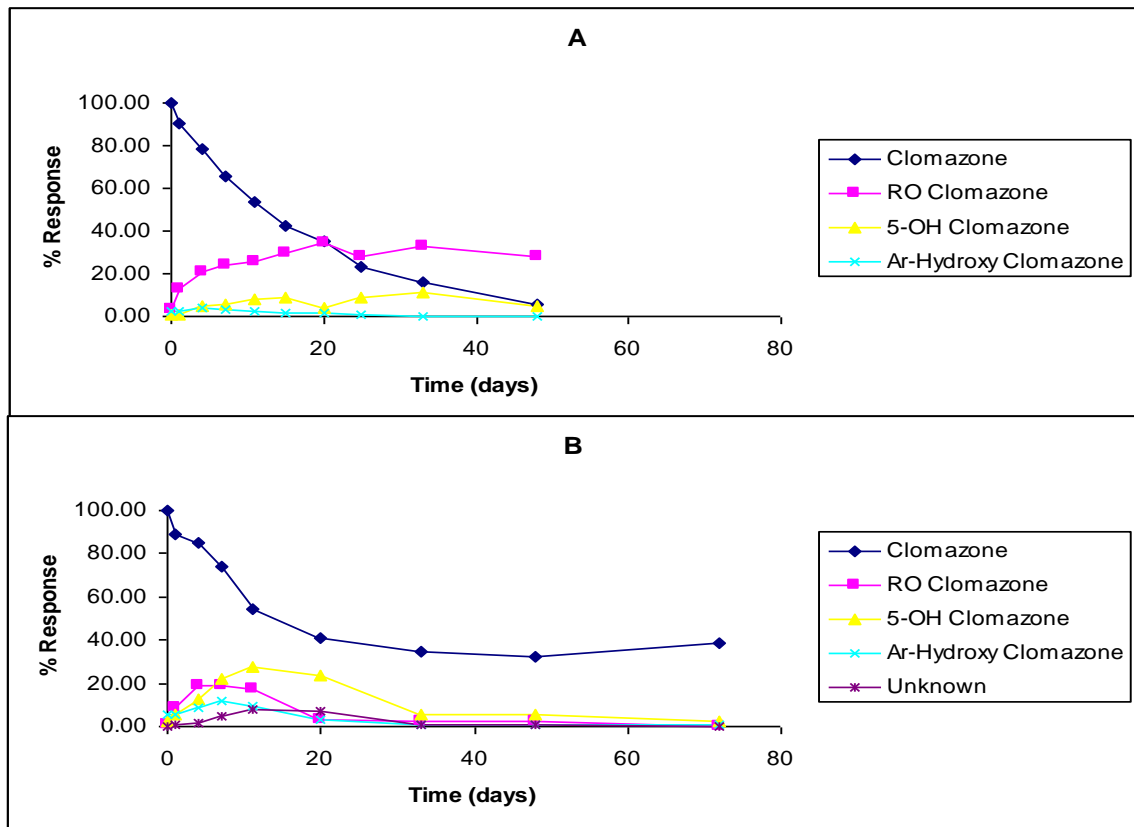
Our preliminary data predicts that Cerano will degrade anaerobically via pseudo first-order kinetics with a half-life (DT-50) of 11.8 days (Figure 3). Three metabolites were identified at levels >1% of the initial parent application (Figure 4). The primary metabolite observed was ring-open clomazone (RO), which attained 34% response of the initial application at day 20, and the response slowly tapered off thereafter. Two other pathways include hydroxylation at the 5 position (5-OH) and hydroxylation on the aromatic ring (Ar-OH), which follows similar kinetics to RO. Aerobically; Cerano degrades much slower, and does not fit a classical first-order model (Figure 5). A lag (growth) phase is evident from 0-7 days, followed by a period of rapid degradation from day 7 to day 20; thereafter the response does not decrease appreciably. Four metabolites were observed, including an unknown having a mass of 268.1 g/mol. Two of these, RO clomazone and 5-hydroxy clomazone, attained responses of 19% and 27% at day 7 and 11, respectively. Liu, et al (1996) proposed 5-OH to be a precursor to RO formation, and our findings are ambiguous in this regard, both under aerobic and anaerobic conditions.



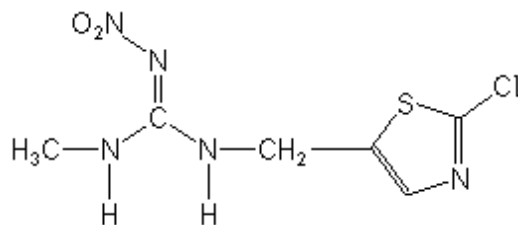
**Figure 3.** Anaerobic clomazone biodegradation.



**Figure 4.** Clomazone microbial degradation pathway in Biggs Soil (A = Aerobic, N = Anaerobic).



**Figure 5.** Degradation kinetics of (A) anaerobic microcosms, and (B) aerobic microcosms.



**Figure 6.** Structure of clothianidin.

### Objective III

#### *Introduction*

Clothianidin, (E)-1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine (Figure 6), is a novel neonicotinoid insecticide that exhibits a good systemic action and high insecticidal activity against various sucking insect pests (Umene *et al.*, 2006). It has been registered for foliar spray and seed treatment applications for food crops in various countries such as Japan and Europe (Franklin *et al.*, 2004) and is of a current interest for rice culture in California due to its effectiveness against the water weevil. Due to its efficient mode of action (acting selectively on the insect central nervous system as agonists of the post-synaptic nicotinic acetylcholine receptors), neonicotinoid insecticides show no cross-resistance to conventional insecticide classes and therefore have begun replacing those long-established classes of insecticide such as pyrethroids, chlorinated hydrocarbons, organophosphates and carbamates (Jeschke *et al.* 2008).

Two mechanisms are of primary importance when considering the abiotic dissipation of the insecticide clothianidin from rice fields: 1) chemodynamic transport (movement of the compound via air-water partitioning and/or soil-water partitioning, and 2) degradation (destruction of the compound via reactions mediated by either sunlight or microbes). This past year, we began investigating the potential volatility of the compound, or more specifically, the Henry's law constant for clothianidin since air-water partitioning is dependent on both water solubility and vapor pressure, as measured by the Henry's constant (Schwartzbach *et al.*, 2003).

#### *Methods*

The experimental determination of Henry's constant for clothianidin was performed by the gas stripping apparatus method (Lau *et al.*, 2006). Custom-made gas stripping columns (1 m x 51 mm id Pyrex cylinders) containing approximately 1.5 L of a 0.25 mg L<sup>-1</sup> clothianidin solution in 0.01 M CaCl<sub>2</sub> and 200 mg L<sup>-1</sup> sodium azide (to prevent microbial degradation of the insecticide) were run in duplicates. The columns were wrapped in aluminum foil to prevent photodegradation of the analyte, and the column temperature was maintained at 20°C by a recirculating water bath. A stream of N<sub>2</sub> gas (filtered through a hydrocarbon trap and saturated with water) at a flow rate of 100 mL/min was introduced to the column through a tube insert located at the bottom of the cylinder. Aqueous samples (10 mL) were collected at various time intervals over the course of the experiment (48-h time period) to measure the disappearance of clothianidin from the aqueous solution. The collected samples were stored in sealed glass test tubes at 4°C for analysis at a later date.

**Table 3.** Solvent gradient program for LC/MS analysis of clothianidin spiked samples.

Time (min)	Water (%)	Acetonitrile (%)
0.00	70	30
10.00	30	70
10.01	0	100
11.00	0	100

### Method Validation

*Extraction.* Sample solutions (10 mL), spiked with analytical-grade clothianidin (Valent, U.S.A.) at 0.25, 0.50 and 0.75 ppm in 0.01 M CaCl<sub>2</sub>, were prepared in triplicate and extracted using BAKERBOND™ SPE Octadecyl (C<sub>18</sub>) Disposable Extraction Columns (J.T. Baker). Cartridges were conditioned with 3 mL of methanol followed by 3 mL D.I. water. After loading an aqueous sample, each cartridge was dried under vacuum for approx. 1 h. The analyte was then eluted twice with 3 mL aliquots of ethyl acetate, which were then evaporated under a stream of N<sub>2</sub> gas at room temperature. The residues were dissolved in 2 mL of acetonitrile and analyzed by LC/MS/MS.

*LC/MS Analysis.* LC/MS/MS analysis of spiked samples was performed on an HP Series 1100 HPLC (Hewlett Packard, Inc.) coupled with API 2000 LC/MS/MS System (Applied Biosystems, Inc.). A Titan C<sub>18</sub> analytical column (5 μm particle size, 2.1 mm id x 100 mm; Peeke Scientific) was used at ambient temperature, via solvent gradient, at a flow rate of 0.15 mL/min (Table 3). Injection volume was 20 μL, using an HP Series 1100 Autosampler, and the column eluent was directed to the MS for the entire run time of 11 min. Positive ion electrospray ionization was used with optimized MS parameters (Table 4), and the ion transition (m/z 250.0→169.4) of clothianidin was acquired by multiple reaction monitoring mode. A seven-point external calibration curve with weighed (1/X<sup>2</sup>) linear regression was generated by potting the instrumental response of clothianidin for m/z 250.0→169.4 transition calculated with Analyst Software Version 1.4.2.

### Results

*Air-Water Partitioning Experiment Status.* The Henry's law constant ( $K_H$ ) for clothianidin was estimated according to the vapor pressure and water solubility of the insecticide. By definition:

$$K_H = \frac{\text{Vapor Pressure (Pa)}}{\text{Solubility (mol/m}^3\text{)}}$$

Therefore, the Henry's law constant at 20°C was calculated using the chemical properties of the insecticide provided by the manufacturers:

$$K_H = \frac{3.8 \times 10^{-11} \text{ Pa}}{0.327 \text{ g/L}} = \frac{3.8 \times 10^{-11} \text{ Pa}}{1.3 \text{ mol/m}^3} = 2.9 \times 10^{-11} \text{ Pa}\cdot\text{m}^3/\text{mol}$$

In general, chemicals with Henry's law constants lower than  $3 \times 10^{-7} \text{ Pa}\cdot\text{m}^3/\text{mol}$  are considered to have low volatility. The calculated  $K_H$  value for clothianidin suggests that the insecticide is not volatile in an aqueous environment. Therefore, we hypothesize that the insecticide will remain in

**Table 4.** Detailed mass spectrometer parameters for LC/MS/MS analysis.

Parameters	Clothianidin m/z 250 → 169.4
Gas	Nitrogen
Curtain Gas	20
Collision Gas	4
Ionspray Voltage	5500
Temperature (°C)	375
Ion Source Gas 1	30
Ion Source Gas 2	0
Declustering Potential (V)	26
Focusing Potential (V)	360.0
Entrance Potential (V)	11.0
Collision Energy (V)	19.0
Collision Cell Exit Potential (V)	6.0

water, rather than dissipating into the atmosphere, after being applied to a rice field. Our experimental determination of the  $K_H$  should verify the calculated result.

Aqueous samples were collected at certain time intervals from the gas stripping columns (described above) and are currently stored at 4°C. They are scheduled to be analyzed by LC/MS/MS upon completion of the method validation.

*Method Validation Status.* MS parameters in optimum condition for the analysis of clothianidin (Table 3) were determined by injecting 10 ppm of a clothianidin standard into the MS; the retention time for clothianidin was at 2.9 min. The transition at m/z 250.0→169.4, occurring due to cleavage of the nitro- and the chlorine- moieties from the parent compound under the optimized collision conditions, was the most abundant transition for clothianidin and therefore used for quantitation of the analyte. The calibration curve correlation coefficient was 0.9757, and the range of spiked recoveries were 73.4-106 % (n=3), 94.8-104 % (n=2) and 86.5-116 % (n=3) for 0.25, 0.5 and 0.75 ppm spiked samples, respectively. Both the limits of detection and quantitation for the instrument will to be determined.

Method validation is currently ongoing and the first priority of the air-water partitioning experiment. A well-developed analytical method for LC/MS/MS analysis of the insecticide will benefit not only the air-water partitioning study but also future experiments regarding the environmental fate of clothianidin (i.e., soil-water partitioning, microbial degradation and photolytic degradation).

## REFERENCES

California Department of Pesticide Regulation, 2006 Summary Report: Indexed by Commodity, <http://www.cdpr.ca.gov/docs/pur/pur06rep/comrpt06.pdf>.

Gunasekara, A. S., I. D. de la Cruz, V. P. Claassen, T. M. Young and R. S. Tjeerdema. The sorption and desorption of clomazone to soils: Sorbent contributions. *Pest. Manage. Sci.* (in press).

Liesack, W., Schnell, S., Revsbech, N.P. Microbiology of flooded rice paddies. *FEMS Microbiology Reviews*, 2000, 24, 625-645.

Rabus, R., Kube, M., Heider, J., Beck, A., Heitmann, K., Widdel, F., and Reinhardt, R. (2005) The genome sequence of an anaerobic aromatic-degrading denitrifying bacterium, strain EbN1. *Arch Microbiol* 183: 27–36.

Schmelzer, K. R., Johnson, C. S., Viant, M. R., Williams, J. F., Tjeerdema, R. S. 2005. Influence of organic carbon on reductive dechlorination of thiobencarb in California rice field soils. *Pest Manage. Sci.* 61:68-74.

Franklin, M. T., Winston, M. L., and Morandin, L. A. 2004. Effects of clothianidin on *Bombus impatiens* (Hymenoptera: Apidae) colony health and foraging ability. *J. Econ. Entomol.* 97 (2): 369-373.

Jeschke, P., and Nauen, R. 2008. Review: Neonicotinoids – from zero to hero in insecticide chemistry. *Pest Management Science.* 64: 1084-1098.

Lau, F. K., Charles, M.J., *et al.* 2006. Evaluation of gas-stripping methods for the determination of Henry's law constants for polybrominated diphenyl ethers and polychlorinated biphenyls. *J. Chem. Engineer. Data.* 51: 871-878.

Liu, S.Y.; Shocken, M.; Rosazza, J.P.N. Microbial Transformations of Clomazone. *Journal of Agricultural and Food Chemistry.* 1996. 44, 313-319.

Schwarzenbach, R. P., Gschwend, P.M., and Imboden, D.M. 2003. *Environmental Organic Chemistry*, 2<sup>nd</sup> edition. John Wiley & Sons Inc., New Jersey.

Umene, H., Konobe, M., Akayama, A., Yokota, T. and Mizuta, K. 2006. Discovery and Development of a Novel Insecticide “Clothianidin.” *Sumitomo Kagaku*, vol. 2006-II.

## **PUBLICATIONS OR REPORTS**

### *Abstracts in Meeting Proceedings*

1. Vasquez, M. E. and R. S. Tjeerdema, 2008. Partitioning of etofenprox under simulated California rice field conditions. *Proceedings of the American Chemical Society*. Philadelphia, PA.

### *Manuscripts (new in print or press this year)*

1. 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.

2. Gunasekara, A. S., I. D. de la Cruz, V. P. Claassen, T. M. Young and R. S. Tjeerdema. The sorption and desorption of clomazone to soils: Sorbent contributions. *Pest. Manage. Sci.* (in press).

### **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 processes that can contribute to such dissipation that are investigated: volatilization to air, sorption (reversible bonding) to soils, degradation by sunlight, and degradation by soil microbes.
2. For etofenprox, a method was developed and validated for the analysis of the insecticide and its metabolites using LC/MS/MS. It will be used to characterize its dissipation rate and half-life via microbial and photochemical processes under California rice field conditions.
3. Experiments designed to characterize the anaerobic microbial degradation of etofenprox in flooded soils are currently in progress.
4. For Cerano, an advanced method involving LC/MS/MS was developed for the analysis of the herbicide in both soil and water samples.
5. Preliminary experiments have been completed and indicate that Cerano is efficiently degraded by soil microbes under both aerobic and anaerobic conditions. Additional experiments are currently underway.
6. For clothianidin, the extraction method for analysis of the insecticide was developed. Via the spike-recovery approach, reverse-phase SPE cartridges were found to be optimal for extracting clothianidin from soil and water samples.
7. Optimized conditions for the instrumental analysis of clothianidin were also investigated. LC/MS/MS was chosen due to the high water solubility of the insecticide.
8. Preliminary results indicate that the calculated Henry's law constant of clothianidin is relatively low, indicating that it is not likely to dissipate from rice fields via volatilization; an experimental determination of the constant is underway.