

**ANNUAL REPORT  
COMPREHENSIVE RESEARCH ON RICE**

January 1, 2006 – December 31, 2006

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

**PROJECT LEADER:** Ronald S. Tjeerdema, Professor and Chair, 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), Amrith Gunasekara (UCD), Donald Crosby (UCD)

**LEVEL OF 2006 FUNDING:** \$49,712

**OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO ACCOMPLISH OBJECTIVES:**

**Objective 1.** To investigate the natural factors governing the dissipation of pesticides in California rice fields. Emphasis for 2006 was to characterize the volatilization and soil sorption of the insecticide etofenprox under California rice field conditions.

**Objective 2.** To investigate the natural factors governing the dissipation of pesticides in California rice fields. Emphasis for 2006 was on the soil sorption of clomazone (Cerano 5 MEG) in California rice field soils.

**SUMMARY OF 2006 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:**

***OBJECTIVE 1***

*Introduction*

A synthetic pyrethroid insecticide, etofenprox is of current interest to rice farmers in the Sacramento Valley due to its effectiveness against the rice water weevil. It is also effective against green leafhoppers and plant hoppers resistant to the commonly used organophosphorus insecticides. While this particular compound is not yet registered in California for use on rice fields, it is currently used effectively for rice culture in both Japan and Spain (United Nations, 1993). Etofenprox belongs to the ether class of pyrethroid insecticides, named from the novel ether linkage in the structure. Currently used pyrethroids belong to the carboxyl ester pyrethroid group, as also defined by the presence of this functional group in the structure.

Two mechanisms are of primary importance when considering the abiotic dissipation of the pesticide etofenprox 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). The first parameter includes the potential volatility of the compound, or more specifically, the Henry's law constant for etofenprox since air-water partitioning of any chemical is dependent on both its water solubility and its vapor pressure, as measured by the Henry's constant (Schwartzbach *et al.*, 2003). Another important abiotic factor that can greatly affect field dissipation of a pesticide is its soil-water partitioning, which is representative of both the soil sorption and desorption processes. A high degree of soil sorption can contribute significantly to pesticide dissipation from field water; however, it may also limit the bioavailability of the pesticide, thus potentially limiting an agent's effectiveness. In addition, soil sorption may reduce a pesticide's availability for degradation via abiotic or biotic means, thus contributing to its persistence in the environment.

### *Methods*

The gas stripping apparatus method was used for the experimental determination of Henry's constant for etofenprox (Lau *et al.*, 2006). Gas stripping columns (1 m x 51 mm id) were run side by side for duplicate determinations. Approximately 1.5 L of dilute etofenprox solution (2-5 ppb) and 200 ppm sodium azide (to prevent microbial degradation of the insecticide) were added to the gas stripping columns. Column temperature (25°C) was maintained with a recirculating water bath, and columns were wrapped in foil to prevent photodegradation of etofenprox over course of experiments. High purity nitrogen gas (45-60 mL/min flow rate) was filtered through a hydrocarbon trap and saturated with water before entering the bottom of the water column in the gas stripping apparatus. Volatilized etofenprox was captured on polyurethane foam (PUF) plugs. A mist trap separating the water column and the PUF plugs was used to prevent splashing water from landing on the PUF plugs and biasing the results. Water samples (10 mL) were collected from the column at various time intervals over the course of the experiment to measure aqueous decrease over time. At the end of the experiments the columns were rinsed with solvent and analyzed to determine the amount of etofenprox sorbed to the apparatus, and the PUF plugs were analyzed to determine the amount volatilized from the water column.

### *Extraction and Analysis*

To each 10 mL water sample, 1 µL of internal standard (dicyclohexylphthalate) was added. Extraction blanks and control spikes were analyzed along with each sample set extracted. Extraction began by adding 0.5 g NaCl and 0.1 mL acetone to water samples and then mixing until the salt dissolved. Hexane (3 mL) was used 3 times to extract etofenprox from the water, after which the hexane layers were dried with sodium sulfate, combined, and evaporated to 50 µL under nitrogen gas before analysis by GC/MS. This procedure was adapted from methods provided by the manufacturer (Mitsui, Japan).

The column apparatus was drained of remaining aqueous solution and then rinsed with hexane to remove sorbed etofenprox. As above, the hexane rinse was collected, dried

with sodium sulfate and evaporated under nitrogen gas to 50  $\mu\text{L}$ . Internal standard was added before analysis by GC/MS. PUF plugs were spiked with internal standard before extraction with 30 mL hexane on a rotary shaker overnight. Hexane extracts were evaporated to 50  $\mu\text{L}$  under nitrogen gas before analysis by GC/MS.

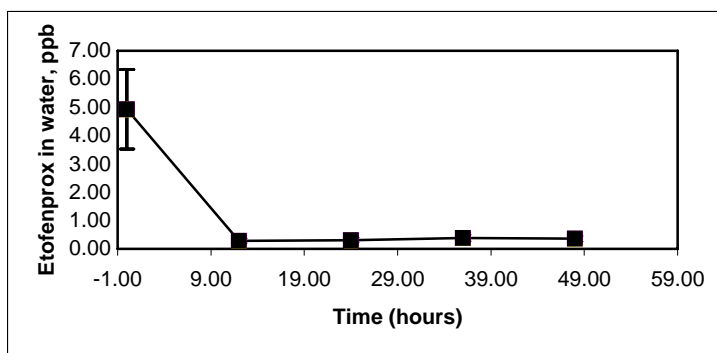
GC-MS analysis was performed on a HP 5890 gas chromatograph coupled to a HP 5971 mass selective detector. The analytical column was a Zebron ZB-5 ms capillary column (30 m x 0.25 mm id x 0.25  $\mu\text{m}$  film thickness). The initial GC oven temperature was 50°C (0 min), which was then ramped at 50°C/min to 200°C and held for 4 min. The final ramp was at 20°C/min to 280°C and held for 6 min. The injector was in splitless mode at a temperature of 250°C and a constant flow of pressure (15.1 psi). Helium flow rate through the column was set at 1.8 mL/min, and the GC-MS interface was held at 280°C.

The mass spectrometer was run in SIM mode (135, 163, 376 m/z for etofenprox; 83, 122, 167 m/z for the internal standard). Sample and calibration standard aliquots (both 5  $\mu\text{L}$ ) were injected using a HP 7673 autosampler. Total abundance for all ions monitored was used for quantification. The relative response of etofenprox to internal standard was used to generate the calibration curve in Microsoft Excel. Linear regression was applied to the calibration points and the intercept was not forced through the origin. The analytical method was adapted from methods provided by the manufacturer (Mitsui, Japan).

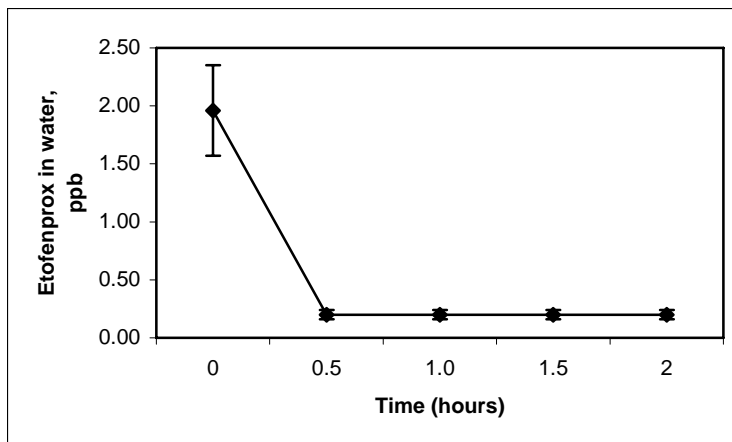
### *Results and Discussion*

The first attempt to measure Henry's constant began with an initial water concentration of 5 ppb etofenprox and a 12-h sampling interval. As shown in Figure 1, the aqueous etofenprox concentration decreased to levels at or below the detection limit for the method (0.2 ppb) within 12 h.

The next approach was to shorten the sampling interval to try to observe the aqueous decrease in a concentration range that is quantifiable. Figure 2 shows the aqueous etofenprox concentration after 30-min sampling intervals.



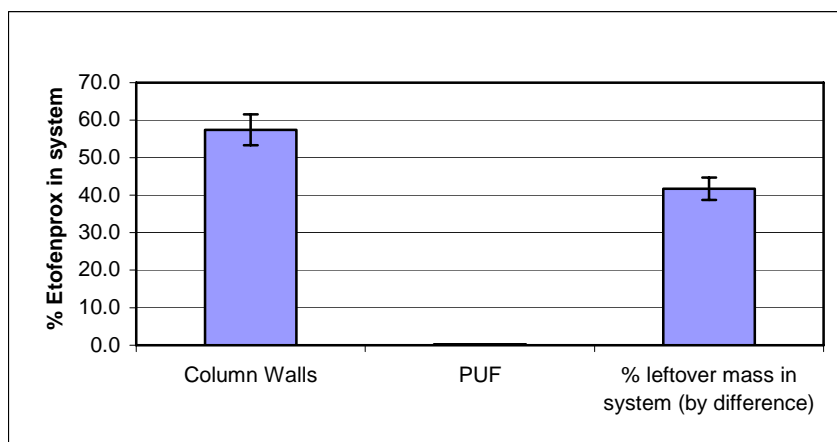
**Figure 1.** Air-water partitioning of etofenprox in the gas stripping during experiment 1.



**Figure 2.** Air-water partitioning of Etofenprox: aqueous concentration vs. time in the gas stripping during experiment 2.

As in experiment 1, etofenprox levels decreased to below the detection limit within 30 min. Analysis of the column rinse samples and PUF samples from experiments 1 and 2 showed the mass distribution within the system over the course of the study. The relative percent of mass distribution is summarized in Figure 3 for both experiments.

Approximately 60% of the mass in the system partitioned onto the apparatus walls. This behavior has been reported previously for pyrethroids by other researchers. (Zhou *et al.*, 1995) The mass balance approach allowed confirmation that the aqueous phase decrease was not only due to volatilization but also sorption. The significance of the degree of sorption to the apparatus has plagued other Henry's constant experimental determinations of very insoluble compounds, such as the heavier PBDE congeners as reported by Lau *et al.* (2006). Since the compound adsorbed to the apparatus with significant affinity, the mass remaining in aqueous solution was not enough to overcome analytical limitations.



**Figure 3:** Percent mass distribution of etofenprox in gas stripping apparatus over the course of 2 separate experiments

Analytical limitations led to inconclusive results of the measured Henry's constant due primarily to the extreme insolubility of etofenprox in water (22.5 ppb). These limitations include 1) a fixed volume of water for extraction due to apparatus limitations, and 2) use of a dilute solution of etofenprox while still maintaining the concentration above instrumental detection limits. If these parameters and assumptions could have been modified, then more conclusive measurements may have been obtained. However, as the data show, experimental limitations and assumptions limited a complete understanding of the Henry's constant for etofenprox under California rice field conditions.

Despite these analytical difficulties, the experiments demonstrate that air-water partitioning will not be a major dissipation route for etofenprox. Rather, the hydrophobic nature of etofenprox predisposes it to partitioning to soils and sediments. This is indeed the case for currently used pyrethroids in agriculture (Zhou *et al.*, 1995). The results of the on-going soil sorption studies for etofenprox will allow evaluation of this hypothesis.

### *Calculations*

Henry's constants can be calculated according to the vapor pressure and water solubility of a chemical:

$$K_H = \frac{\text{vapor pressure}}{\text{solubility}}$$

Using the manufacturer's reported values for vapor pressure and solubility at 25 °C, the Henry's constant at 25°C was calculated as follows:

$$K_H = \frac{8.13 \times 10^{-7} \text{ Pa}}{5.98 \times 10^{-5} \text{ mol/m}^3} = 0.0136 \text{ Pa}\cdot\text{m}^3/\text{mol} \text{ at } 25^\circ\text{C}$$

In order to determine  $K_H$  at temperatures relative to California rice field conditions, the vapor pressure and solubility values of the compound must be determined or calculated at the temperatures of interest. Therefore, vapor pressures were calculated according to the boiling point group contribution method outlined by Schwartzenbach *et al.* (1993). Estimated vapor pressures at relevant rice field temperatures are presented in Table 1. When comparing the manufacturer-determined vapor pressure and the calculated vapor pressure at 25°C, there was agreement to within less than an order of magnitude.

Experimentally-determined solubility data for hydrophobic compounds is scarce and prone to analytical error. Because solubility is temperature dependent, the solubility must be experimentally determined or estimated from chemical structure. Currently used methods to estimate solubility of a compound from its chemical structure do not suffice for extremely large and insoluble compounds, such as etofenprox (Schwartzenbach *et al.*, 2003). In comparing the calculated solubility to the manufacturer determined solubility at 25 °C, the results were not similar. As a result, water solubilities at different rice field temperatures were not calculated and must be experimentally determined as performed by the manufacturer. Without reliable solubility data, the calculation of Henry's constants at different temperatures cannot be reliably completed.

Temperature °C	Calculated Vapor Pressure (Pa)	Manufacturer Reported Vapor Pressure (Pa)
5	$4.48 \times 10^{-9}$	
15	$1.11 \times 10^{-8}$	
20	$1.71 \times 10^{-8}$	
25	$2.58 \times 10^{-8}$	$8.13 \times 10^{-7}$
35	$5.64 \times 10^{-8}$	

**Table 1:** Estimated vapor pressures of etofenprox at various temperatures.

### *Conclusions*

Etofenprox is an ether pyrethroid with a water solubility of 22.5 ppb. Based on its behavior during Henry's constant experiments, it is suggested that it will very strongly sorb to soil and its organic matter components. It is highly unlikely that it would move with percolation into groundwater due to its hydrophobic nature. Thus, the hydrophobic nature of etofenprox may predispose it to strongly partition out of water. This is indeed the case for currently used pyrethroids in agriculture (Zhou *et al.*, 1995). The results of the on-going soil sorption studies for etofenprox will facilitate full evaluation of this hypothesis.

### *Soil-Water Partitioning Experiment Status*

As a result of not being able to obtain  $^{14}\text{C}$ -labeled etofenprox in a timely manner from the manufacturer (Mitsui, Japan), it was necessary to modify the proposed procedures for the soil sorption experiments. Labeled compounds provide extreme sensitivity at low concentrations. Without labeled etofenprox, the experiments can still be conducted using the non-labeled insecticide but the total mass in the system must be increased to provide analytical sensitivity. Thus, using 125-mL serum bottles for sorption studies instead of the 8-mL vials should allow for sufficient mass in the system for analytical quantification. This work is currently ongoing.

## **OBJECTIVE 2**

### *Introduction*

Clomazone (2-[2-chlorophenyl)methyl-4,4-dimethyl-3-isoxazolidinone) is an herbicide used in rice culture to control pre-emergent and post-emergent grasses such as barnyard, sprangletop, and water grasses. Herbicide uptake is via plant roots and translocation occurs via the xylem to the leaves. Consequently, clomazone inhibits the production of chlorophyll in the leaves. Its effectiveness against weed grasses has made it a popular herbicide. For instance, in California, 50,000 lbs were used on rice fields in 2004 (CDPR, 2004). In general, clomazone is moderately soluble in water (1100 mg/L), has a relatively low organic carbon partition coefficient ( $K_{oc}$ ), and is both hydrolytically and photolytically stable in the environment.

Considerable data exists regarding the sorption of clomazone to different soils. However, to date there is little information available on the its sorption to rice field soils. To our knowledge there are only an handful of papers that directly examine the sorption of clomazone to rice field soils (Mervosh *et al.*, 1995; Li *et al.*, 2004; Quayle *et al.*, 2006). None characterize the sorption of clomazone to the unique rice field soils of the Sacramento Valley. Thus, there is an important lack of information regarding the use of clomazone in relation to the soils of California's major rice producing region. In this study we collected soils from two different rice fields in the Sacramento Valley. We then studied the sorption of clomazone to these two rice soils under controlled laboratory conditions which simulated California rice field conditions.

### *Methods*

*Soils.* Soils were collected from two separate rice fields in the Sacramento valley, CA. They were located near the towns of Princeton and Richvale, and the soils are thus named as such. Historically, the Princeton rice farm incorporated post harvest straw but instead over the last four years it has burned the straw. In contrast, Richvale is an organic rice farm and therefore the post harvest straw has always been incorporated into the field. Several kilograms of soil were collected randomly from the 0-10 cm layer of each field in the spring (2005) prior to planting but after field preparation. The soils were air dried, ground to pass through a 2-mm sieve, further ground to a powder for sorption isotherms in the lab, and stored at 4°C until used.

*Soil characterization.* Soils were characterized for a number of chemical properties by the Division of Agriculture and Natural Resources (DANR) Analytical Laboratory at the University of California (Davis, CA). Results are shown in Table 1. Description of the methods of analysis can be found in Schmelzer *et al.* (2005) or the DANR website (<http://danranlab.ucdavis.edu>).

*Sorption and desorption experiments.* Ring-UL-<sup>14</sup>C and unlabeled clomazone (>98% purity) were obtained gratis from FMC Corp. All sorption isotherms were run according to the batch equilibration technique (Xing *et al.*, 1996) at 20 ± 1°C in 8-mL screw cap vials with Teflon-lined septa. The background solution was 0.01 M CaCl<sub>2</sub> in deionized water with 200 mg/L sodium azide as a biocide. Clomazone concentrations ranged from 0.067 to 500 mg/L. Clomazone was prepared at a high concentration in methanol prior to its addition to the vials. However, the final methanol concentration did not exceed 0.1% by volume to the background solution. Based on initial kinetic studies, clomazone was mixed with all sorbents for seven days to reach apparent equilibrium. The quantity of sorbent was adjusted to maintain sorption of clomazone between 30 and 70%; approx. 1 g of Princeton and Richvale soil was used with 6 mL background solution. All samples, including the blanks (no sorbent), were run in triplicate. After mixing, vials were centrifuged at 1000 x g for 30 min, followed by a 1-mL removal of supernatant. The supernatant was added to 6 mL Ultima Gold XR<sup>TM</sup> cocktail (Fisher Scientific, Pittsburgh, PA) prior to scintillation counting (Beckman LS 3801, Fullerton, CA).

Sorbed clomazone concentration was determined by mass balance calculations because sorption to the vials of similar model compounds has been found to be insignificant (Yuan and Xing, 2001). Desorption was conducted by sequential decant-refill steps after the completion of the sorption experiments (Chen *et al.*, 2000). After the 1-mL aliquot was withdrawn, as part of the sorption procedure, about 5 mL of the remaining supernatant was discarded and replaced by the

fresh background solution (dilution). Following dilution, the vials were mixed for the same equilibration time (7 days) as used in the sorption experiments. After mixing, the vials were centrifuged and an aliquot (approx. 1 mL) of the supernatant was taken out for scintillation analysis. The remaining supernatant was replaced by the fresh background solution and the above process was repeated for two more cycles. Mass balance calculations were conducted to determine the amount of clomazone desorbed in each cycle.

*Data analysis.* All sorption data were fit to the logarithmic form of the Freundlich equation:

$$\log S = \log K_F + N \log C_e$$

S is the total sorbed concentration ( $\mu\text{g/g}$ ),  $C_e$  is the solution phase concentration ( $\mu\text{g/mL}$ ), and  $K_F$  ( $\mu\text{g/g}$ ) ( $\mu\text{g/mL}$ )<sup>-N</sup> and N are constants with N often <1 for sorption of hydrophobic organic chemicals to soils. Isotherms were plotted by log S vs. log C, and log  $K_F$  and N were obtained from the fitting. Because the units of  $K_F$  depend on the N value for a given sample (Bowman, 1981),  $K_F$  values cannot be compared between different isotherms. However, the  $K_F$  value from different isotherms can be compared with each other after normalizing it by the organic carbon content of the soil at a specific concentration. This method of normalization generates the modified organic carbon normalized Freundlich parameter,  $K_{oc}$ .

### *Results and Discussion.*

Table 1 shows the physical-chemical properties of the two soils collected from the Sacramento Valley, CA. There were several similarities and differences in the two soils. For example, the Princeton soil had less clay and more silt (akin to riverbed sediment) than Richvale which was more similar to a rice field soil with high clay content (Table 1). The organic matter content was greater in the Princeton soil even though post-harvest straw had not been incorporated after recent harvests as it was burned. Total nitrogen was similar at both sites but nitrate content was high in Princeton soil. Subtle differences were observed for exchangeable potassium, sulfate, and phosphorus (Table 1) between the two soils.

**Table 1.** Soil properties showing physical and chemical similarities and differences of the Princeton and Richvale soils (0-10 cm depth).

Soil property	Soil	
	Princeton	Richvale
Sand (%)	14	23
Silt (%)	49	26
Clay (%)	37	51
Organic matter (%)	3.10	2.18
Total available nitrogen ( $\mu\text{g/g}$ )	0.175	0.142
Nitrate ( $\text{NO}_3$ ) nitrogen ( $\mu\text{g/g}$ )	8.6	0.3
Exchangeable K ( $\mu\text{g/g}$ )	157	178
Exchangeable S ( $\text{SO}_4^-$ ; $\mu\text{g/g}$ )	23	41
Phosphorus ( $\mu\text{g/g}$ )	6.2	2.4

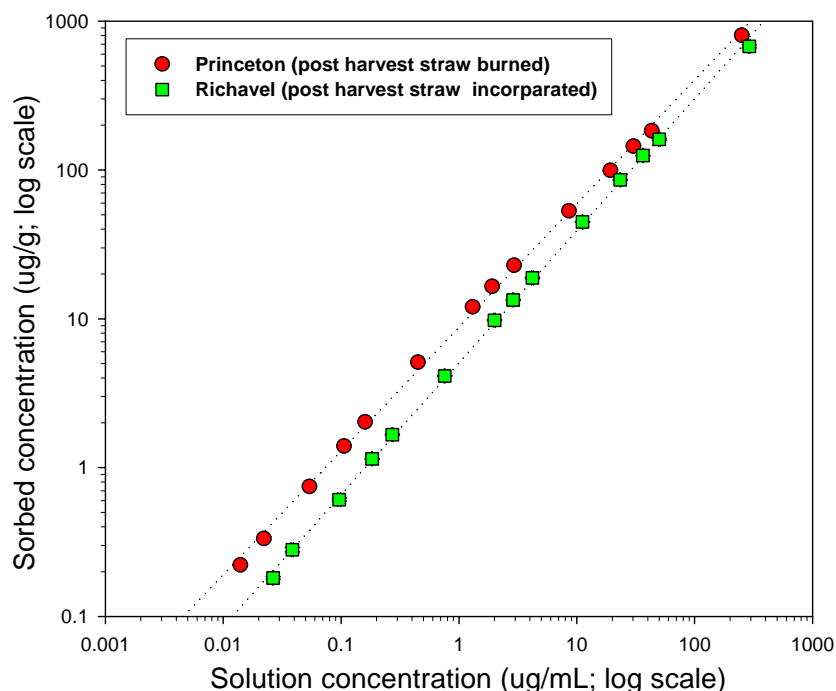
Figure 1 shows the detailed sorption isotherm data for clomazone in the Princeton and Richvale soils. The data show that sorption to the Princeton soil is slightly greater in relation to the Richvale soil. Table 1 indicates that the Princeton soil has greater organic matter content than the Richvale soil. There are many sorption studies that have associated organic matter content with increased sorption (Fingler *et al.*, 2004; Li and Pan, 2005). This could explain the slightly larger sorption affinity of clomazone for the Princeton soil. However, others factors could also explain the data. For instance, in the recent sorption literature, the role of burned residues (black carbon or charcoal) has been explored. Reports showed that such residues in soils have a very high affinity for hydrophobic organic compounds mainly due to their large surface area (Huang *et al.*, 2003; Yu *et al.*, 2006). Thus, post-harvest straw management practices (burning versus incorporation) could be responsible for the observed sorption deviation between the two soils – Princeton rice straw was burned first and then incorporated while the Richvale soil had straw directly incorporated. A greater understanding of the data presented in Figure 1 can be obtained from the Freundlich fitting parameters presented in Table 2.

Table 2 provides two important parameters extrapolated from the clomazone sorption isotherm data. The first is the exponent N which is the linearity (slope) of the data for each soil presented in Figure 1. Linear isotherms ( $N = 1$ ) are indicative of a dissolution sorption process. The dissolution environment is considered to be expanded with sorption sites that have a momentary existence similar to dissolved molecules in a viscous liquid. In contrast, if the  $N < 1$  in addition to the dissolution process there is high-energy “hole filling” site-specific sorption that takes place. The region in the soil is postulated to be condensed with specific sites for molecular sorption. Table 2 shows that clomazone sorption to both soils does not follow a simple linear, dissolution only, sorption process. Rather sorption is nonlinear indicating that dissolution and more specific sorption processes are taking place. This specific sorption process involves clomazone sorption to high energy sorption sites or “holes” within the organic matter fractions of the Princeton and Richvale soils even though the organic matter content of the soils is only 2-3%. Additionally, voids and layers within the inorganic clay fractions may contain such sites for clomazone sequestration. Char or burned soil residues could also be responsible for the nonlinearity. Nonlinear sorption processes are well described by the dual-mode sorption models proposed recently (Xing and Pignatello, 1997; LeBoeuf and Weber, 2000; Zhou *et al.*, 2001).

Sorption capacity or  $K_F$  is the other important parameter obtained from the mathematical fitting of the Freundlich equation. Essentially, the value is obtained by extrapolating the sorbed concentration ( $\mu\text{g/g}$ ) at a clomazone solution concentration of 1 ppm (Figure 1). The sorption capacity of clomazone to these soils is low when compared to other more hydrophobic soils (Table 4). Thus, clomazone is not expected to sorb appreciably by rice field soils of the Sacramento Valley, which are rich in clay and silt but low in organic matter (~2-3%).

**Table 2.** Clomazone sorption isotherm results after fitting the data to the Freundlich equation.

Sorbent	$K_F$ [( $\mu\text{g/g}$ )/ $\mu\text{g/mL}$ ]	N	$r^2$
Richvale soil (post harvest straw incorporated)	$5.06 \pm 0.007$	$0.887 \pm 0.005$	0.999
Princeton soil (post harvest straw burned)	$8.76 \pm 0.010$	$0.831 \pm 0.008$	0.999



**Figure 1.** Sorption of clomazone to two different rice field soils from the Sacramento Valley.

The sorption capacity data from Table 2 was used to obtain the distribution coefficient ( $K_D$ ) and organic carbon-normalized sorption capacity coefficient ( $K_{oc}$ ), as summarized in Table 3.  $K_D$  and  $K_{oc}$  (based on  $K_F$ ) cannot be directly compared between isotherms because the exponent  $N$  from the Freundlich equation might not be the same, as in this case: the Princeton  $N$  is 0.831 and the Richvale  $N$  is 0.887. However, they can be compared at specific concentrations, as summarized in Table 3. Results show that there is a greater affinity for clomazone at lower concentrations ( $C_e = 2 \mu\text{g/mL}$ ) as compared to the higher ones ( $C_e = 500 \mu\text{g/mL}$ ) for both soils. This is expected since soils contain a fixed number of sorption sites. At low concentrations, there are plenty of sites (with high energies) for the small number of clomazone molecules in solution. However, these same sites become saturated at higher clomazone concentrations and their energies diminish. They are primarily located in a soil's organic matter fraction. The benefit of calculating  $K_D$  and  $K_{oc}$  is that they can be compared to the same values from other compounds (usually at a solution concentration of  $1 \mu\text{g/mL}$ ; Table 4).

**Table 3.** The distribution coefficient ( $K_D$ ) and organic carbon-normalized sorption capacity coefficient ( $K_{oc}$ ) for Princeton and Richvale soils at specific solution concentrations.

Sorbent	$K_D$ at specific $C_e$ ( $\mu\text{g/mL}$ )			$K_{oc}$ (mL/g) at specific $C_e^*$		
	$C_e = 2$	$C_e = 25$	$C_e = 500$	$C_e = 2$	$C_e = 25$	$C_e = 500$
Richvale soil (post harvest straw incorporated)	5.46	4.00	2.33	432	317	184
Princeton soil (post harvest straw burned)	11.40	6.19	3.20	633	344	178

\*  $K_{oc}$  is based on the findings that organic matter is 58% organic carbon.

**Table 4.** The organic carbon-normalized sorption capacity coefficient ( $K_{oc}$ ) in relation to solubility for two herbicides and a model sorption compound.

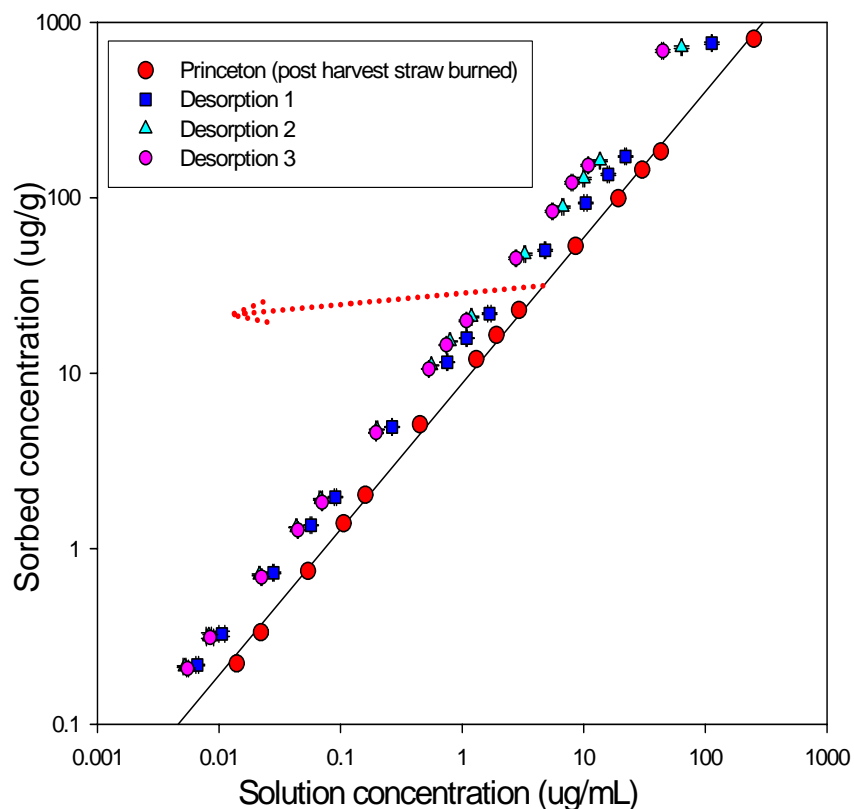
Herbicide	$K_{oc}$ (mL/g) at $C_e \sim 1$ mg/mL	Solubility (mg/L in water)
Clomazone	$\sim 500$	1100
Thiobencarb (2003-05 study)	$\sim 11500$	31
Phenanthrene	$\sim 80000$	1

Table 4 is a comparison of the  $K_{oc}$  for clomazone with another commonly used rice herbicide, thiobencarb, and a model hydrophobic organic compound, phenanthrene. It is evident that clomazone does not sorb appreciably to either the Princeton or Richvale soils. The thiobencarb results, which were obtained by the same laboratory with the same soils, show considerably more sorption. Phenanthrene is a model compound and its sorption to soils is generally very high. Such results can be explained when taking into consideration the solubility of the three compounds. Clomazone being the most soluble is least sorbed by the soils whereas thiobencarb, which is several times less soluble in water, has a greater soil affinity. The results show that clomazone is less likely to move from the water phase to the soil phase given its high solubility and the low organic carbon content of the rice field soils.

Finally, we examined whether clomazone is effectively desorbed from the two soils. Figure 2 shows desorption of clomazone from Princeton soil; desorption of clomazone from Richvale soil was very similar. Hysteresis or deviation from the sorption line was observed for all clomazone desorption experiments (total of 3). At all concentration points in both Princeton and Richvale soils clomazone had difficulty exiting the soil matrix. According to the sorption literature, this is mainly due to the entrapment of clomazone molecules in soil organic matter and/or the inorganic matrix. More specifically, since such soils have low organic matter ( $\sim 2$ -3%) entrapment of the clomazone molecules may involve meso/microporous entrapment within the inorganic matrix of the two rice field soils (Huang *et al.*, 2003). The desorption results have direct implication towards clomazone degradation as hysteretic desorption process mean that herbicide molecules are not readily available for biological degradation or root uptake. However, it does provide lower overall toxicity since clomazone is effectively sequestered within the soil matrix.

## REFERENCES

- Bowman, B.T. 1981. Anomalies in the log Freundlich equation resulting in deviations in adsorption K values of pesticides and other organic compounds when the system of units is changed. *J. Environ. Sci. Health. B.* 16: 113–123.
- Celis, R., De Jonge, H., De Jonge, L. W., Real, M., Hermosin, M. C., Cornejo, J. 2006. The role of mineral and organic components in phenanthrene and dibenzofuran sorption by soil. *Europ. J. Soil Sci.* 57: 308-319.



**Figure 2.** Desorption of clomazone from Princeton soil (desorption from Richvale soil was very similar and thus the data is not shown). The arrow indicates the pathway of clomazone desorption from the soil.

Chen, W., Kan, A. T., Tomson, M. B. 2000. Irreversible adsorption of chlorinated benzenes to natural sediments: Implications for sediment quality criteria. *Environ. Sci. Technol.* 34: 385–392.

Fingler, S., Stipicevic, S., Drevenker, V. 2004. Sorption behavior of chlorophenols and triazine herbicides in reference euro-soils. *Intern. J. Environ. Anal. Chem.* 84: 83-93.

Huang, W., Peng, P., Yu, Z., Fu, J. 2003. Effects of organic matter heterogeneity on sorption and desorption of organic contaminants by soils and sediments. *Appl. Geochem.* 18: 955-972.

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.

LeBoeuf, E. L., Weber, W. J. Jr. 2000. Macromolecular characteristics of natural organic matter. 2. Sorption and desorption behavior. *Environ. Sci. Technol.* 34: 3632-3640.

Li, J. H., Pan, G. X. 2005. Sorption of pyrene on two paddy soils and their particle-size fractions. *J. Environ. Sci. China.* 17: 962-965.

Li, L. F., Li, G. X., Yang, R. B., Guo, Z. Y., Liao, X. Y. 2004. Clomazone dissipation, adsorption and translocation in four paddy topsoils. *J. Environ. Sci. China*. 16: 678-682.

Mervosh, T. L., Sims, G. K., Stoller, E. W., Ellsworth, T. R. 1995. Clomazone sorption in soil: incubation time, temperature, and soil moisture effects. *J. Agric. Food Chem.* 43: 2295-2300.

Quayle, W. C., Oliver, D. P., Zrna, S. 2006. Field dissipation and environmental hazard assessment of clomazone, molinate, and thiobencarb in Australian rice culture. *J. Agric. Food Chem.* 54: 7213-7220.

*Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment. Geneva, Switzerland, September 20-29, 1993.* Food and Agricultural Organization of the United Nations: 357-381.

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.

Schwarzenbach, R. P., Gschwend, P.M., and Imboden, D.M. 2003. *Environmental Organic Chemistry*. New Jersey, John Wiley & Sons, Inc.

Xing, B., Pignatello, J. J., Gigliotti, B. 1996. Competitive sorption between atrazine and other organic compounds in soils and model sorbents. *Environ. Sci. Technol.* 30: 2432-2440.

Xing, B., Pignatello, J. J. 1997. Dual-mode sorption of low polarity compounds in glassy polyvinylchloride and soil organic matter. *Environ. Sci. Technol.* 31: 792-799.

Yu, X. Y., Ying, G. G., Kookana, R. S. 2006. Sorption and desorption behaviors of diuron in soils amended with charcoal. *J. Agric. Food Chem.* 54: 8545-8550.

Yuan, G., Xing, B. 2001. Effects of metal cations on sorption and desorption of organic compounds in humic acids. *Soil Sci.* 166: 107-115.

Zhao, D. Y., Pignatello, J. J., White, J. C., Braida, W., Ferrandino, F. 2001. Dual-mode modeling of competitive and concentration-dependent sorption and desorption kinetics of polycyclic aromatic hydrocarbons in soils. *Water Resour. Res.* 37: 2205-2212.

Zhou, J. L., Rowland, S., *et al.* 1995. Partition of Synthetic Pyrethroid Insecticides between Dissolved and Particulate Phases. *Water Res.* 29:1023-1031.

## **PUBLICATIONS OR REPORTS:**

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

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.

Jabusch, T. W. and R. S. Tjeerdema, 2006. Microbial degradation of penoxsulam in flooded rice field soils. *J. Agric. Food Chem.* 54, 5962–5967.

Jabusch, T. W. and R. S. Tjeerdema, 2006. Photochemical degradation of penoxsulam. *J. Agric. Food Chem.* 54, 5958–5961.

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.

#### *Meeting Proceedings*

Gunasekara, A. S., T. Young, K. P. Nambiar and R. S. Tjeerdema, 2006. The sorption of thiobencarb to soils: Mechanistic findings. Division of Agrochemicals. *Proceedings of the American Chemical Society*. San Francisco, CA.

#### **CONCISE GENERAL SUMMARY OF CURRENT YEAR'S RESULTS:**

1. The new insecticide etofenprox, as an ether-based pyrethroid, is extremely insoluble in water (based upon the information provided by the manufacturer). Therefore, measurement of its potential to volatilize from rice fields via air-water partitioning (Henry's law) is technically very difficult.
2. The vapor pressure of etofenprox can be calculated using structural modeling, which provides insight into its ability to volatilize from solid surfaces in the environment (which is quite low). However, its water solubility cannot be reliably modeled, which limits the potential for estimating air-water partitioning from rice fields based upon calculated Henry's law values.
3. The high degree of sorption of etofenprox to apparatus walls during Henry's law experiments indicated the likelihood for extensive soil sorption in the field. Experiments are under way but progress has been delayed by our inability to obtain the radiotracer originally promised by the manufacturer (Mitsui, Japan). Alternative analytical methods have been developed and are being used, but efforts also continue to obtain the needed radiotracer.
4. Soil sorption of the herbicide clomazone was compared using two representative rice field soils from the Sacramento Valley – one from the Princeton area and the other from the Richvale area.
5. Freundlich isotherms were developed to compare the soil sorption capacities of the two soils for clomazone.
6. Clomazone, which has relatively high water solubility, does not appreciably sorb to soils, especially when compared to the less water soluble herbicide thiobencarb. While this could make clomazone more mobile (particularly when rice fields are drained), it also may enhance the degradation of clomazone via sunlight or microbial actions. Experiments are under way to characterize its degradation by soil microbes present in California rice fields.