

**ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE**

January 1, 2007 – December 31, 2007

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

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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 2007 was to complete the characterization of the volatilization and soil sorption of etofenprox – both under California rice field conditions.

Objective II. To investigate the natural factors governing the dissipation of pesticides in California rice fields. Emphasis for 2007 was to complete characterization of the soil sorption (via organic carbon) of clomazone (Cerano 5 MEG) under California rice field soils.

SUMMARY OF 2007 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

OBJECTIVE I

Introduction

Etofenprox is a synthetic ether pyrethroid of current interest to California rice farmers due to its effectiveness against the rice water weevil. This compound is not yet registered in California for use on rice but it is currently used in Spain and Japan for rice culture. (FAO, 1993) Etofenprox is of environmental interest because it belongs to the pyrethroid class of compounds. (Udagawa, 1988) 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. These compounds are increasing in usage since they are seen as replacements for the organophosphorus class of pesticides. (Oros *et al.*, 2005) The OP pesticides are associated with mammalian toxicity whereas pyrethroids are associated with low mammalian toxicity. (Park *et al.*, 2004) Despite this advantage of pyrethroid usage over OP usage (toxicity concerns), pyrethroids are not without

Table 1. Estimated physical and chemical properties for etofenprox at different temperatures.

ETOFENPROX PHYSICAL/CHEMICAL PROPERTY	ESTIMATED VALUE	MANUFACTURER REPORTED VALUE
BOILING POINT	461°C	NA
VAPOR PRESSURE (Pa)		
5°C	4.48E-09	
15°C	1.11E-08	
20°C	1.71E-08	
25°C	2.58E-08	8.13 X10 ⁻⁷ (exp)
35°C	5.64E-08	
40°C	8.16E-08	
AQUEOUS SOLUBILITY (mg/L)		
5°C	0.275	
15°C	0.357	
20°C	0.405	0.0225 (exp)
25°C	0.457	
35°C	0.575	
40°C	0.641	
HENRY'S CONSTANT (Pa·m³/mol)		
5°C	1.80E-05	
15°C	1.80E-05	
20°C	1.80E-05	1.36E-02
25°C	1.80E-05	
35°C	1.80E-05	
40°C	1.80E-05	

NA – not applicable.

exp – experimentally determined by Mitsui Chemicals, Inc.

adverse affects. Pyrethroids, in general, are very insoluble in water and thus are predisposed to partition into organic components of soil.

The physical-chemical properties of a compound dictate its fate and transport in the environment. 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.

This study aims to describe the partitioning of etofenprox under simulated rice field conditions by determination of the Henry's law constant (H , as an estimate of volatilization), the soil-water distribution coefficient (K_d), and the organic carbon-normalized distribution coefficient (K_{oc}) – all at representative temperatures.

Materials and Methods

Chemicals and soils. Etofenprox was supplied by Mitsui Co. Stock solutions of etofenprox were prepared in acetone and used to prepare aqueous samples. Soils were collected from two separate rice fields in the Sacramento valley, CA. The first was collected in Princeton, California, on the west side of the Sacramento valley, whereas the second soil was collected in Richvale, California, on the east side of the valley. Several kilograms of soil were collected randomly from the 0-10 cm layer of each field. 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 then stored until used.

Volatilization. The Henry's law constant (H) can be calculated by dividing the vapor pressure of a compound by its aqueous solubility at a given temperature. If data is not available at the temperature of interest, it can be estimated using the chemical structure. To estimate vapor pressure at various temperatures, the boiling point must also be estimated. The group contribution method described by Stein and Brown, 1979, was used to find the boiling point of etofenprox and subsequently used to find vapor pressure ranging from 5 – 40°C, while the Kistiakowsky-Fishtine equation was used to solve for vapor pressure, as described by Schwartzenbach *et al.*, 2003:

$$\ln P^* (\text{bar}) = - K_F (4.4 + \ln T_b [(1.8(T_b/T) - 1) - 0.8 \ln(T_b/T)])$$

The aqueous solubility of etofenprox at different temperatures was estimated based on the AQUAFAC group contribution method described by Myrdal *et al.*, 1995.

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>).

Soil-water partitioning. All sorption isotherms were run similar to the batch equilibration technique described by Zhou *et al.*, 1995 except on a larger scale. Briefly, 150 mL glass serum bottles were used for sorption studies. The background solution consisted of 0.02 M NaHCO₃ in HPLC water with 200 mg/L sodium azide as a biocide. Initial aqueous etofenprox concentrations ranged from 5 – 15 µg/L. Initial solvent concentration did not exceed 0.06% v/v upon addition of etofenprox. The quantity of sorbent was adjusted to maintain sorption of individual pyrethroids to between 15 and 85%. The soil to solution ratio was 1:1250 in order to maintain a measurable aqueous concentration at equilibrium (Fig. 1). Initial kinetic studies showed sorption equilibrium was achieved within 72 h (Fig. 2). All samples, including the controls (no sorbent), were run in triplicate. Etofenprox recovery in control samples ranged from 77%-124% of initial mass applied over course of experiment. After mixing at 25°C, bottles were centrifuged at 1000 x g for 20 min,

Table 2. Soil Properties 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 (NO ₃) nitrogen ($\mu\text{g/g}$)	8.6	0.3
Exchangeable K ($\mu\text{g/g}$)	157	178
Exchangeable S (SO ₄ ²⁻ ; $\mu\text{g/g}$)	23	41
Phosphorus ($\mu\text{g/g}$)	6.2	2.4

followed by transfer of supernatant to pre-weighed extraction bottles. Since soil concentrations were determined by the difference in initial aqueous concentration and the equilibrium aqueous concentration, it was crucial to determine amount of mass adsorbed to container walls. Pyrethroid sorption to glassware has been shown to be significant and can not be ignored (Zhou *et al.*, 1995) As a result, serum bottles were rinsed with solvent and analyzed under the same conditions as aqueous extracts. As a result, the actual mass bound to the soil can be calculated and used to generate the isotherm. To investigate the effect of temperature on partitioning, the Princeton soil was used to generate an isotherm at 35°C and compared to the Princeton isotherm at 25°C.

To investigate desorption of etofenprox from the representative rice soils, triplicate isotherm samples were prepared and allowed to equilibrate for 72 hours. The samples were then centrifuged and the supernatant decanted. A measured amount of clean background solution was added to replace the discarded supernatant. The samples were then allowed to equilibrate for another 72 hours at which time the samples were processed as described previously. The mass desorbed from the soil was calculated based on the percent mass in the aqueous phase after correction for mass remaining in water from the incomplete decant.

Extraction and analysis. To each water sample, 5 μL of internal standard (dicyclohexylphthalate) was added. Extraction begins by adding 5 g NaCl and 1 mL acetone to water samples and then mixing until the salt dissolves. Hexane (20 mL) is used 3 times to extract etofenprox from the water, after which the hexane layers are dried with sodium sulfate, combined, and evaporated to 250 μL 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 μm 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.

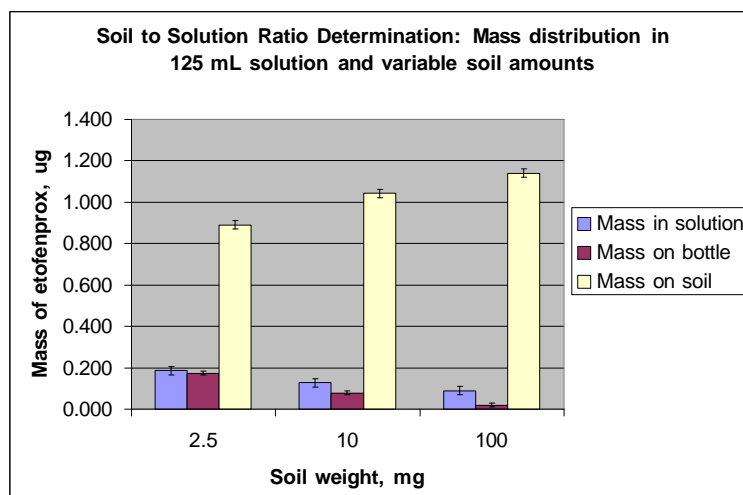


Figure 1. Soil-water distribution of etofenprox after incubation with variable amounts of soil.

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 μ 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).

Data analysis. Differences between initial and equilibrium concentrations are due to etofenprox sorption and were calculated from the following equation:

$$\text{Mass bound to soil} = \text{Initial applied mass} - (\text{Mass in water} + \text{Mass on bottle})$$

Mass balance calculations were used to reveal the sorption affinity, capacity, and mechanism. These results were extrapolated using the linear partitioning model (the Freundlich equation where $n=1$):

$$C_s = K_d C_w^{1/n}$$

The soil concentration is denoted by C_s (ug/g), C_w is the aqueous-phase solute concentration (ug/mL), and K_d [(ug/g)(ug/mL)⁻ⁿ] and n are constants. To facilitate direct comparison of sorption affinities among samples, organic carbon normalized parameters were used [$K_{oc} = (C_s / C_w) / f_{oc}$ where f_{oc} is the fraction of soil organic carbon in the sample]. Sorption capacity and affinity can be obtained from K_d while the sorption mechanism is explained by the values obtained for n .

Results and Discussion

Volatilization. The calculated H was different than the value calculated based on the manufacturer's reported vapor pressure and solubility: 1.8×10^{-5} Pa·m³/mol at 5 to 40°C versus

Figure 2. Kinetic study at 25°C to determine time to equilibrium in soil-water system.

$1.3 \times 10^{-2} \text{ Pa}\cdot\text{m}^3/\text{mol}$ at 20°C. (Table 1) The manufacturer used vapor pressure and solubility values from a different temperature to compute H , since etofenprox solubility was determined at 20°C and vapor pressure at 25°C. Ideally, both properties would be determined at the same temperature and then H would be calculated. Despite the difference in the two values, both imply that volatilization will not be a major dissipation pathway. The estimated values for H remained constant between 5 and 40°C. Thus, etofenprox will not partition to air from water as temperature increases.

Soil-water partitioning. Table 2 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 2). 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 2) between the two soils.

As demonstrated in the Henry's constant experiment, etofenprox showed a strong tendency to partition out of water and sorb to both the soil and glassware. The mass distribution within the system during the soil to solution study showed an increase partitioning to the glassware as the amount of sorbent decreased (Fig. 1).

The system using 100 mg soil was chosen for isotherm construction because it provided the greatest difference between the mass in the water and the mass on the bottle wall. The kinetic study at 25°C revealed equilibrium was achieved within 72 hours and this time frame was used to incubate soil-water systems to construct the isotherm (Fig. 2).

The Richvale soil showed greater potential for uptake of etofenprox than the Princeton soil but both soils have great affinity for etofenprox with $\log K_{oc}$ values of 6.3 and 6.0 respectively. The uptake of etofenprox in the Princeton soil showed a more leveling trend in uptake compared to the Richvale soil (Fig. 3). Linear correlation coefficients (r^2) for each soil (Table 3) were very close to 1, implying a linear partitioning phenomenon occurring in both soils, where $n=1$.

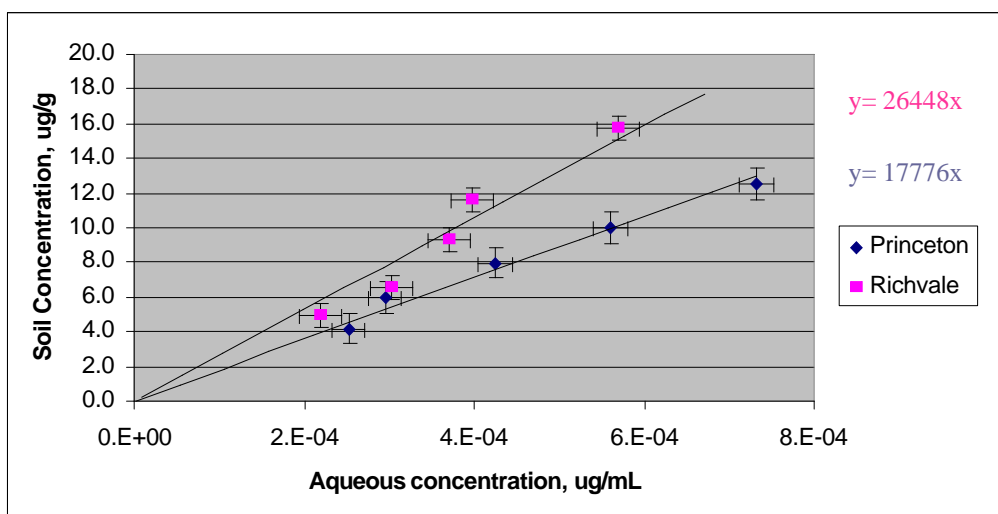


Figure 3. Isotherm (25°C) for etofenprox on two different California rice field soils.

Hydrogen bonding is thought to be the dominant force and mechanism of interaction between hydrophobic chemicals and soil organic matter. (Gauthier, 1987) Sorption to organic matter has been shown not only to depend on the quantity, but amount of aromatic components in the soil organic matter. Greater O:C ratios within soil organic matter has been correlated to less sorption by hydrophobic chemicals. (Grathwohl, 1990) This is not to rule out mineral interaction in etofenprox sorption, as seen from the necessity to account for etofenprox sorption to glassware (Fig. 4).

Further work is required to unravel the individual composition of each soil to better understand the sorption mechanism. It was unexpected to find that the Princeton soil had a higher percentage of organic matter yet had a smaller soil-water distribution coefficient than the Richvale soil. This could be due to the quality of the organic matter in the different soil types. Management practices can greatly influence the quality and type of soil organic matter, from straw burial to straw burning. The Princeton field had a history of burning the rice straw after harvest whereas the Richvale field reincorporated the straw into the field after harvest. The structure and composition of soil organic matter is heterogeneous within a single soil sample and across soil types. This could be an explanation for the greater capacity for uptake of etofenprox in the Richvale soil.

The desorption experiments at 25°C further showed the propensity of etofenprox to remain sorbed once it has partitioned out of water. For the Princeton soil, 1%-3% ($\pm 1\%$) of the initial sorbed mass was desorbed and 2%-5% ($\pm 2\%$) for the Richvale soil. Thus, desorption of

Table 3. Summary of soil-water partitioning coefficients (25°C) for etofenprox.

Soil	K_d (mL/g)	f_{oc}	K_{oc}	$\log K_{oc}$ (mL/g)	N	r^2
Princeton	17776	1.8	988654	6.0	1	0.9758
Richvale	26448	1.3	2091743	6.3	1	0.9351

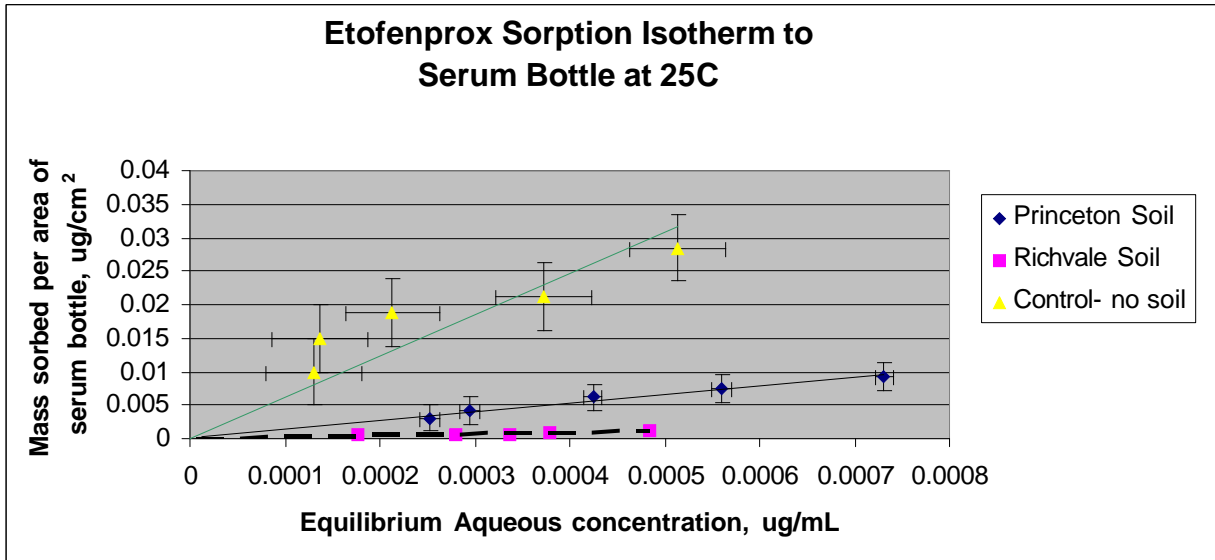


Figure 4. Isotherm for etofenprox on bottle walls at 25°C.

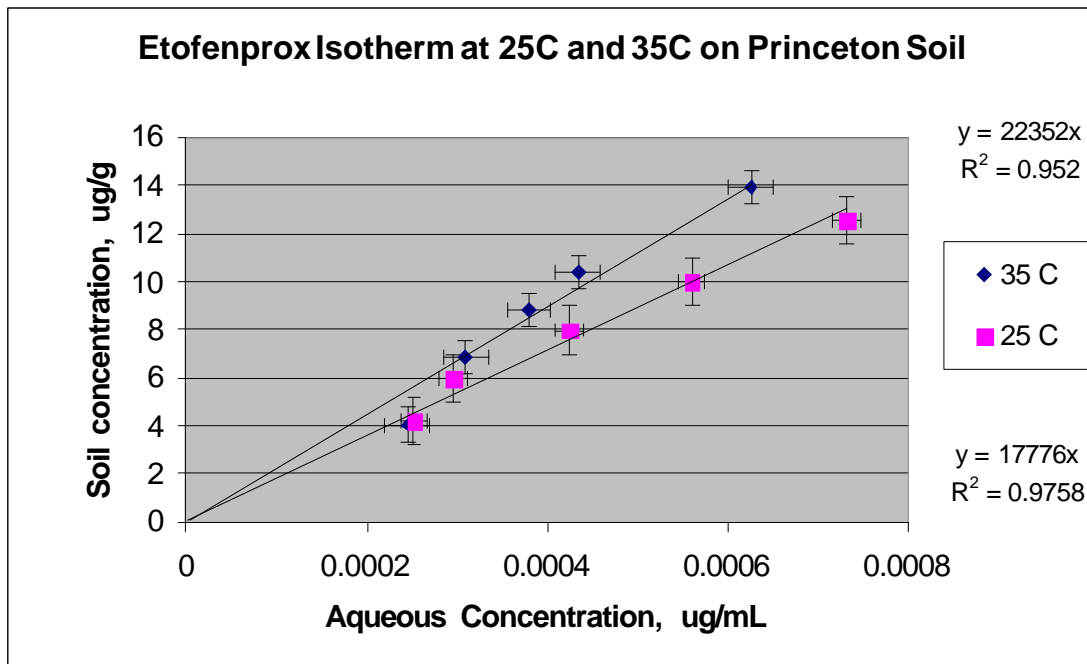


Figure 5. Isotherm for etofenprox on Princeton rice soil at 25°C and 35°C

Table 4. Soil-Water Partitioning Coefficients for Etofenprox at Different Temperatures

Temp (°C)	Soil	K_d (mL/g)	foc	K_{oc}	log K_{oc} (mL/g)	N	r^2
25	Princeton	17776	1.8	988654	6.0	1	0.9758
35	Princeton	22352	1.8	1241778	6.1	1	0.952

etofenprox from rice soils is suggested to be minimal.

The effect of temperature on the sorption process was investigated by constructing the isotherm at 35°C using the Princeton soil in same manner as described previously (Fig. 5). The resulting log K_{oc} was 6.1 compared with 6.0 at 25°C.

There was slightly greater uptake of etofenprox to the soil at 35°C compared to 25°C but essentially the same log K_{oc} was found for both temperatures (Table 4). Thus, temperature showed little effect on etofenprox sorption to the Princeton rice soil.

Conclusions

The extreme hydrophobicity of etofenprox drives its partitioning from the aqueous phase to a sorbed state. The log K_{oc} for etofenprox ranged from 6.0-6.3 depending on temperature and rice soil type. Desorption from soils was less than 5% of initially sorbed mass. Based on etofenprox behavior during air-water and soil-water partitioning studies, etofenprox will sorb before it volatilizes. Offsite transport of etofenprox via drainage of field water is unlikely as a result of high affinity for soil, unless transported in a bound state. Sorption to soils is likely to be the major dissipation pathway from California rice fields with microbial populations in charge of the final chemical degradation and transformation of soil residues. Future studies will be focused on this fate pathway.

OBJECTIVE II

Introduction

In this investigation we evaluated the herbicide clomazone for its sorption to soils and their major organic matter fraction, humic acid (HA). Clomazone (2-[2-chlorobenzyl]-4,4-dimethyl-1,2-oxazolidin-3-one) is an isoxazolidinone herbicide developed in the early 1980s and commercialized under the trade name Command[®] (TenBrook and Tjeerdema, 2006). It is popular for use with many crops, including soybeans (*Glycine max*), cotton (*Gossypium hirsutum*), and corn (*Zea mays*) among others (Leibl and Norman, 1991; Culpepper *et al.*, 2001). In the last decade clomazone has also been applied to flooded rice fields to control broad leaf weeds and grasses (Webster *et al.*, 1999; Bollich *et al.*, 2000). Its popularity for use with rice is increasing; use in California has increased from 550 in 2002 to 50,000 lbs in 2004 (CDPR, 2007).

Physical-chemical properties indicate that clomazone is relatively water soluble (1100 mg/L at 25°C). Therefore, it may effectively leach to groundwater if its solubility, K_{oc} (organic carbon normalized sorption coefficient) and K_d (distribution coefficient) are approx. 30 mg/L, 300-500

Table 5. The fire effected (BCF and RF) and protected (BCNF and RNF) forest and rice soils.

Soil property	Whole soil			
	BCF	DPNF	RF	RNF
Sand (%)	69	57	21	22
Silt (%)	16	21	28	27
Clay (%)	15	22	51	51
pH	6.1	5.7	4.7	6.4
Organic matter (%)	4.54	4.30	2.14	2.11

mL/g, < 5 mL/g, respectively (Hatrik and Tekel, 1996; Wintersteiger *et al.*, 1999; Barcelo and Hennion, 1997; Zanella *et al.*, 2003). Thus, sorption/desorption processes to soils are important.

To date, only a few reports have characterized sorption of clomazone to soils and even fewer have examined sorptive processes in flooded rice field conditions (Kirksey and Mueller, 1995; Mervosh *et al.*, 1995; Cumming *et al.*, 2002; Li *et al.*, 2004; Quayle *et al.*, 2006). Also, we evaluated the structural composition of HA sorbents by solid state ¹³C magic angle spinning (MAS) NMR to evaluate if specific functional groups in the sorbent promotes or limits clomazone sorption and/or desorption.

Materials and Methods

Sorbates and sorbents. Technical grade ring-labeled ¹⁴C and unlabeled clomazone were obtained *gratis* from FMC Corporation. Eight sorbents were used, of which four were whole soils and the others HA extracted from the soils. Two soils were collected from rice fields in the Sacramento Valley, CA. The two sites differed in post-harvest rice straw management practices: the Richvale rice farm (RNF) practiced conservation tillage whereas the UC Rice Research Station (RF) continuously burned their straw (information supplied via the landowners). For comparison, two additional soils were collected from pine forested sites in the Lassen National Forest California that had either been fire affected or protected. Historically, fire events have occurred at Beaver Creek Pinery (BCF) but have not been able to cross Dear Creek which separated the two locations to affect Devils Parade Ground (DPNF). Both sites have the same soil profile, elevation (~2800 feet), and environmental conditions.

Soils were randomly collected from the 0-10 cm depth from all sites, transported on ice in plastic bags, preserved at 4°C in the laboratory, air dried, ground and sieved (100 μ m), and stored in sealed plastic bags until use. Properties were characterized by the Agricultural and Natural Resources (ANR) Analytical Laboratory at UCD (Table 5; Schmelzer *et al.* 2005). Humic acid was extracted from the whole forest soils via previously described methods (Swift, 1996).

Sorption experiments. The batch equilibration technique ($23 \pm 1^\circ\text{C}$) was used to obtain isotherms for the four whole soils and their corresponding HAs (Wang and Xing, 2005a). Isotherms were obtained using 8-mL screw cap vials with Teflon-lined plastic caps. The background solution consisted of 0.01 M CaCl₂ and 200 μ g/mL of NaN₃ as a biocide. Both ¹⁴C-labeled and non-labeled clomazone were added to the background solution and mixed for approx. 1 hour before

Table 6. Freundlich coefficients (K_f and N) for whole soils and corresponding HA.

Sorbent	K_f ($\mu\text{g}/\text{g } \mu\text{g}/\text{mL}^{-1}$)	N	r^2
RF whole soil (straw burned)	8.76 ± 0.01	0.831 ± 0.008	0.999
RNF whole soil (straw incorporated)	5.06 ± 0.01	0.887 ± 0.005	0.999
BCF whole soil (fire affected)	9.20 ± 0.01	0.848 ± 0.006	0.999
DPNF whole soil (fire protected)	6.78 ± 0.01	0.893 ± 0.006	0.999
RF HA	71.80 ± 0.01	0.988 ± 0.008	0.999
RNF HA	83.14 ± 0.01	0.999 ± 0.005	0.999
BCF HA	75.25 ± 0.01	0.954 ± 0.006	0.999
DPNF HA	37.14 ± 0.01	0.979 ± 0.006	0.999

addition to the sorbent. Mixing was then initiated continuously for seven days in a rotary shaker (to allow the sorbates to reach sorption equilibrium). In previous experiments, no significant increase in sorption was observed after seven days nor was there sorption to the glass vials (data not shown). The vials were centrifuged at 3000 g for 20 min (IEC Centra 8 – International Equipment Company) and 1 mL of supernatant was added to 6 mL Ultima Gold XRTM cocktail (Fisher Scientific) prior to liquid scintillation counting. All isotherms were obtained using triplicate samples and blanks to calculate standard deviation, and sorbed concentrations were determined by mass balance calculations. The quantity of soil and HA added to the background solution was adjusted to maintain clomazone sorption of between 30 and 70% of maximum. Clomazone concentration points (14 in total) ranged from 0.067 to 500 $\mu\text{g}/\text{mL}$. Approximately 1-2 g of whole soil and 75-160 mg of HA per vial were used to construct the isotherms.

All sorption data were fitted to the logarithmic form of the Freundlich equation (1), where S is the total sorbed concentration ($\mu\text{g}/\text{g}$), C_e is the final solution phase concentration ($\mu\text{g}/\text{mL}$), and K_f ($\mu\text{g}/\text{g } \mu\text{g}/\text{mL}^{-1}$) and N are constants with N often <1 for sorption of compounds such as naphthalene in soils or soil organic matter. We also obtained the distribution coefficient or K_d (2) and organic carbon (f_{oc}) normalized sorption coefficient or K_{oc} (3) from the isotherm data at several solution concentration (C_e) points.

$$\log S = \log K_f + N \log C_e \quad (1)$$

$$K_d = S / C_e \quad (2)$$

$$K_{oc} = K_f / f_{oc} \quad (3)$$

Spectroscopy. All samples were treated with dilute HCl-HF to reduce ash and paramagnetics that would interfere with the acquisition of NMR spectra. The HA samples were subjected to ^{13}C MAS NMR using a Bruker 500 MHz NMR spectrometer. Spectra were acquired at a frequency of 125 MHz for ^{13}C and 500 MHz for ^1H , MAS spinning rate of 15 kHz in a 4 mm rotor probe, contact time of 2 ms, 1 sec recycle delay with approx 1000-2000 scans per sample, and line broadening of 50 Hz.

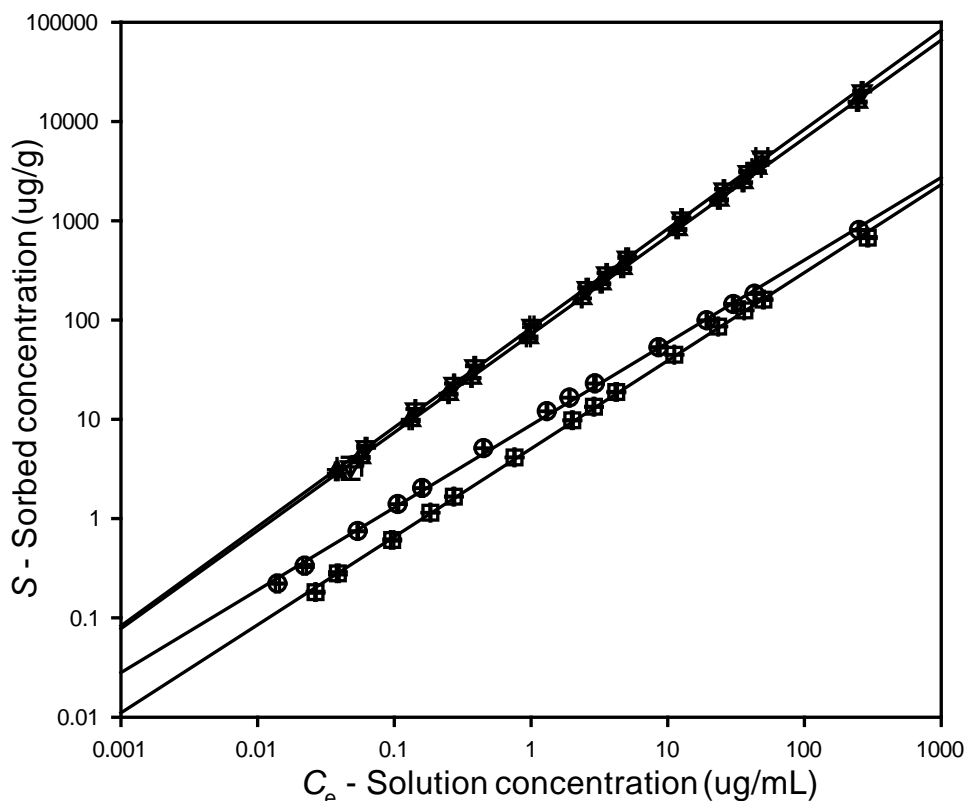


Figure 6. Sorption to whole rice fire-affected (circle, RF) and protected (square, RNF) soils and their HA fractions, triangle-up (RF HA) and triangle-down (RNF HA), respectively.

Results and Discussion

Sorption. Isotherms of clomazone sorption to whole rice (RF and RNF) and forest soils (BCF and DPNF) and their corresponding HAs is shown in Figs. 6 and 7, respectively. Sorption was low with all the whole soils tested, which would be predicted from its high water solubility (1100 mg/L). The isotherms show that the fire-affected whole soils (RF and BCF) exhibited slightly more clomazone sorption than the fire protected soils (RNF and DPNF) at all concentrations.

The Freundlich sorption coefficients in Table 6 show more clearly the trends; K_f values for the RF and BCF whole soils were 8.76 and 9.20 $\mu\text{g}/\text{g}$ $\mu\text{g}/\text{mL}^{-1}$, while they were 5.06 and 6.78 $\mu\text{g}/\text{g}$ $\mu\text{g}/\text{mL}^{-1}$ for RNF and DPNF whole soils, respectively. Greater nonlinearity (N) was also observed (Table 6) for the whole soils that had fire events (0.831-0.848) compared to the protected soil (0.887-0.893), suggesting that fire residues (e.g. black carbon) may minimally contribute to clomazone sorption.

Sorption to the isolated HAs, while also low, was higher than that for the whole soils (Figs. 6 and 7). Freundlich data (Table 6) show that HA sorbed approx. 6-16 times more clomazone than their corresponding whole soils. For example, the K_f of BCF whole soil was 9.20 $\mu\text{g}/\text{g}$ $\mu\text{g}/\text{mL}^{-1}$ while its HA was 75.25 $\mu\text{g}/\text{g}$ $\mu\text{g}/\text{mL}^{-1}$. The RF HA and RNF HA were very similar in Fig. 5 as observed by isotherm overlap but produced slightly different K_f (Table 6). The forest soil HA

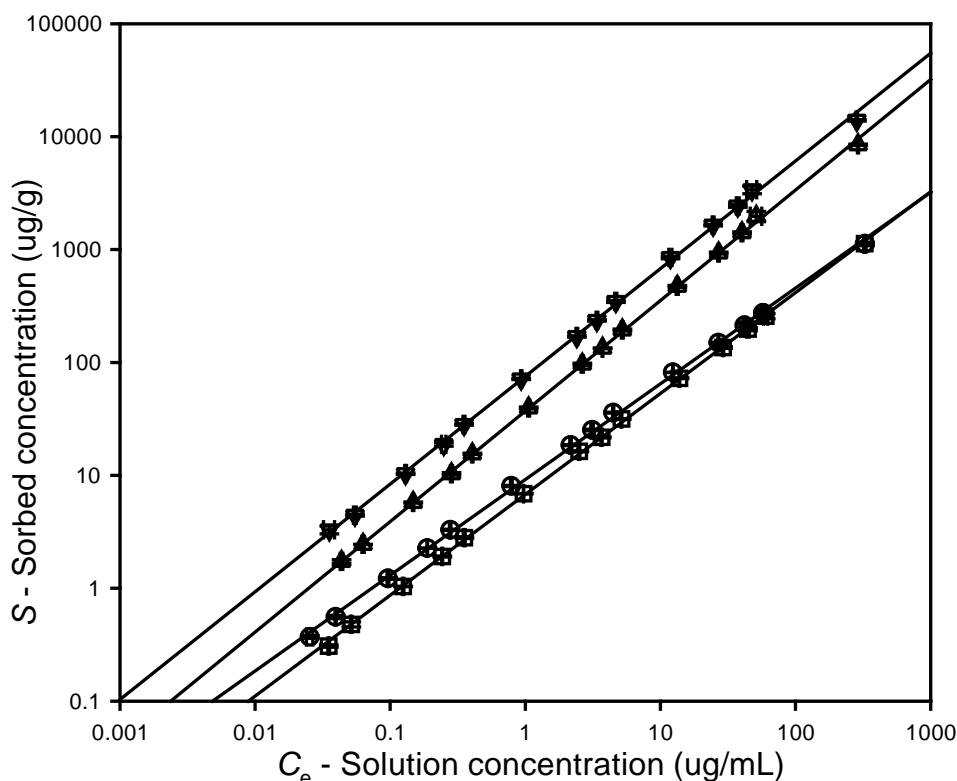


Figure 7. Sorption to whole forest fire-affected (circle, BCF) and protected (square, DPNF) soils and their HA fractions, triangle-down (BCF HA) and triangle-up (DPNF HA), respectively.

isotherms in Fig. 7, however, do not follow the same trend as RF HA and RNF HA and deviate from one another. For instance, BCF HA had greater sorption ($75.25 \text{ } \mu\text{g/g } \mu\text{g/mL}^{-1}$) than the fire protected site (DPNF HA; $37.14 \text{ } \mu\text{g/g } \mu\text{g/mL}^{-1}$). All the isolated HA isotherms are more linear ($0.980 = \text{average of four HA}$) than the whole soils ($0.865 = \text{average of four whole soils}$).

Calculated K_d and K_{oc} values for three different C_e points spanning three orders of magnitude (2, 25, and 500 $\mu\text{g/mL}$) are presented in Table 7. Overall, K_d data confirm that the sorption of clomazone to both rice field and forest whole soils, as well as to their HA fractions, is low overall. Sorption is higher to HA than whole soils, with lower concentrations having twice the clomazone sorption than higher concentrations; higher K_d values are present at C_e of 2 $\mu\text{g/mL}$ for both the whole soils and their corresponding HA (Table 6). The K_{oc} data for the whole soils confirm that sorption is greatest at low concentrations than the high concentrations and that fire effected whole soils (RF and BCF) have values (472 and 388 $\mu\text{g/mL}$) higher than the respective fire protected soils (RNF and DPNF).

Desorption. Hysteresis was observed for clomazone desorption from the RF HA (Fig. 8), as well as from the four whole soils and their respective HA (data not shown). In Fig. 8, not all data points are presented to maintain clarity. For each desorption data point the slope was calculated and these numbers are presented in Fig. 8 for RF HA and Table 8 for all other sorbents. A slope value closer to zero indicates greater hysteresis while a higher number indicates (0.354) less hysteresis. For example, in Fig. 8 low concentrations of clomazone experience greater hysteresis

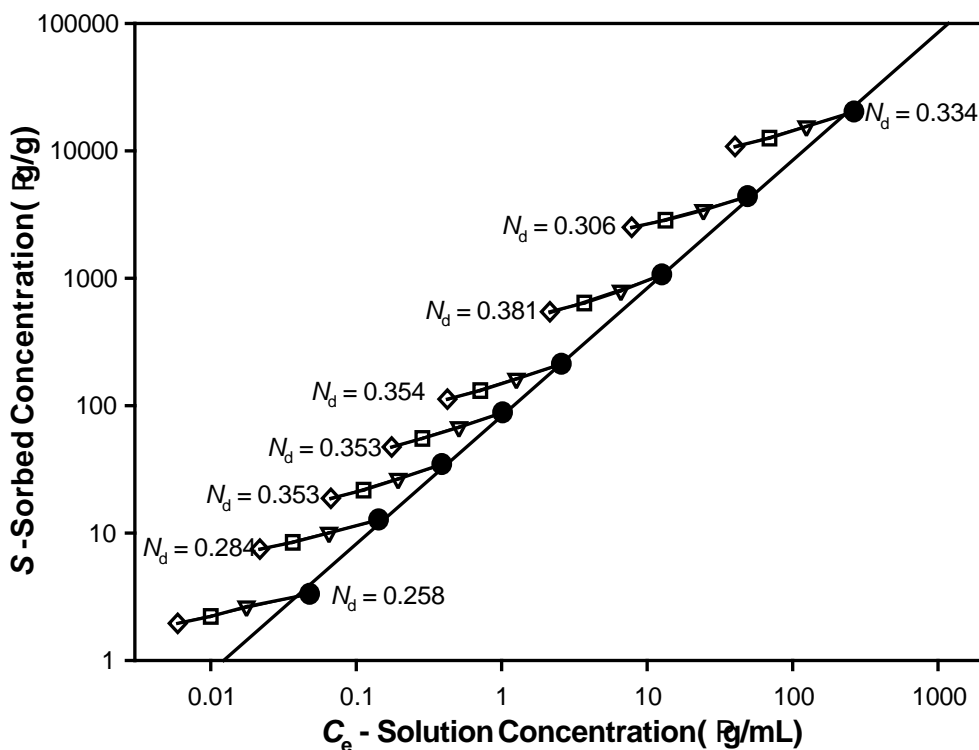


Figure 8. The desorption of clomazone from rice field soil HA (RF). Black circles show the sorption data while triangle-down, square, and diamond data points reflect the 1st, 2nd, and 3rd desorption, respectively. N_d is the slope of desorption at each sorption data point.

Table 7. The sorption (K_d) and organic carbon-normalized sorption (K_{oc}) coefficients.

Sorbent	K_d at specific C_e (mL/g)			K_{oc} at specific C_e (mL/g)*		
	$C_e = 2$	$C_e = 25$	$C_e = 500$	$C_e = 2$	$C_e = 25$	$C_e = 500$
RF whole soil (straw burned)	11.40	6.19	3.20	472	257	133
RNF whole soil (straw incorporated)	5.46	4.00	2.33	446	327	191
BCF whole soil (fire affected)	10.20	6.60	3.44	388	250	131
DPNF whole soil (fire protected)	7.07	5.24	3.46	238	210	140
RF humic acid	69.7	69.7	64.1	-	-	-
RNF humic acid	86.8	84.4	76.7	-	-	-
BCF humic acid	76.6	71.6	49.2	-	-	-
DPNF humic acid	37.3	35.4	29.2	-	-	-

(e.g., N_d is 0.258 at 0.07 $\mu\text{g/mL}$) than concentrations that are four orders of magnitude higher (e.g., N_d is 0.381 at 50 $\mu\text{g/mL}$). Similar slope data was obtained for the whole soils and their corresponding HA (Table 8).

There was also a clear distinction of greater hysteresis at low concentrations (C_e of 0.067 and 0.25 $\mu\text{g/mL}$) for both the whole soils and their corresponding HA (Table 8). Desorption then became less strained at higher concentrations (C_e from 0.75 to 12 $\mu\text{g/mL}$), as observed by the

Table 8. Slope (N_d) values for desorption from the sorbents and to specific concentrations (C_e).

C_e ($\mu\text{g/mL}$)	Sorbent							
	RSF Soil	RNF Soil	BCF Soil	DPNF Soil	RSF Humic acid	RNF Humic acid	BCF Humic acid	DPNF Humic acid
0.067	0.052	0.100	0.116	0.165	0.216	0.258	0.205	0.182
0.25	0.071	0.116	0.149	0.194	0.259	0.284	0.246	0.221
0.75	0.093	0.137	0.180	0.222	0.320	0.353	0.289	0.260
2	0.110	0.148	0.203	0.248	0.328	0.353	0.315	0.271
5	0.123	0.152	0.220	0.242	0.336	0.354	0.309	0.271
12	0.134	0.147	0.227	0.262	0.352	0.381	0.323	0.275
100	0.124	0.141	0.214	0.254	0.282	0.306	0.257	0.223
500	0.090	0.138	0.166	0.205	0.307	0.334	0.278	0.237

larger N_d values for the whole soil and HA. At the highest clomazone concentrations, C_e of 100 and 500 $\mu\text{g/mL}$, desorption again become more difficult as observed from the lower N_d values. Thus, hysteresis is greatest at both the lowest and highest C_e concentrations. To our knowledge such observations have not been previously reported for relatively polar organic compounds.

¹³C MAS NMR. To evaluate if structural components may contribute to deviations in the sorption of clomazone in HA, ¹³C MAS NMR was used to obtain the carbon chemical group distribution (Table 9). Rice field HA analysis confirmed that despite different treatments to the straw (burning vs. incorporation), the carbon species distribution was relatively the same for the aliphatic, aromatic, and O-containing groups. This data is supportive of the overlapping sorption isotherms for these HA sorbents. However, the forest soil HA was not the same as evident in Table 9, as variations existed in the aliphatic and aromatic carbons but not in the O-containing carbon group. The aromatic carbon groups were reduced in the fire protected HA (DPNF HA) by about 13% while inversely the fire effected HA (BCF HA) had greater aromatics and reduced aliphatics. Such a trend is consistent with the ¹³C NMR spectrum of charcoal (Fig. 3 in Braida *et al.*, 2003), which shows mainly aromatic moieties.

Several important findings are evident. First, clomazone does not possess a great sorption affinity (K_f) nor capacity (K_{oc}) for sandy or clay soils. Similar K_d values (1.7-3.6 mL/g) were obtained for clomazone sorption to four Australian soils with soil physical-chemical properties akin to those used in this study (Table 1; Cumming *et al.*, 2002). Benzene, a model compound whose solubility (1790 mg/L) is close to that of clomazone (1100 mg/L) also has similar K_d values (2.86 mL/g) as described here (Baek *et al.*, 2003). More hydrophobic models, such as phenanthrene, possess K_d and K_{oc} values of about 100 and 5000 mL/g, respectively, for soils that are similar to the rice field soils used in this study (2% organic carbon; Bonin and Simpson, 2007). In general, clomazone sorption to rice field whole soils (RF and RNF) was not very different. The same is true for the forest whole soils (BCF and DPNF). However, soils from fire events (BCF and RF whole soils) possessed significantly more, albeit slight, sorption compared

to the protected soils. Given the high solubility and low sorption of clomazone, soils are not expected to efficiently sequester the herbicide.

Table 9. Carbon group distribution of fire affected and protected rice field and forest soil HAs.

HA Sample	0-108 Aliphatic	108-162 Aromatic C	162-220 O-Containing C
RF	64.64	26.22	9.18
RNF	65.24	26.32	8.40
BCF	49.37	40.01	10.5
DPNF	63.40	27.13	9.42

Isolated HA yielded considerably higher sorption (approx. 6 – 16 fold) than whole soils. Humic acid has been previously found to possess significantly more sorption potential for model HOCs, when compared to whole soils, and the present findings are consistent with this trend. For instance, Gunasekara and Xing (2003) demonstrated that sorption of naphthalene (solubility of 31 mg/L) to HA was also greater than to its corresponding soil. In another study, even though the phenanthrene K_d (1500-12000 mL/g) and K_{oc} (3320-9220 mL/g) values are significantly greater to HA than those reported here for clomazone (K_d from 37-86 mL/g), phenanthrene sorption to HA was about 5-15 times greater than their respective whole soil with < 5% organic matter (Bonin and Simpson, 2006). Thus, the observed increase in clomazone sorption by HA is consistent with literature reports that have evaluated other HOCs.

In contrast to the whole forest soils (BCF and DPNF), where little deviation existed between the isotherms, their corresponding HA isotherms were more separated from one another. Clomazone sorption by BCF HA is double that of DPNF HA at all concentration points as observed by K_f and K_d , respectively. Contributing to this increase in sorption for BCF HA are aromatics since this sorbent has about 13% more of these carbon species than the fire protected forest HA (DPNF HA). These aromatics in BCF HA could stem from the fire events since they are absent in the fire protected site (DPNF HA). Numerous studies have shown that fire residues (e.g., black carbon or soot) contribute to greater aromaticity of the sorbent and increased sorption of HOCs (Glaser *et al.*, 2002; Gunasekara *et al.*, 2003; Braida *et al.*, 2003; Tinoco *et al.*, 2006). Supporting these findings is the degree of nonlinearity. It is clear that BCF HA has greater nonlinearity (0.954) than DPNF or the fire protected soil HA (0.979). Several studies have shown that nonlinearity can occur as a result of high surface area carbonaceous materials (HSACM). We show that indeed HSACM such as fire residues can contribute to isotherm nonlinearity and increased sorption but the natural environmental contributions are much lower than presented in some reports (Accardi-Dey and Gschwend, 2003; Cornelissen *et al.*, 2005).

The nonlinear clomazone isotherms presented here can be described well by using the “dual-mode” or “dual reactive domain” sorption model based on a rubbery-glassy polymer model (Huang *et al.*, 1997; Pignatello and Xing, 1996; Chefetz *et al.*, 2000). The organic matter of soils have been found to have a heterogeneous amorphous polymer-like characteristics with both glassy and rubbery phases (Young and Leboeuf, 2000; Wang and Xing, 2005b; Ju and Young, 2005). According to the dual-mode model, sorption of HOCs to SOM is non-ideal resulting in

isotherm nonlinearity, a result of HOC sorption to high energy sites located within a glassy or condensed region of the HA matrix. The composition of the rubbery (flexible) and glassy (condensed) matrix is still under debate but studies have shown that the glassy matrix might be composed of aromatic carbon groups (Gunasekara *et al.*, 2003).

An alternative carbon contribution from aliphatic groups to the formation of the glassy phase in the presence of a mineral has been recently proposed by Gunasekara and Xing (2003). This mechanism involves organic matter samples with large aliphatic contributions that come in contact with the mineral to form a more condensed phase which then contributes to greater isotherm nonlinearity due to the newly formed high energy sorption sites or holes. In this study, the HA sample had high aliphatic carbons, and their interaction with the mineral surface (e.g., whole soil) led to great isotherm nonlinearity. Thus, the results here are explained best when considering that mineral bound HA produced additional binding sites for clomazone, compared to isolated HA, and led to greater isotherm nonlinearity. We rule out that the mineral component directly contributes to clomazone sorption since the whole soils isotherms are lower than the HA isotherms in Figures 6 and 7. Details of this mechanism is clear when considering desorption of clomazone which produced hysteresis in all the whole soil and HA isotherms. Further, hysteresis is greatest at the very lowest isotherm concentrations where high energy sorption sites produced as a result of HA binding to the mineral is readily available to the low number of clomazone molecules. However, as the concentration increases and thus the number of clomazone molecules, the limited high energy sorption sites become saturated, leading to easier desorption as observed by the N_d values in Figure 8. At the very highest concentrations, clomazone sorption again become difficult. Here, we invoke the “conditioning effect” proposed by Lu and Pignatello (2002). The sorbent is infused with the sorbate at a concentration above its glass transition concentration and then removed. Conditioning occurs when new high affinity holes (sites) are produced as a result of greater energy infused into the matrix by the high sorbate concentration.

The results show that clomazone sorption to soil is low, as it sorbs more to the major organic matter fraction of soil than their corresponding parent material, and the mechanism of sorption is different with the two sorbents. Whole soil sorption is more nonlinear than the isolated HA fraction and a dual-mode sorption as well as a recently proposed aliphatic-mineral based mechanism is supported. We also observed the “condition effect” taking place as a result of desorption studies where hysteresis is observed. Fire residues do contribute to aromaticity in HA as well as to slightly greater sorption of clomazone but not to the extent reported for some model HOCs. Overall, this study shows that although clomazone does not sorb appreciably to soils, it has difficulty in desorbing from the soils HA-mineral matrix. Therefore, leaching from soils is a possibility as well as reduced availability to microbial degradation. Given that clomazone also has a high water solubility, microbial degradation is important and should be characterized.

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PUBLICATIONS OR REPORTS

Manuscripts (new in print or press this year)

1. Gunasekara, A. S., J. Troiano, K. Goh and R. S. Tjeerdema. Chemistry and fate of simazine. *Rev. Environ. Contam. Toxicol.* 189, 1–24 (invited).
2. Gunasekara, A. S., K. Goh and R. S. Tjeerdema. Chemistry and fate of fipronil. *J. Pestic. Sci.* 32, 189–199 (invited).
3. Jabusch, T. W. and R. S. Tjeerdema. Chemistry and fate of triazolopyrimidine sulfonamide herbicides. *Rev. Environ. Contam. Toxicol.* (invited; in press)
4. Gunasekara, A. S., K. Goh, F. Spurlock, A. L. Rubin and R. S. Tjeerdema. Environmental fate and toxicology of carbaryl. *Rev. Environ. Contam. Toxicol.* (invited; in press).

Abstracts in Meeting Proceedings

1. Gunasekara, A. S. and Tjeerdema, 2007. Clomazone adsorption and desorption to soils. Division of Agrochemicals. *Proceedings of the American Chemical Society*. Boston, MA.
2. Vasquez, M. E. and R. S. Tjeerdema, 2007. Air-water partitioning of etofenprox under simulated California rice field conditions. *Proceedings of the Northern California Chapter of the Society of Environmental Toxicology & Chemistry*. Berkeley, CA.

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 flooded California rice field conditions. Therefore, there are generally four processes that can contribute to such dissipation that are investigated: volatilization to air, sorption (adherence) to soils, degradation by sunlight, and degradation by soil microbes.
2. Volatilization capability of the insecticide etofenprox was characterized by the calculation of its Henry's constant (H). The estimated values for H remained both extremely small and constant between 5 and 40°C. Thus, volatilization will not be a major dissipation pathway for etofenprox from flooded rice fields at any temperature.
3. Using the Freundlich isotherm approach, sorption (adherence) of etofenprox to soil organic carbon was compared using two representative Sacramento Valley rice field soils – one each from the Princeton and Richvale areas. In addition, the influence of temperature on sorption was compared at 25°C and 35°C using the Princeton soil.
4. The measured soil organic carbon sorption coefficients ($\log K_{oc}$ s) for etofenprox ranged between 6.0 and 6.3, indicating that sorption to soil versus rice field water would be on the order of a million-to-one, and would not vary with either soil type or temperature.

5. In conclusion, its very low H and very high K_{oc} indicate that etofenprox will quickly dissipate from rice field water via rapid and strong sorption to soils. Volatilization will not significantly contribute to dissipation. Offsite transport of etofenprox via drainage of field water is highly unlikely unless significant, simultaneous soil erosion occurs. Ultimately, sunlight may degrade waterborne etofenprox, and soil microbes may likewise degrade sorbed insecticide. Future studies will be focused on characterizing degradation rates and pathways.
6. In order to characterize the dissipation of the herbicide Cerano (clomazone) from flooded rice fields, its sorption was characterized by also using the Princeton and Richvale soils.
7. Using the Freundlich isotherm approach, the role of soil organic carbon was also considered in characterizing the soil sorption of Cerano.
8. The relatively water-soluble Cerano was not found to appreciably sorb to either soil type. While it was found to sorb more effectively to soil organic carbon (whether or not burned), even this was relatively low, as the measured K_{oc} s (not in log values) ranged between 100 and 500, indicating that sorption to soil organic carbon versus rice field water would be at best at a ratio of some 500-to-one.
9. Dissipation of Cerano from flooded rice fields is not likely to be through soil sorption. However, it may very well be efficiently degraded via sunlight and/or microbial actions. Therefore, future studies will focus on characterizing Cerano's degradation by sunlight and the soil microbes present in California rice fields.