

ANNUAL REPORT
COMPREHENSIVE RESEARCH ON RICE
January 1, 2011 – December 31, 2011

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 pesticide dissipation in California rice fields. Emphasis for 2011 was on characterizing volatilization of clothianidin (Poncho, Belay) under California rice field conditions.

Objective II. To investigate the natural factors governing pesticide dissipation in California rice fields. Emphasis for 2011 was on characterizing volatilization of imazosulfuron (Brazzos, League) under California rice field conditions.

SUMMARY OF 2011 RESEARCH (MAJOR ACCOMPLISHMENTS) BY OBJECTIVE:

In general, two chemodynamic processes are important when considering dissipation of a pesticide from rice fields (particularly field water) – air-water partitioning (volatilization) and soil-water partitioning (sorption). The first describes the potential volatility of the compound, or more specifically its Henry's law constant, since air-water partitioning of a chemical is dependent on both its water solubility and its vapor pressure (Schwarzenbach *et al.*, 2003). Soil-water partitioning involves soil sorption (bonding), which can also contribute significantly to dissipation from field water. During the past year the focus has been on characterizing volatilization as a significant contributor to field dissipation.

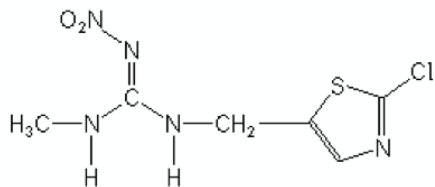


Figure 1: Structure of clothianidin, a neonicotinoid insecticide.

Objective I – Volatilization of Clothianidin (Poncho, Belay)

Introduction

Clothianidin (trade names include Poncho and Belay), (E)-1-(2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine (Figure 1) 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 throughout Europe and Asia (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 their efficient mode of action (involving cholinergic properties of the central nervous system), neonicotinoids show no cross-resistance to conventional insecticide classes and thus have begun replacing established classes such as the pyrethroids, organophosphates and carbamates (Jeschke *et al.*, 2008).

Two chemodynamic mechanisms are of primary importance when considering the abiotic dissipation of an insecticide from rice fields: 1) air-water partitioning, and 2) soil-water partitioning. The first describes the potential volatility of the insecticide, or more specifically its Henry's law constant, since air-water partitioning is dependent on both water solubility and vapor pressure, as compared by the constant (Schwarzenbach *et al.*, 2003). The second parameter, soil-water partitioning, describes the contribution to field dissipation of an insecticide via the sorption-desorption process. The degree of soil sorption can contribute to insecticide dissipation from field water where a large organic carbon-water partitioning coefficient (K_{oc}) is indicative of high soil sorption.

The objective of this study was to describe the air-water partitioning of clothianidin under simulated rice field conditions. While in 2009 we began investigating the potential volatility of clothianidin, unfortunately the student researcher was not able to complete the characterization prior to discontinuing her graduate work. Therefore, the project was transferred to a new graduate student in 2010. During the past year we both verified the experimental measurements and estimated values (via modeling) of the Henry's law constants for clothianidin under both standard and rice field conditions.

Materials and Methods

Estimation of physical properties including Henry's Law. The partitioning behavior of a pesticide can be predicted by estimating its chemical properties from its structure. Most established methods for estimating properties such as aqueous solubility, vapor pressure or partitioning coefficients such as air-water deviate from experimentally-determined

Table 1: Estimated Physical-Chemical Properties of Clothianidin

Physical Chemical Property	Estimated Value	Manufacturer Reported Value
Boiling Point (°C)	351.51	n/a
Excess Enthalpy Vaporization (kJ/mol)	72.26	n/a
Aqueous Solubility (mg/L)		
5 °C	160	327 ^a
15 °C	200	
25 °C	253	
35 °C	324	
Henry's Law Constant Pa*m ³ /mol		
5 °C	1.43E-10	---
15 °C	4.40E-10	---
20 °C	7.50E-10	---
25 °C	1.25E-09	2.90E-11 ^b
35 °C	3.34E-09	---

^a reported by Sumitomo Chemical

^b reported by Bayer

values for polar molecules such as clothianidin. When experimentally determined phase descriptors are available, linear solvation energy relationships (LSERs) can be used to estimate air-water partitioning coefficients. Using the phase descriptors for clothianidin previously published, we estimated the Henry's law value at 25°C (Tulp *et al.*, 2008). For estimation at temperatures other than 25°C, a form of the van't Hoff equation was used (Schwarzenbach *et al.*, 2003):

$$\frac{d \ln K_{iaw}}{dT} = \frac{\Delta_{aw} H_i}{RT^2}$$

In this model K_{iaw} is a dimensionless Henry's law constant and $\Delta_{aw} H_i = 72.26 \text{ kJ/mol}$, the excess enthalpy of vaporization, which is obtained from the slope of the natural log of the aqueous solubility versus $1/T$ where T is temperature and is assumed to be constant for temperatures between 5-35°C (Table 1).

Materials. Clothianidin (99.6%) was supplied by Bayer Co. HPLC-grade acetonitrile and ACS grade calcium chloride (CaCl_2) were purchased from Fisher.

Gas-stripping method. Henry's law constants were measured via the gas-stripping method described by Mackay *et al.* (1979), and using custom-made gas stripping columns (1 m x 51 mm id Pyrex cylinders). They were wrapped in aluminum foil to prevent photodegradation of the analyte, and experiments were performed at 20°C and 37°C (representative field temperature) in duplicate for each temperature. Nitrogen gas was streamed through a 5 ppm stock solution of Poncho in 0.01M CaCl_2 at 0.05 m³/hr. A

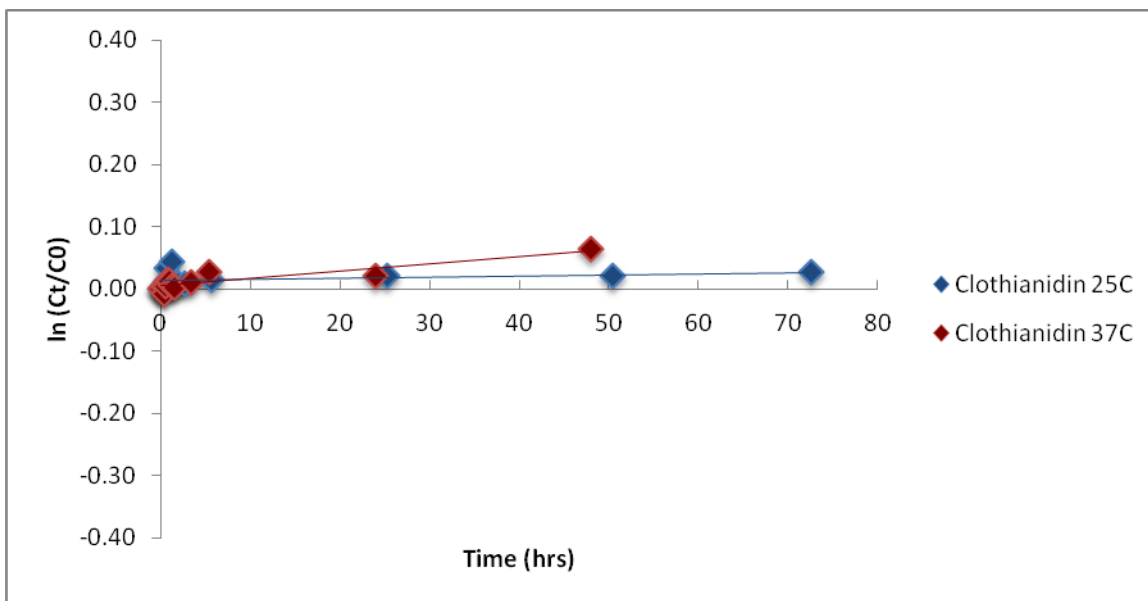


Figure 2. $\ln C_t/C_0$ vs. time was plotted in order to determine Henry's law constant of clothianidin. Experimental conditions were: $T=25^\circ\text{C}$ (298.15°K) and 37°C (310.15°K), $V= 0.0015\text{ m}^3$, and $G= 0.05\text{m}^3/\text{h}$. The values of slope, $-(HG/VRT)$, yielded from the plots at 25°C and 37°C were 0.0002 and 0.0011, respectively.

circulating water bath was used to insure that each column was maintained at a constant temperature. Aqueous samples were collected at fixed time intervals and were immediately transferred to and stored in sealed amber HPLC vials.

HPLC-DAD. Aqueous samples were analyzed via high-pressure liquid chromatography (HPLC) using an Agilent 1100 HPLC (Agilent Technologies, Santa Clara, Ca.) with an Agilent 1100 autosampler coupled to a diode-array detector (DAD) and controlled by Agilent Chem Station interface. The HPLC was equipped with a $3.5\ \mu$ particle size, $4.6 \times 150\text{ mm}$ ID Xterra C_{18} column (Waters, Milford, MA) and using an isocratic mobile phase with a $0.5\text{ mL}/\text{min}$ flow rate at ambient temperature.

Results and Discussion.

Group Contribution LSER. The Henry's law constant (H) calculated via group contribution method was two orders of magnitude larger than the value reported by the manufacturer: 1.25×10^{-9} versus $2.9 \times 10^{-11}\text{ Pa} \cdot \text{m}^3/\text{mol}$ at 20°C (Table 1). The difference between the H values could have been due to the fact that the H value reported by the manufacturer was calculated using experimentally determined vapor pressure. Tulp *et al.* (2008) observed systematic deviations between experimental- and LSER-generated partitioning coefficients. Specifically they observed that predicted values were larger than experimentally determined values for polar compounds such as clothianidin. Despite the difference in the two values, *both indicate that volatilization will not be the major dissipation pathway.* In addition, the constant remained low over the range of $5\text{-}35^\circ\text{C}$ as shown on Table 1. Thus, volatilization of clothianidin is negligible for the range of

temperatures typically found in California rice fields.

Gas Stripping Method. As described by Mackay *et al.* (1979), when the aqueous phase is well mixed, the rate of mass transfer of pesticide in aqueous phase into air phase follows the first-order decline in aqueous pesticide concentration, shown as the equation below:

$$-V \frac{dC}{dt} = HG/RT$$

where V is the volume of aqueous solution in m³, C is the pesticide concentration, t is the time in hours, H is the Henry's law constant in Pa·m³/mol, G is the gas flow rate in m³/h, R is the universal gas constant and T is the temperature of the system in (°K). Integrating this equation from initial condition when t=0 and C=C₀ gives:

$$\ln (C_t/C_0) = - (HG/VRT) t$$

The natural log of the aqueous clothianidin concentration over time was plotted (Figure 2). The resulting graph yielded slopes 0.0002 and 0.0011 for 25°C and 37°C, respectively. A plot of log C against time yields a linear relationship with a slope of – (HG/VRT). However, because the aqueous concentration of clothianidin did not decline, no measurable volatilization occurred. Thus, Henry's law constant values could not be measured due to the extremely low vapor pressure of the insecticide. *Thus, volatilization represents a negligible dissipation pathway for clothianidin in flooded rice fields.*

Objective II – Volatilization of Imazosulfuron (Brazzos, League)

Introduction

Imazosulfuron (trade names include Brazzos, League; Figure 3) is a sulfonylurea herbicide of interest to California rice farmers due to its rice selectivity and high effectiveness at a low application rate (75-95 g ha⁻¹; Tomlin, 1997). The USEPA registered imazosulfuron for commercial and residential use in 2010. Imazosulfuron's mode of action involves inhibiting the enzyme acetolactate synthase, a critical component to the production of amino acids necessary for new cell generation. Imazosulfuron-tolerant plants are thought to rapidly metabolize the herbicide (Tanaka & Yoshikawa, 1994).

Volatilization is an important factor in determining the fate and transport of a chemical in the environment. A common measure of a compound's propensity to volatilize is the Henry's law constant (H), which incorporates the vapor pressure and water solubility of a chemical. No experimentally-determined Henry's law constant has been published for imazosulfuron. This lack of data was sought to be remediated by the investigation of air-water partitioning using the gas stripping method and by estimation based on known chemical properties.

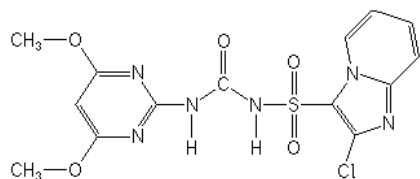


Figure 3. Structure of imazosulfuron.

Materials and Methods

Experimental Design and Sampling. Imazosulfuron (1-(2-chloroimidazo[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl) urea) was purchased from Santa Cruz Biotechnologies, Inc. (Santa Cruz, CA). Standard solutions were prepared in acetonitrile and kept at -20°C. All solvents were HPLC grade.

The gas-stripping method was used to determine imazosulfuron's Henry's constant (*H*) (Lau *et al.*, 2006). Glass columns (1 m x 51 mm i.d.) were run in duplicate with 1.5 L of a 100 ug/L solution of imazosulfuron in 0.01 M CaCl₂ and 200 mg/L HgCl₂. High purity N₂ gas (99.998%) was passed through activated carbon filters and bubbled through the solution at a flow rate of 20 – 130 mL/min. Two temperatures were investigated; 25°C, to reflect standard conditions, and 35°C, to reflect California summer conditions. Columns were wrapped in foil to protect from ambient light and kept isothermal via a recirculating water bath. Two polyurethane foam (PUF) plugs were placed atop the columns to collect the volatilized fraction. Mist traps were placed between the column and the PUF plugs to protect from enrichment by splashing. Samples were taken at approx. 12-h intervals over a period of over 100 h and immediately frozen at -20°C.

Extraction and Analysis. Prior to analysis, aqueous samples were thawed and sonicated for at least 10 min, and the PUF plugs were extracted with two 75 mL washes of acetone for 4 h on a rotary shaker. The columns, mist traps, and PUF plug holders were drained and rinsed with acetone to remove glass-sorbed imazosulfuron. The acetone extracts from the plugs and glassware were evaporated in a warm water bath under N₂ flow to dryness, reconstituted with acetonitrile and filtered.

LC/MS/MS analysis was performed on an Agilent 1100 liquid chromatograph coupled to an AB MDS Sciex API 2000 quadrupole mass spectrometer. A needle wash with acetone and a 0.5 min auto-equilibration time was included prior to each injection. The analytical column was an Allure C18, 30 x 2.1 mm i.d., 5 μm particle size (Restek). The column temperature was held at 25°C. Imazosulfuron was eluted under a mobile phase gradient consisting of 1% acetic acid and acetonitrile. The flow rate was 0.25 mL/min from the start of the run until 11 min, where it was ramped to 1 mL/min to rapidly equilibrate the column. Percent acetonitrile was ramped from the initial condition of 25% to 50% at 5-10 min, where it was ramped to 95% at 11 min and until 15 min, where it was returned to 25%. Total time was 22 min, but only eluent from 8-11 min was sent to the MS.

MS data were acquired in positive ion ESI mode. Ions monitored, collision energies and collision cell exit potentials are listed in Table 2.

Table 2: Ions Monitored for Imazosulfuron Analysis

Parent Ion <i>m/z</i>	Daughter Ion <i>m/z</i>	Collision Energy (V)	Collison Cell Exit Potential (V)
413	156.2	29.0	6.0
413	153.0	23.0	6.0
413	257.8	33.0	12.0

The dwell time for all ions was 150 msec, and source temperature was 400°C. The first quadrupole was set at high resolution mode, and the ionspray voltage was 5500 V. Curtain gas, ion source gas #1, ion source gas #2 and the collision gas were 50 psi, 15 psi, 50 psi and 8 psi, respectively. The de-clustering and focusing potentials were 11.0 and 37.0 V, respectively, and the entrance potential was 6.5 V.

Quantification was performed by comparison with a seven point calibration curve using the peak areas of imazosulfuron and a 1/x weighted linear regression. The 413.0 → 156.2 *m/z* transition was used in quantification while 413.0 → 153.0 and 413.0 → 257.8 were used as a qualifier ions. Accuracy and precision of the method were determined by analyzing a third party certified reference material purchased from AccuStandard (New Haven, CT). The chemical standard (10 µg/mL in acetonitrile, 1 mL) was diluted in the CaCl₂ and HgCl₂ solution to 100 µg/mL. Accuracy within ±10% was considered acceptable.

Estimation. Henry's constants can be calculated by dividing the vapor pressure by the aqueous solubility at the same temperature. Where this experimental data is unavailable, H can be estimated based on the structure. This approach was not useful in the case of imazosulfuron, where estimated vapor pressures were skewed dramatically (10 orders of magnitude), by erroneously high estimated boiling points. Imazosulfuron has no true boiling point, as it decomposes at high temperatures.

Results and Discussion

At 25°C, the concentration of imazosulfuron remained fairly constant throughout the run (Figure 4). Extraction post-run showed a small portion (>0.15% of total mass) of imazosulfuron had sorbed to the glassware, while extraction of the PUF plugs yielded concentrations below the limit of detection. A minimum of 15 ng (0.01% of total mass) was needed in order to quantify the PUF plug extraction and yield a Henry's law constant. The mass distribution at the end of the experiment (Figure 5) shows that the vast majority of imazosulfuron remained in the aqueous phase, suggesting little propensity for imazosulfuron to volatilize at 25°C.

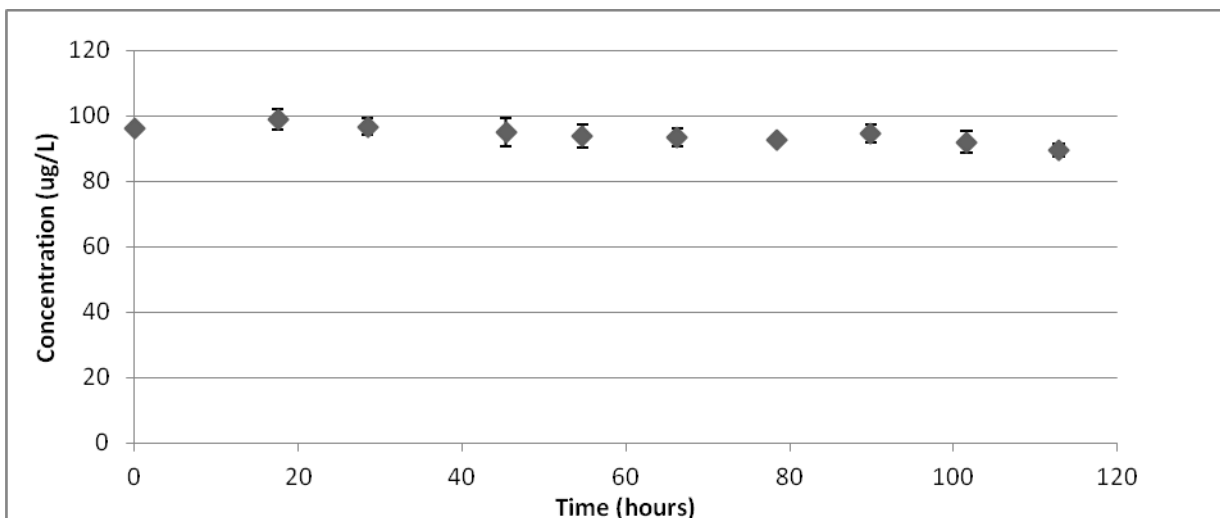


Figure 4. Concentrations of the aqueous phase in the 25°C gas stripping experiment. Points represent averages of the two columns and bars represent SE.

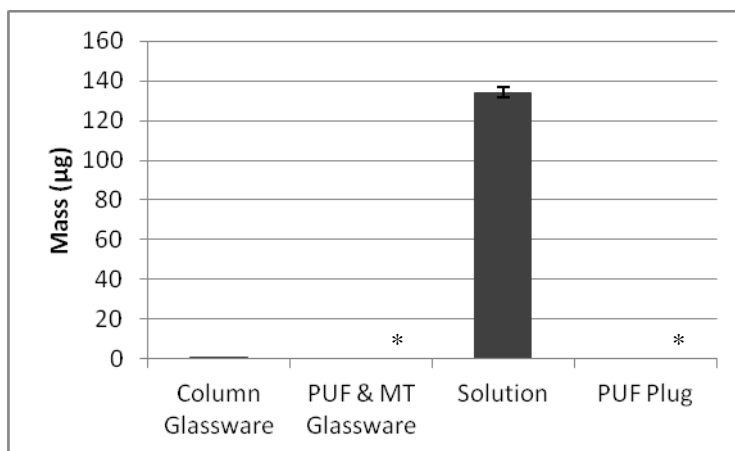


Figure 5. Mass distribution of imazosulfuron post-25°C run. *Below limit of detection.

The gas stripping experiment was repeated at 35°C in order to account for CA summer temperatures, and the results were similar to those at 25°C (Figure 6). The mass of imazosulfuron in the aqueous phase decreased more dramatically than at the lower temperature, but extraction of the PUF plugs indicates that this was not due to volatilization (Figure 7); PUF plug extracts were once again below analytical capabilities.

Morrica *et al.* (2001) found that imazosulfuron hydrolysis (reaction with water) rates increased under more acidic conditions. The aqueous solution was slightly acidic (pH 5.6), as imazosulfuron is an acid ($pK_a = 4.0$; Tomlin, 1997). It is likely that the loss of imazosulfuron from the aqueous phase was due to hydrolysis, as less than 15 ng was extracted from the PUF plugs. Other sulfonylurea herbicides have also shown susceptibility to hydrolysis, commonly occurring at the sulfonylurea bridge, and

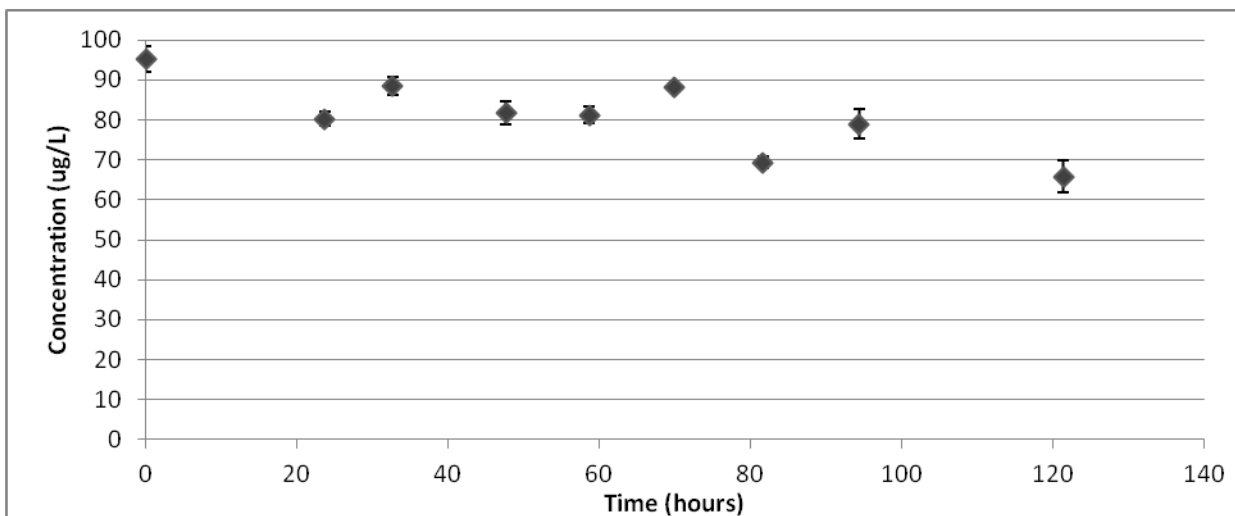


Figure 6. Concentration of the aqueous phase in the 35°C gas stripping experiment. Points represent averages of the two columns and bars represent SE.

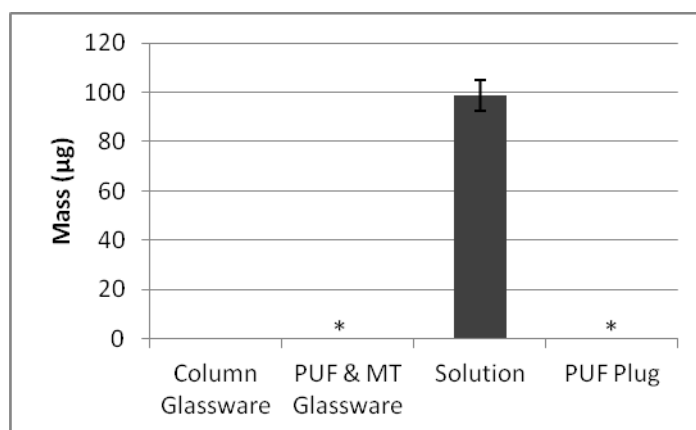


Figure 7. Mass distribution of imazosulfuron post-35°C run. *Below limit of detection.

occurring more rapidly under higher temperatures and more extreme pHs (Genari *et al.*, 2008, Saha *et al.*, 2008; Zheng *et al.*, 2008).

A maximum detection limit of the Henry's law constant, calculated using the air and water detection limits, represents the upper limit of H for imazosulfuron and was estimated to be $9.66 \times 10^{-3} \text{ m}^3 \text{ Pa mol}^{-1}$. The estimated H, derived by dividing the vapor pressure by the water solubility at 25°C, is $6.03 \times 10^{-7} \text{ m}^3 \text{ Pa mol}^{-1}$. These small constants correlate to the low vapor pressures of other sulfonylureas (Schmuckler *et al.*, 2000).

Conclusions

Imazosulfuron is a sulfonylurea herbicide with high water solubility (308 mg/L). Due to this high solubility and the results of the Henry's law constant experiments, *it is unlikely*

Table 3: Summary of Dissipation Results

Agent	Volatility ($H=P/S$)	Sorption (log K)	Photolysis (half life)	Biodegradation (half life)
Granite	4.6×10^{-15} (calculated)	0.1 - 5.1 (not log)	5-8 days	3-12 days (anaerobic)
Cerano	1.6×10^{-6}	0.5 - 5.3 (not log)	ND	47 days (aerobic) 8 days (anaerobic)
Trebon	2.9×10^{-1} (calculated)	6.0-6.4	10-18 days	27 days (aerobic) 100 days (anaerobic)
Poncho, Belay (clothianidin)	3.3×10^{-9} (calculated)			
Brazzos, League (imazosulfuron)	6.0×10^{-7} (calculated)			

that volatilization is a significant mode of dissipation in California rice fields. An estimated Henry's law constant, calculated to be $6.03 \times 10^{-7} \text{ m}^3 \text{ Pa mol}^{-1}$, indicates that the herbicide has low volatility. It is possible that hydrolysis may be the cause of imazosulfuron degradation in both the gas stripping experiments and in rice fields. This potential, along with soil-water partitioning, will be investigated in future work.

Overall Summary

Over the past decade our focus has been on a number of pesticides of interest to the RRB. Early on our focus was on the delayed phytotoxicity syndrome caused by Bolero (thiobencarb; Palumbo *et al.*, 2004; TenBrook *et al.*, 2004; Gunasekara *et al.* 2005; Schmelzer *et al.*, 2005), while more recently (with Professor Albert Fischer) we have focused on the mechanism of action of Cerano (clomazone; TenBrook and Tjeerdema, 2005, 2006; Yasuor *et al.*, 2008, 2010), as well as pesticide dissipation. To date, we have completed characterization of the field dissipation properties of Granite (penoxsulam; Jabusch and Tjeerdema, 2005, 2006a, 2006b, 2008), Cerano (Gunasekara *et al.*, 2009; Tomco *et al.*, 2010), and Trebon (etofenprox; Vasquez *et al.*, 2010); additional papers will be published shortly (Table 3). We are now focusing on two other compounds (Table 4). Thus, during the next year we propose to continue our ongoing research with the neonicotinoid insecticide Poncho (clothianidin) and herbicide imazosulfuron.

Table 4: Summary of Ongoing Dissipation Research

Agent	Volatilization	Soil Sorption	Microbial Degradation	Photodegradation
Granite	completed	completed	completed	completed
Cerano	completed	completed	completed	completed
Trebon	completed	completed	completed	completed
Poncho, Belay	completed	in progress		
Brazzos, League	completed	in progress		

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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 (bonding) to soils, and degradation by either sunlight or soil microbes.
2. For the insecticide clothianidin (Poncho, Belay), the capacity to volatilize from a flooded rice field was characterized via calculation of a Henry's law constant (3.3×10^{-9}). In summary, the insecticide is not prone to volatilization due to the low constant value.

3. For the herbicide imazosulfuron (Brazzos, League), the capacity to volatilize from a flooded rice field was characterized via calculation of a Henry's law constant (6.0×10^{-7}). In summary, the insecticide is not prone to volatilization due to the low constant value.
4. For both pesticides, dissipation from flooded rice fields will not be significantly influenced by volatilization.
5. Sorption to representative rice field soils will be characterized next year to determine its contribution to dissipation from field water.