

ANNUAL REPORT  
COMPREHENSIVE RESEARCH ON RICE  
January 1, 2012 – December 31, 2012

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

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OBJECTIVES AND EXPERIMENTS CONDUCTED BY LOCATION TO  
ACCOMPLISH OBJECTIVES:

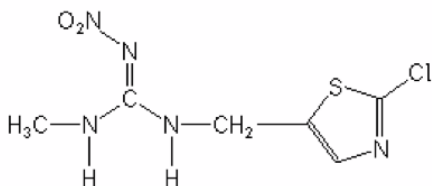
Objective I. To investigate the natural factors governing pesticide dissipation in  
California rice fields. Emphasis for 2012 was on characterizing soil sorption of Belay  
(Belay) under California rice field conditions.

Objective II. To investigate the natural factors governing pesticide dissipation in  
California rice fields. Emphasis for 2012 was on characterizing volatilization of League  
(League) under California rice field conditions.

Objective III. To investigate the natural factors governing pesticide dissipation in  
California rice fields. Emphasis for 2012 was on characterizing volatilization of Butte  
(Butte) under California rice field conditions (objective added later).

SUMMARY OF 2012 RESEARCH (MAJOR ACCOMPLISHMENTS) BY  
OBJECTIVE:

**Objective I – Soil-water partitioning of Clothianidin (Belay)**



**Figure 1:** Structure of Belay, a neonicotinoid insecticide.

## *Introduction.*

Belay, a synthetic neonicotinoid insecticide, is registered for foliar-spray and seed-treatment applications for rice in Japan and is of current interest to California rice farmers due to its effectiveness against the rice water weevil, chinch bug, thrips, aphids and grape colaspis (Franklin *et al.*, 2004, Umene *et al.*, 2006, T van der Velde-Koerts, 2009) (*Figure 1*). Belay is not yet registered in California for use on rice, and the bulk of available fate data pertain to environmental systems different from California rice fields.

Two partitioning processes are of primary importance when considering the abiotic dissipation of a pesticide from rice fields: 1) air-water partitioning, and 2) soil-water partitioning. The tendency of a chemical, such as a pesticide, to volatilize from water into the atmosphere (air-water partitioning) is related to its Henry's law constant ( $H$ ); a pesticide with a very high  $H$  will move from water into the atmosphere more readily than a chemical with a low  $H$ . Likewise, the tendency of a chemical to move from water into soil (soil-water partitioning) is related to its soil-sorption coefficient ( $K_d$ ); a pesticide with a high  $K_d$  will move from water into the soil more readily than a pesticide with a very low  $K_d$  (Schwarzenbach *et al.*, 2003). Both  $H$  and  $K_d$  are kinetic parameters derived from the chemical properties of a pesticide and environmental factors, including temperature, pH and soil characteristics.

Air-water partitioning coefficient ( $H$ ) values reported by the US EPA for Belay are low, indicating that it will not readily vaporize from water to the atmosphere (US EPA, 2010). However, the reported  $H$  values were calculated by measuring the ratio of its vapor pressure to water solubility at 25°C (no values are reported for elevated temperatures; US EPA, 2010; Umene, 2006; Federoff, 2005). In 2011, we determined that the air-water partitioning coefficients ( $H$ ) for Belay, at temperatures relevant to California rice fields, are low ( $1.2\text{E}^{-9}$  and  $3.34\text{E}^{-9}$  Pa m<sup>3</sup> mol<sup>-1</sup> at 22°C and 35°C, respectively). Our results suggest that volatilization will not be a significant route of dissipation for Belay.

According to the *Environmental Fate and Ecological Risk Assessment Registration Report* on Belay (US EPA in 2010),  $K_d$  coefficients for Belay are generally low but correlate to the amount of organic matter present in the soil. This indicates two things: 1) the tendency for Belay to move from water to soil is low, and 2) the tendency for Belay to move from water to soil significantly increases in soils with higher concentrations of organic matter (US EPA, 2010). Studies have noted that the concentration of organic matter in California rice soils is highly variable, meaning that the mobility of Belay within rice soils will be highly variable. Thus, our objective for 2012 was to determine soil-water partition coefficients for Belay in California rice soil systems. In order to determine  $K_d$  values predictive for partitioning under California rice field conditions, sorption isotherm experiments were run on four different soils collected from rice fields in the Sacramento Valley.

## Materials and Methods

**Materials and soils.** Analytical grade Belay was purchased from Sigma Aldrich. Stock solutions of Belay were prepared in  $\text{CaCl}_2$  and used to prepare aqueous samples. Several kilograms of soil samples were randomly collected from the 0-10 cm layer at three locations in northern California: Biggs, Davis and from two different fields in Richvale. Following collection, soils were air dried and ground to pass through a 2 mm sieve. In order to inhibit microbial activity, they were autoclaved at  $120^\circ\text{C}$  for 1 hour and dried at  $105^\circ\text{C}$  for 5 hours.

**Soil Characterization.** The soils were analyzed for physical and chemical characteristics by the Division of Agriculture and Natural Resources (ANR) Analytical Laboratory at the UCD. Results are shown in Table 1. Description of the methods can be found in Schmelzer *et al.*, 2005, or the ANR website (<http://danranlab.ucdavis.edu>). Post harvest rice straw management practices varied between sites – Richvale (RV-B) and Biggs (BF) field sites burned post-harvest rice straw, whereas Richvale (RV-T) and Davis (DF) field sites tilled the straw into the field.

**Table 1.** Soil Properties of Davis, Biggs and Richvale Soils (0-10 cm depth).

	California Rice Field Soil			
	Richvale	Richvale	Biggs	Davis
Post Harvest Straw Disposal	Tilled & Flooded	Burned	Burned	Tilled & Flooded
foc	0.012	0.0175	0.0145	0.0195
Clay (%)			44	47.5
Sand (%)			28	13.5
Silt (%)			28	39
pH	4.46	4.56	4.69	6.6
CEC (estimated)	5.97	5.88	20.05	37.95

**Soil-water partitioning.** Soil isotherms were constructed from triplicate samples created using the batch equilibration method as previously described by the (US EPA, 2008). Preliminary kinetic experiments determined that a soil-to-solution ratio of 1:2 allowed for 20-85% sorption, and apparent sorption equilibrium was reached after 72 hours. For each soil sample, 5.0 g was transferred into a 50 mL amber polytetrafluoroethylene (PTFE) screw top centrifuge tube and suspended in 9 mL of 0.01M  $\text{CaCl}_2$ . Soil suspensions were equilibrated on a rotary shaker for 12 hours prior to the addition of Belay stock solution. An aliquot of 1mL of Belay stock solutions in 0.01M  $\text{CaCl}_2$  was added to each experiment, and concentrations ranged between 0.05 and 10  $\mu\text{g/mL}$ . Suspensions were agitated on a rotary shaker at room temperature ( $22^\circ\text{C} \pm 2^\circ\text{C}$ ) at 200 rpm for 72 hours. After shaking, each suspension was centrifuged at  $2,000 \times g$  for 30 minutes, and 7 mL of supernatant was decanted from each experiment and a 1 mL aliquot of supernatant was passed through a 0.45 $\mu\text{m}$  PTFE syringe tip filter into an amber HPLC vial.

Controls either without soil or without Belay stock solution showed that 1) no interfering compounds were detected in the soil, and 2) Belay was stable and did not sorb to surface of the centrifuge tube. All experiments and controls were performed in triplicate.

*Analysis by LC-MS/MS.* An Agilent 1100 (Agilent, Santa Rosa, CA) HPLC with an 1100 series autosampler coupled to PE SCIEX triple quadrupole mass spectrometer (AB Sciex, Foster City, CA) model AP2000 equipped with a heated nebulizer ionization source (APCI) and controlled by Analyst interface software version 1.4.2 was used. The HPLC was equipped with a 3.5  $\mu\text{m}$  particle size, 4.6 x 250 mm ID Xterra C18 column (Waters, Milford, MA) using an isocratic mobile phase of 70% methanol with 0.1% formic acid and 30% water with 0.1% formic acid at 400  $\mu\text{L}/\text{min}$  flow rate at ambient temperature with a 50  $\mu\text{L}$  injection volume. Detection used MRM in the positive ion mode using the protonated molecular ions  $(\text{M}-\text{H})^+$  as the precursor ion. The retention time, product ion, transition, dwell time, collision energy and collision cell exit potential are listed in Table 2. Other MS parameters are as follows: heated drying gas temperature 425  $^{\circ}\text{C}$ , curtain gas pressure 50 psi, collision gas pressure 4 psi, ion source gas ( $\text{N}_2$ ) GS<sub>1</sub>/ GS<sub>2</sub> 75 psi/15 psi, focusing potential 370V, entrance potential 8V, declustering potential 16V. A 7-point external calibration curve was constructed from the peak area of Belay in a range of 0.005 to 10  $\mu\text{g}/\text{mL}$  using standards prepared in 0.01M  $\text{CaCl}_2$ .

**Table 2:** APCI-MS/MS optimized parameters for Belay.

Compound	Retention Time (min)	Precursor Ion (m/z)	Product Ion (m/z)	Collision Energy (V)	Collision Cell Exit Potential (V)	Dwell time (ms)
Clothianidin	8.49	250	169	19	6	150

### Data Analysis.

The amount of Belay sorbed by soil was calculated from the analytically determined equilibrium concentrations,  $C_{\text{eq}}$ , of Belay in the aqueous phase according to the following equation:

Equation 1

$$C_s \left[ \frac{\mu\text{g}}{\text{g}} \right] = \frac{(C_o - C_{\text{eq}}) \cdot V_w}{m_s}$$

where  $C_o$  is the initial spike concentration of Belay in aqueous phase ( $\mu\text{g}/\text{mL}$ ),  $V_w$  is the volume of water in the aqueous phase (mL), and  $m_s$  is the mass of soil in the test tube (g). Sorption isotherms were fitted to the logarithmic form of the Freundlich equation:

Equation 2

$$\log C_s \left( \frac{\mu\text{g}}{\text{g}} \right) = \log K_f + N \log C_w$$

where  $C_s$  is the total sorbed concentration (ug/g),  $C_w$  is the aqueous-phase concentration (ug/ mL) at equilibrium, and  $K_f$  [(ug g<sup>-1</sup>)/(ug mL<sup>-1</sup>)] is the Freundlich coefficient constant and  $N$  is the Freundlich exponent.

*Distribution Coefficients.* The sorption coefficient value  $K_d$  is a direct measure of sorption for a pesticide between the soil and water for one set of conditions. Unfortunately, environmental conditions governing the sorption are not constant— several factors including changes in soil or water chemistry or changes in the concentration of a pesticide. Sorption isotherms were used to investigate the effect pesticide concentration on sorption to California rice field soils.

It is well documented that the sorption affinity of Belay significantly increases with small increases in the concentration of organic matter. The  $K_d$  and organic carbon (OC)-normalized sorption coefficient ( $K_{oc}$ ) were calculated from the isotherms for a field-relevant concentration of 0.15 ug/mL ( $C_w$ ) via the equations below.

*Equation 4*

$$K_d = K_f \cdot C_w$$

*Equation 5*

$$K_{oc} = \frac{K_d}{f_{oc}}$$

In these equations  $f_{oc}$  is the fraction of organic carbon in each soil sample (Table 1).

## Results

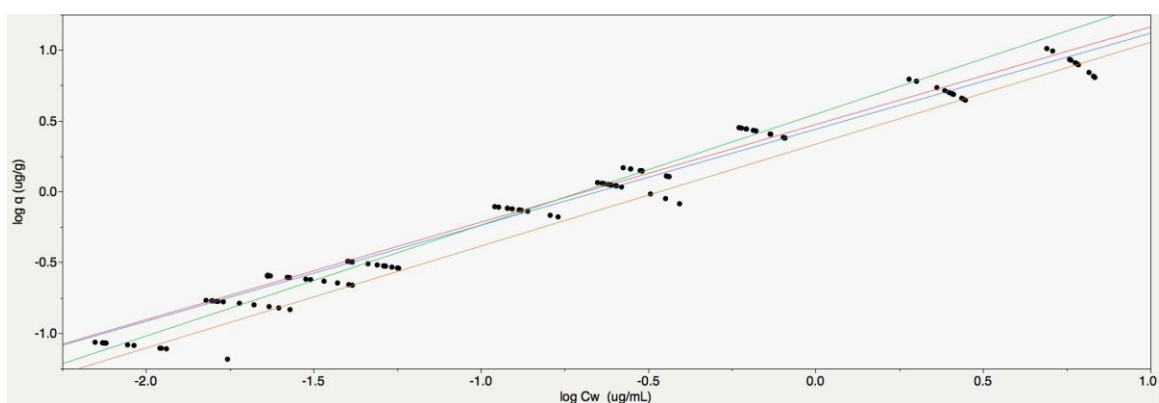
The amount of Belay sorbed to soils increased with decreasing initial concentrations and ranged between 14% to 68%. Distribution coefficients,  $K_d$ , and log  $K_{oc}$  values were calculated from the isotherms for the field-relevant concentration of 0.15 ug/mL ( $C_w$ )— values ranged from 0.324 to 0.532 L kg<sup>-1</sup> and 1.07 to 1.48 L kg<sup>-1</sup> respectively (Table 3). The low  $K_d$  and  $K_{oc}$  values indicate that sorption of to rice soils is weak. The organic carbon content of the rice soils used in this study ranged between 1.12 to 1.92%, and a correlation between organic carbon content for all but the Davis field soil was observed.

The sorption isotherms of Belay for the four rice field soils studied are shown in Figure 2. Data from the isotherm experiments for the four rice soils were log transformed to fit the Freundlich model using *Equation 2* and the corresponding Freundlich parameters are listed in *Table 3*— the model offered a good fit with  $R^2 \geq 0.982$  for each isotherm. All isotherms were non-linear ( $N < 1$ ) indicating that Belay is bound with successively less favorable free energy as the initial concentration of the pesticide increases. This indicates that sorption of Belay is likely restricted to specific sorption sites, such as those located within soil organic matter.

**Table 3:** Freundlich sorption coefficient  $K_f$ , exponent  $N$ , distribution coefficient  $K_d$  ( $\text{L kg}^{-1}$ ), and log of organic carbon normalized sorption coefficient  $K_{oc}$  ( $\text{L kg}^{-1}$ ) values for Belay on four rice field soils at 22°C.

Soil	Co Range (ug/mL)	$K_f$	$N$	$R^2$	$K_d$ [L/kg]	log $K_{oc}$
Richvale, Tilled	0.05 - 10	2.163	0.720	0.982	0.324	1.43
Richvale, Burned	0.05 - 10	2.755	0.680	0.995	0.413	1.37
Davis, Tilled	0.05 - 10	3.548	0.780	0.994	0.532	1.44
Biggs, Burned	0.05 - 10	2.951	0.690	0.988	0.443	1.48

**Figure 2:** Log transformed Freundlich sorption isotherms of Belay to soils: Biggs, burned (red), Davis, tilled (green), Richvale, burned (blue), Richvale, tilled (orange).



## Conclusions

Belay is a moderately polar compound with low vapor pressure and moderate water solubility ( $327 \text{ mg L}^{-1}$ ), and is uncharged at environmentally relevant pH. These properties drive Belay to partition to the aqueous phase rather than volatilize or sorb to soil. The log  $K_{oc}$  is low and ranged from 1.37 to 1.48 at 22°C. Desorption isotherms for the same soils will be constructed in order to gain a better understanding of the potential mobility of Belay from rice fields and further work is underway to determine how sorption and desorption will be effected by temperature. However, the data in this study indicate that soil partitioning represents a negligible dissipation pathway for Belay from flooded rice fields.

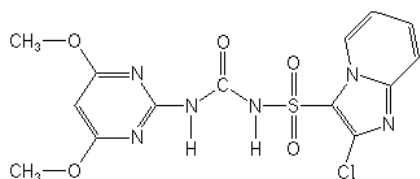
## Objective II – Sorption of Imazosulfuron (League)

### Introduction

Imazosulfuron (trade names include 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 ( $75\text{-}95 \text{ g ha}^{-1}$ ; Tomlin, 1997). The US EPA registered League for commercial and residential use in 2010. League's mode of action involves inhibiting the enzyme acetolactate synthase, a critical component to the production of amino acids

necessary for new cell generation. League-tolerant plants are thought to rapidly metabolize the herbicide (Tanaka & Yoshikawa, 1994).

Sorption to soil is an important process in determining the overall fate of a pesticide in the environment. Partitioning coefficients, such as the soil sorption coefficient ( $K_d$ ) and organic carbon partition coefficient ( $K_{oc}$ ), provide quantitative information describing a chemical's sorption. Properties of both the chemical and the soil influence sorption. Previous work describing League's behavior in soils shows its sorption to be moderate and heavily influenced by pH and organic matter (Mikata *et al*, 2000). No previous work has addressed the sorption of League under California rice field conditions.



**Figure 3.** Structure of League.

### *Materials and Methods*

**Experimental Design and Sampling.** League (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, and all solvents were HPLC grade.

Soil was randomly collected from the top 0-10 cm of a rice field in Yolo County and characterized by the Division of Agriculture and Natural Resources Analytical Laboratory at UC Davis. The soil was characterized as clay with a pH of 6.60 and OM content of 3.92%. Soil was sieved to <2 mm and baked to remove moisture.

Soil sorption isotherms (23°C±1) were prepared using the batch equilibrium technique. Slurries were prepared in 60 mL amber serum vials and capped with Teflon lids. Vials and soil were autoclaved at ~121°C and 15 psi for 30 min. A 0.01 M CaCl<sub>2</sub> aqueous solution, adjusted to pH 7 was filtered (0.2 µm) to remove microorganisms and added such that the soil to water ratio was 1:5. Slurries were allowed to equilibrate for 24 hours on a shaker at 200 rpm and then spiked with League (<0.5% solvent). Preliminary studies showed that apparent equilibrium was reached within 4 hours. Samples were then centrifuged at 2000 x g for 30 min. The supernatant was filtered with 0.2µm PVDF syringe filters and frozen at -20°C prior to analysis. Isotherms were run with 4 replicates per concentration and blanks. Loss to glass was negligible. Sorbed concentration was determined from mass balance. Sorption of League ranged from 8.5 – 29.7% for the eight spike levels, ranging from 40 – 3000 µg L<sup>-1</sup>.

**Analysis.** Samples were thawed and spiked with an internal standard, halosulfuron-methyl. 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

and a 0.5 min auto-equilibration time was included prior to each injection. The column was an Elclipse XDB-C18, 150 x 4.6 mm i.d., 5  $\mu$ m particle size (Agilent). The column temperature was held at 25°C. League was eluted via a mobile phase gradient consisting of 0.15% acetic acid and 0.15% acetic acid in acetonitrile. The flow rate was 0.25 mL/min from the start of the run until 16.5 min, then ramped to 1 mL/min to rapidly equilibrate the column. Percent acetonitrile was ramped from the initial condition of 50% to 90% at 0-7.5 min, then held for 9 min, before ramping down to 50% from 16.5 - 19.5 min. Total run time was 21 min, but only eluent from 12-16.3 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 4.

**Table 4:** Ions Monitored for Analysis

Compound	Parent Ion <i>m/z</i>	Daughter Ion <i>m/z</i>	Collision Energy (V)	Collision Cell Exit Potential (V)
League Halosulfuron- methyl (IS)	413	156.2	29.0	6.0
	413	153.0	23.0	6.0
	413	257.8	33.0	12.0
	434	182	33.0	8.0

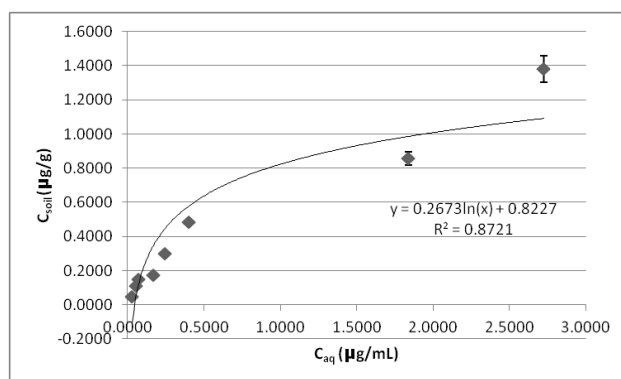
The dwell time for all ions was 150 msec and the source temperature was 400°C. The first quadrupole was set at high resolution mode, and the ionspray voltage was 5500 V. Curtain gas, ion source gas #1, ion source gas #2 and the collision gas were 50 psi, 15 psi, 50 psi and 8 psi, respectively. The de-clustering 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 six point calibration curve using the peak areas ratio of League to IS and a linear regression. The 413.0  $\rightarrow$  156.2 *m/z* transition was used in quantification while 413.0  $\rightarrow$  153.0 and 413.0  $\rightarrow$  257.8 were used as 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  $\mu$ g/mL in 1 mL acetonitrile, was diluted in the CaCl<sub>2</sub> solution to 100  $\mu$ g/mL. Accuracy within  $\pm$ 10% was considered acceptable.

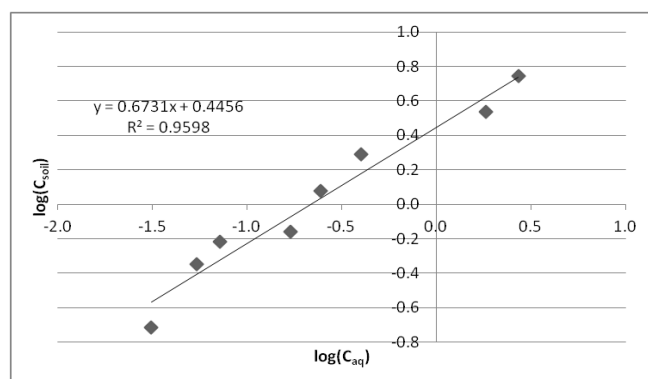
### *Results and Discussion*

League's sorption isotherm (Figure 5) shows that for all concentrations examined, sorption was non-linear and low, with  $K_d$  values ranging from 0.473 – 2.146 cm<sup>3</sup>g<sup>-1</sup>. Greater fractional League uptake was observed at low League concentrations than high. Greater sorption to soil at the highest spike level can likely be attributed to the initial solution's concentration, 300 mg/L, which lies just below the aqueous solubility limit for League, 308 mg/L (Tomlin, 1997). League partitioned to soil to a greater degree due to limits in the solubility of League at this point. Log-transformed data (Figure 6) yielded a Freundlich adsorption coefficient ( $K_f^{ads}$ ) of 2.79 and a regression constant (n) of 1.49.





**Figure 5.** Imazosulfuron concentration in soil vs. aqueous phase.



**Figure 6.** Log transformed soil and aqueous phase concentration data.

### Conclusions

League is sulfonylurea herbicide with high water solubility (308 mg/L). Due to its high solubility and the preliminary sorption results presented, *sorption to soil is expected to be low*. Freundlich adsorption coefficients for League in the literature ( $K_f^{\text{ads}}$ : 0.96-5.27) have good agreement with results from this work ( $K_f^{\text{ads}}$  = 2.79; Mikata *et al.*, 2000). Studies of other sulfonylurea herbicides suggest their sorption is influenced by organic matter and pH (Ren *et al.*, 2011, Vega *et al.*, 2000, Wu *et al.*, 2011). Future work will characterize the sorption and desorption of League for a suite of California rice field soils.

### Objective III. Volatilization of Benzobicyclon (Butte)

#### Introduction

The synthetic herbicide Butte has been proposed as an effective tool for rice farmers in the Sacramento Valley due to its effectiveness against sulfonylurea-resistant weeds such as *Scirpus juncooides*. Though Butte has not yet been registered for use in California, it is currently used in Japan with great success (Koyanagi and Nakahara, 2009). Butte is considered to be a triketone herbicide and inhibits hydroxyphenylpyruvate deoxygenase (HPPD) activity in weeds, leading to chlorophyll destruction, weed bleaching and death.

To understand the behavior of Butte in California rice fields, both chemodynamic transport (the movement of the chemical between phases, such as air-water partitioning and soil-water partitioning) and degradation (destruction of the chemical due to microbial reactions and/or sunlight) need to be considered. The air-water partitioning behavior of Butte is currently under study, which will aid the prediction of the potential volatility of Butte under California rice field conditions. Partitioning depends on both the vapor pressure and the water solubility of the chemical and is measured by Henry's law constant (Schwarzenbach *et al.*, 2003). Prediction of the volatility of Butte under California rice field conditions can be conducted by determining the Henry's law constant for Butte.

*Calculations.* Henry's law constants can be calculated from the vapor pressure and the water solubility of a chemical using the following equation:

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

As the vapor pressure and water solubility are both dependent on temperature, it is important to calculate the Henry's law constant for different temperatures California rice fields might experience. This may be done experimentally and theoretically.

### *Materials and Methods*

The gas stripping apparatus was used to experimentally determine the Henry's law constant for Butte (Lau *et al.*, 2006). Duplicate gas stripping columns (1 m x 51 mm inner diameter) were run simultaneously. Approximately 1.5 L of dilute Butte solution (26 – 39 ppb) was added to each gas-stripping column. High purity N<sub>2</sub> gas was filtered through a hydrocarbon trap with a variable flow rate of 45 – 95 mL/min and saturated with water before being bubbled through the bottom of each water column. Polyurethane foam (PUF) plugs were used to collect volatilized Butte, and a mist trap was used to prevent the exposure of PUF plugs to water droplets, which could bias results. Column temperature was maintained using a recirculating water bath, and columns, polyurethane foam plug holders and mist traps were foil-wrapped to prevent photodegradation. Over the course of the experiment 3 mL water samples were collected to determine the aqueous Butte concentration over time. After experiment completion the Butte solution was drained from the columns, which were rinsed with solvent and analyzed for Butte sorbed to the glass. PUF plugs, the PUF plug holder and mist trap were rinsed with solvent and analyzed for volatilized Butte.

*Extraction and Analysis.* Water samples were extracted via solid phase extraction (SPE) using Waters Oasis® HLB SPE cartridges. Cartridges were activated with 5 mL of methanol, followed by a 10 mL rinse of HPLC grade water. Immediately after the rinse 3mL of water sample was added to the cartridges. After drying under vacuum for one hour, cartridges were rinsed with 1.5 mL of acetonitrile, which was collected and analyzed via HPLC-MS/MS.

After the aqueous Butte solution was drained from the apparatus the columns were rinsed with dichloromethane to remove any Butte sorbed to the glass walls. The solvent was collected and dried to near dryness using a nitrogen evaporator with a 30°C water bath. Acetonitrile was used to reconstitute the samples, which was collected and analyzed via HPLC-MS/MS.

PUF plugs were collected and volatilized Butte extracted via 60 mL of dichloromethane on a rotary shaker for 24 hours. This was repeated four times and all rinses were combined and dried to near dryness with a nitrogen evaporator. Acetonitrile was used to reconstitute the samples, which were analyzed via HPLC-MS/MS.

Time (min)	% A	% B
0	85	15
5	85	15
10	5	95
15	5	95
15.5	85	15

**Table 5:** Gradient of mobile phases for HPLC-MS/MS.

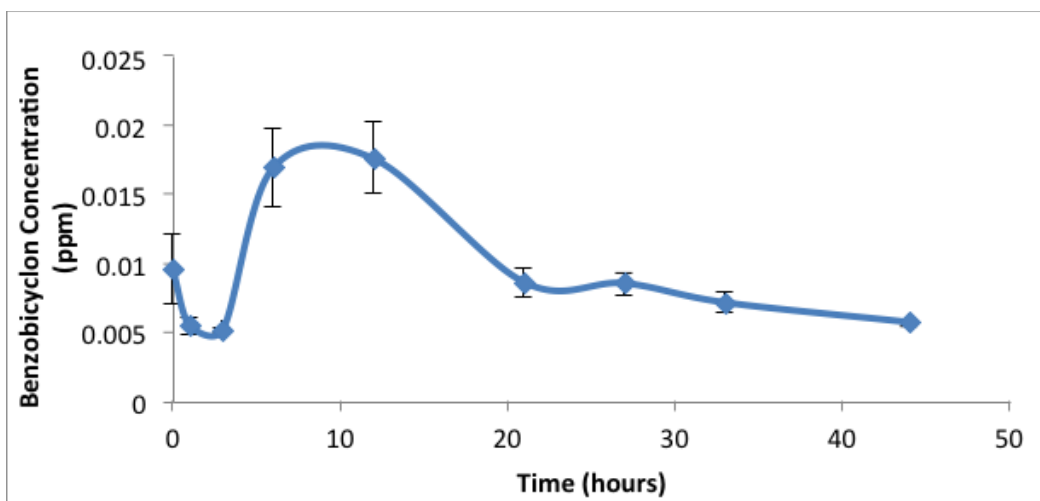
HPLC-MS/MS analyses were performed by an Agilent 1100 LC with PE Sciex API 2000 mass spectrometer (with electrospray (ESI) ionization source). The analytical column was a Restek Allure C18 column (5 cm, 30 mm x 2.1 mm). The mobile phases used were 5 mM ammonium acetate acidified with 0.1% acetic acid (A) and acetonitrile (B). The gradient used is shown in Table 5.

The total run time was set at 15.5 minutes, with an eight minute equilibration time. The injection volume used was 10  $\mu$ L and the flow rate was 0.3 mL/min. The method limit of detection was 4.4 ppb and the method limit of quantification was 10.6 ppb. The mass spectrometer was run in MRM mode with the Q1 mass for Butte set at 446.9 amu and the Q3 mass set at 256.9 amu. Samples and standards were injected using an auto sampler. The linear calibration curve was generated via Analyst software (version 1.4) and the intercept was not forced through the origin.

#### *Preliminary Results and Discussion.*

An aqueous Butte concentration of 26 ppb and a total run time of 44 hours were used for the first attempt to measure Henry's law constant at 25°C. Figure 7 shows the decrease in aqueous Butte over time. The increase in concentration from the third hour to the 12th hour of the experiment suggested that solution had not come to equilibrium prior to the start of the experiment. In addition, SPE spike recoveries were poor (with a 12% average percent recovery) and the mass balance of the system (which accounts for the mass of Butte in solution, sorbed to the columns and volatilized Butte) was also low at 62% recovery of the initial total mass of Butte.

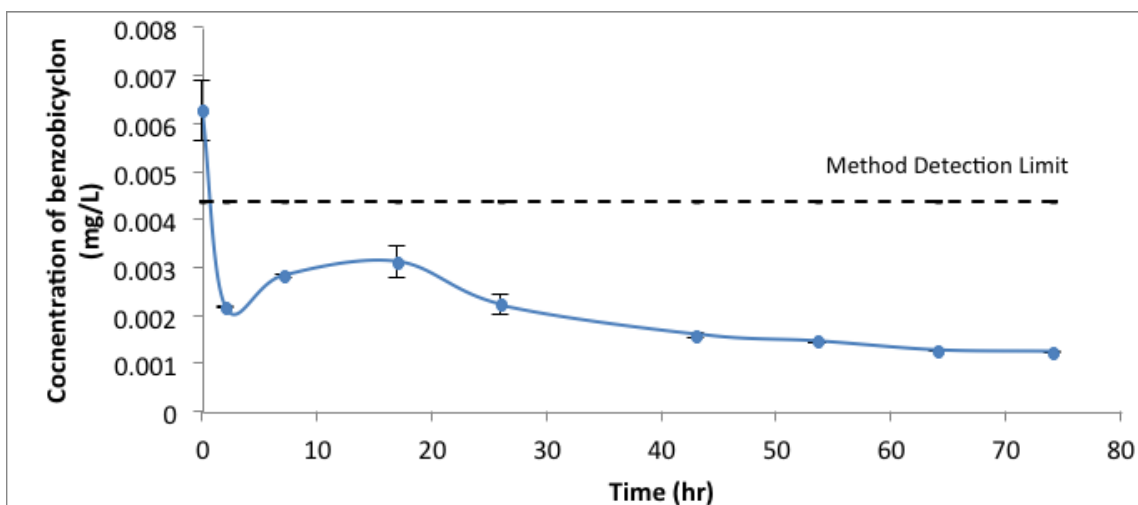
A second attempt addressing these issues was conducted. The concentration of Butte in solution increased to 39 ppb, which was shaken overnight at room temperature to allow the solution to equilibrate. The experiment ran for 74 hours, and the decrease in aqueous Butte concentration is shown in Figure 8.



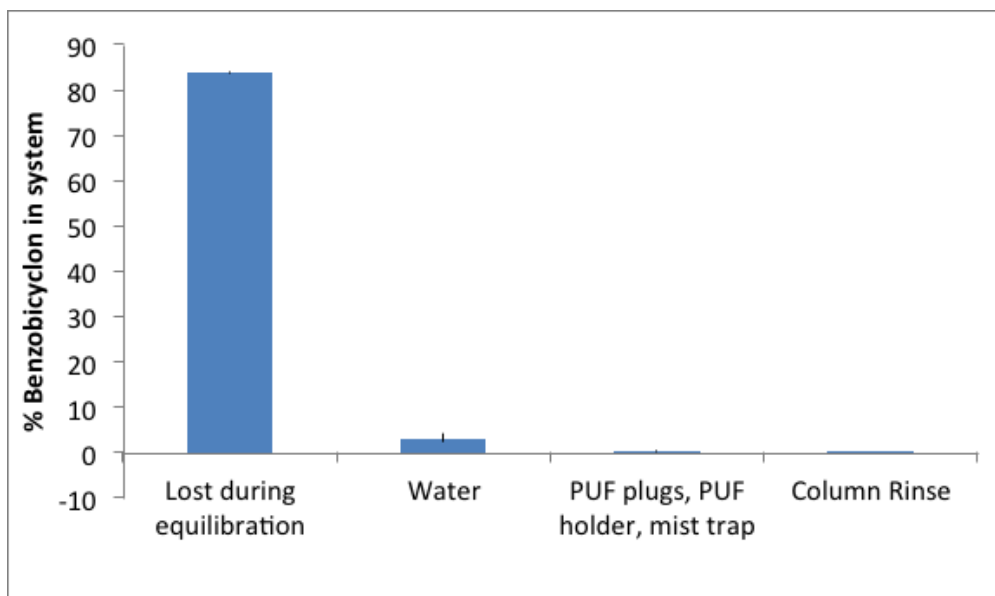
**Figure 7:** Concentration of aqueous Butte over the course of the experiment.

Equilibration of the aqueous Butte solution before adding the solution to the columns severely lowered the soluble Butte in solution and caused a decrease in magnitude of sample concentrations. All samples past the initial water sample registered below the detection limit.

Column rinses and PUF plug extractions were also analyzed for Butte during both experiments. Combining these results with the results from the water sample analysis yields the overall partitioning of Butte in the system over the course of the experiment (summarized in Figure 9).



**Figure 8:** Concentration of aqueous Butte over the course of the experiment.



**Figure 9:** Division of the percent of Butte within the system.

Approximately 80% of the mass of Butte in the system was lost during the equilibration stage prior to the beginning of the experiment. This major loss led to the inability to accurately measure the concentration of Butte in the aqueous phase, sorbed to the column, and in the gas phase. Further trials with altered equilibration methods and water extraction techniques need to be conducted before Henry's law constants can be determined for Butte. This work is currently ongoing.

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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 Belay, the capacity to sorb to rice field soils under standard conditions is moderate and directly correlated to soil organic matter content.
3. For the herbicide League, the capacity to sorb to rice field soils under standard conditions is low and may be significantly influenced by the herbicide's degradation via direct reaction with water.
4. For the herbicide Butte, preliminary results indicate that its ability to dissipate from rice field water via volatilization is minimal.
5. For Belay and Butte, sorption to representative rice field soils under field conditions will be completed next year, as will characterization of volatilization of Butte under similar conditions.