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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 factors governing pesticide dissipation in California rice fields. Emphasis for 2017 will be to focus on the ultimate herbicidal product of Butte (benzobicyclon hydrolysate; BH) by characterizing its soil sorption and photolysis under rice field conditions.

Objective II. To investigate the factors governing pesticide dissipation in California rice fields. Emphasis for 2017 will be to focus on the insecticide Coragen (chlorantraniliprole) by finalizing characterization of its soil sorption under rice field conditions.

Objective III. To investigate the factors governing pesticide dissipation in California rice fields. Emphasis for 2017 will be to focus on the herbicide thiobencarb (Abolish and Bolero) by modeling its dissipation in rice fields during drought years.

Objective I. Aqueous Photolysis of Benzobicyclon Hydrolysate (BH)

Introduction

Recently approved for use on California rice fields by the United States Environmental Protection Agency (USEPA),[1] the herbicide benzobicyclon (Butte®) kills previously resistant weeds via formation of the active herbicide, benzobicyclon hydrolysate (BH; Figure 1). BH works through a new mode of action, inhibition of 4-hydroxyphenylpyruvate dioxygenase (4-HPPD),[2] which has not been previously used on California rice field weeds. The USEPA has advised that Butte® (a granular formulation) can be applied on up to 10% of California rice fields in the upcoming growing season, though the fate of BH in a flooded rice field is still mostly informed from estimated parameters.[1]

Previous studies have experimentally characterized BH hydrolysis and behavior in soil, which indicate a significant portion of BH will remain in the aquatic fraction of a flooded field.[3, 4] The photolysis of BH remains largely unknown, though USEPA registration documentation for BZB reports BH photolysis half-lives of 12.9 and 7.8 d at pH 5 and in field water, respectively.[1] However, these values are estimated to reflect light at 40º latitude and do not indicate when photolysis took place (e.g. summer solstice). The position of the sun over the course of a year can significantly impact photon flux and therefore the rate of photolysis. As BZB will be applied during the early part of the growing season (around early May), photolysis of the active BH should be assessed for both the equinox and summer solstice to better understand the photolytic range for BH.

Based on the registration information and estimated physicochemical properties, the USEPA has recommended floodwater treated with Butte® to be held in the field for 20 days prior to release into the Colusa Basin Drain and eventually the Sacramento River.[1] Currently, the Butte® label suggests a hold time between 0 – 5 days. Depending on when the field is drained, BH may be released into the Sacramento River before it is able to dissipate in the field. Thus, photolysis should be understood in both a flooded rice field and the Sacramento River, especially if the process is slow for BH.

In this investigation, the photodegradation of BH was assessed in high-purity water as well as in filtered rice field water and Sacramento River water in both simulated and natural sunlight. The Pesticide in Flooded Applications Model (PFAM) was used to estimate a floodwater holding time based on the results of this investigation and other experimental BH fate data to better inform safe use practices.

Materials and Methods

Photolysis. Sacramento river water was collected from the Elkhorn Boat Launch Facility and water was obtained from a flooded rice field in the Yolo Bypass Wildlife Area in August 2017, filtered to 0.2 μm prior to use, and stored at 4ºC. The UC Davis Analytical Laboratory characterized the properties of the natural waters (Table 1). A pH 8.00 solution in high-purity water was used to ascertain direct photolysis of BH. Photolysis of BH was determined using both simulated and natural sunlight, and control samples were kept in the dark to account for BH hydrolysis. Chemical actinometers were used to normalize BH photolysis results.

Table 1. Select water properties

Water	pH	Dissolved organic carbon (mg L^{-1})	EC (dS m^{-1})
High-purity	6.52	0.9	< 0.01
Rice field	8.07	10.4	0.95
Sacramento River	7.63	4.2	0.12

Calculations. BH photolysis followed a pseudo first-order decay and rates were determined as:

$$\ln\left(\frac{C_t}{C_0}\right) = -j_{BH}t$$

where C_0 and C_t are the concentration of BH in solution initially and at time t, respectively, and j_{BH} is the pseudo first-order photolysis rate constant of BH (in h^{-1}). The half-life can then be determined as:

$$t_{1/2} = \frac{\ln(2)}{j_{BH}}$$

where $t_{1/2}$ is the half-life of BH in hours.

Pesticides in Flooded Applications Model (PFAM). PFAM is a comprehensive fate model designed to assess the dissipation of pesticides in aquatic systems, particularly rice fields.[5] PFAM was used to estimate the formation and subsequent disappearance timescale of BH in a California rice field using experimentally derived values.[3, 4] PFAM was also used to determine an approximate tailwater holding time for BH prior to release in to the Sacramento River. Input parameters are provided in Table S6 in the supporting information. Weather conditions were approximated using meteorological data for Sacramento, CA between 1961 – 1990, which was provided by the USEPA.[6]

Results and Discussion

BH photolysis. BH in hydrolysis controls was found to be stable for all treatments, as > 90% of the original concentration was retained over the course of each experiment. Simulated sunlight photolysis rates and half-lives were estimated at the summer solstice to approximate light intensities during typical application of BH (May – June).[1] Rates were also estimated at the fall equinox for two reasons: (i) to provide a direct comparison to measured photolysis rates, j_{BH}, in natural sunlight and (ii) to approximate light intensities during the spring equinox (as light intensities are the same during both equinoxes). As expected, summer solstice rates derived from simulated sunlight experiments were faster than those for the fall equinox as light intensities are greater during the summer solstice than either equinox in Davis, CA. Photolysis half-lives in natural sunlight were larger compared to estimated values from simulated sunlight. This is to be expected, as simulated sunlight is typically more intense than natural sunlight.

Table 2. Photolysis rates and half-lives

Treatment	Parameter	Simulated sunlight		Natural sunlight[†]
		Summer solstice	Fall equinox	
pH 8.0 High-purity water	k_p (h^{-1})	0.0178	0.0150	0.00218
	$t_{1/2}$ (h)	39.4	46.6	318
Filtered Rice field water	k_p (h^{-1})	0.0524	0.0443	0.00766
	$t_{1/2}$ (h)	13.3	15.7	90.5
Filtered Sacramento River water	k_p (h^{-1})	0.0244	0.0206	0.00334
	$t_{1/2}$ (h)	28.5	33.7	208
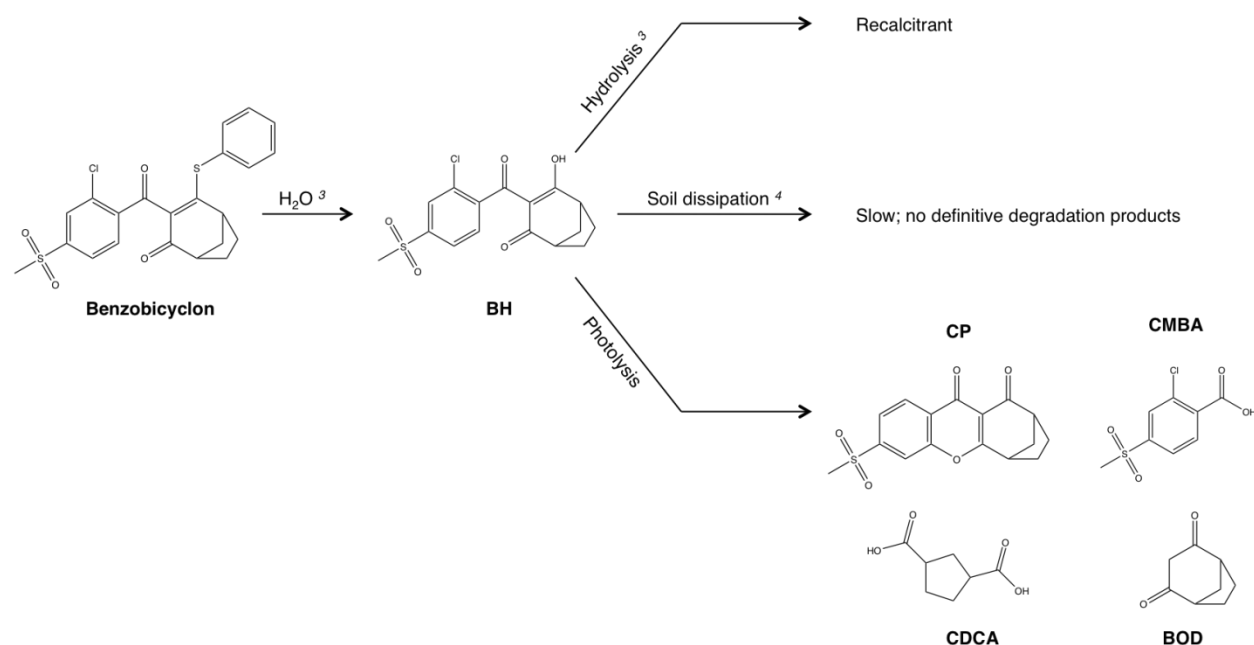
Figure 1. Expected progression of benzobicyclon to BH

BH photolysis in pH 8.0 high-purity water was slow (318 h in natural sunlight; Table 2), whereas photodegradation was much faster in rice field water (91 h in natural sunlight) and Sacramento River water (208 h in natural sunlight). Therefore, indirect photolysis has a major impact on BH photodegradation, especially in rice field water. Dissolved organic matter is known to be a significant driver of indirect photolysis in natural waters (through both sensitizing and quenching processes).[7-9] The measured concentrations of dissolved organic carbon (Table 1) correlate well with the half-lives of BH in the natural waters used in this study, indicating dissolved organic matter may be enhancing BH photolysis through indirect means, especially in rice field water.

California rice fields are typically flooded to approximately 13 cm, which is relatively shallow, though light scattering (attenuation) can still have a significant effect on photolysis near the sediment layer. Accounting for light attenuation, the photolysis half-life of BH in filtered rice field water in natural sunlight increases to 7.4 days (compared to 3.8 days at the surface). Light attenuation is therefore expected to significantly decrease BH photolysis in a flooded rice field by as much as half surface photolysis values.

Degradation products. Figure 1 shows the expected progression of benzobicyclon to BH and secondary degradation products (e.g. CP, CMBA) from all investigated pathways, including this study.[3, 4] Overall, activation of BH was rapid, though degradation via hydrolysis and in soil was slow to nonexistent. Formation of measurable degradation products was only observed for aqueous BH photolysis.

Target photolysis products (BOD, CMBA, CP) were selected to reflect known sulcotrione photolysis products and all were observed in this study (Figure 1).[10-12] Product yields are reported in Table 5. CP formation was initially rapid followed by decay over time, while CMBA was photolytically stable once formed. As with CP, BOD degraded over time after it was formed, however the process was slow. While not an expected photolysis product, CDCA was a major product (up to 39% by mol) in all treatments.

Like CMBA, CDCA appears to be stable to photolysis. The formation pathway is unclear, though it may result from the reaction of reactive oxygen species (such as hydroxyl radical) with BH or possibly BOD. This is supported by CDCA's increased yield in natural waters with dissolved organic carbon content (Tables 1 and 5), as dissolved organic matter is a known source of reactive oxygen species, which enhance indirect photolysis.[7-9]

PFAM and water holding time estimation. PFAM was used to map the fate of BH and its parent, benzobicyclon in both floodwater and benthic sediments (Figure 2). Experimental values from previous studies were used in the model when applicable.[3, 4] In the aqueous fraction, benzobicyclon hydrolyzes to BH over 10 days, while BH takes longer to dissipate, namely via photolysis. After approximately 20 days, the BH concentration falls to a steady state of approximately 2 μg L^{-1}. However, a large portion of benzobicyclon appears to immediately partition into the sediments and slowly partition back into the aqueous fraction, though much of the initial concentration in the sediment is retained over 100 days. The BH fraction in sediments is significantly lower than its parent, though the concentration also remains steady over 100 days after application. This is consistent with findings by the EPA during registration of benzobicyclon for use on California rice fields.[1]

Gowan Co. (the registrant) proposes a floodwater holding time of 0 – 5 days after Butte® application, while the USEPA recommends a holding time of 20 days.[1] Overall, our results indicate a holding time of 20 days should be sufficient to allow the majority of BH, the active herbicide, to dissipate prior to tailwater release into the Sacramento River. However, it is worth noting that significant levels of BH (approximately 2 μg L^{-1}; Figure 2) may remain in the tailwater once it is released. The effects of BH on aquatic plant and algae communities in the Colusa Basin and Sacramento River, as well as its potential effects on other non-target species such as humans and fish, warrant further investigation.
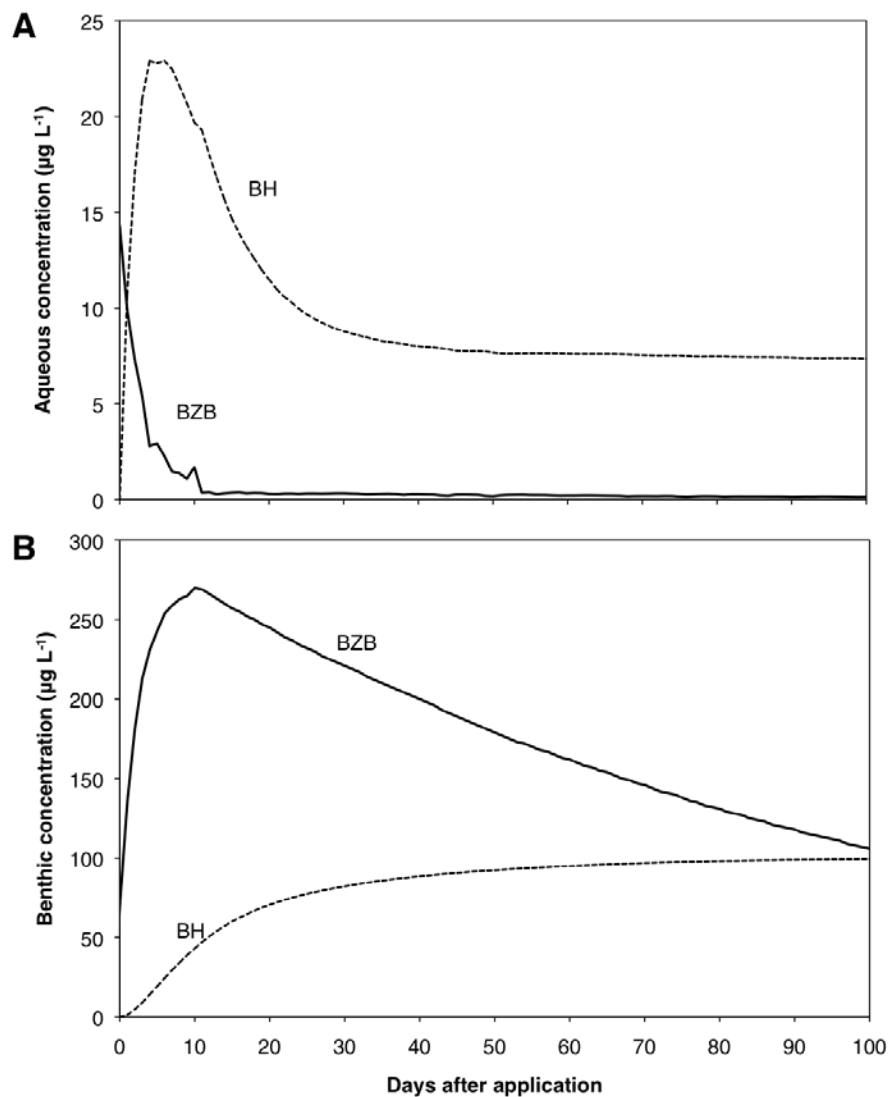
Figure 2. PFAM results for benzobicyclon (BZB; solid line) and benzobicyclon hydrolysate (BH; dashed line) in the aqueous fraction (A) and benthic fraction (B) of a model flooded field.

Objective II. Sorption of Coragen and the Influence of Soil Properties
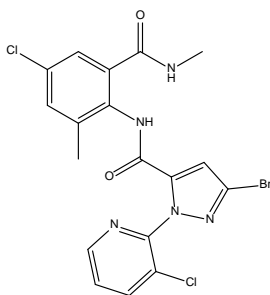

Figure 1. Chlorantraniliprole, the active ingredient of Coragen®

Introduction

Chlorantraniliprole (CAP, trade name Coragen®, Figure 1), an anthranilic diamide insecticide, is a potent insect ryandodine receptor agonist.[1] It was registered for agricultural use with the US Environmental Protection Agency (USEPA) in 2008 and was granted supplemental labeling in 2016 for use on California rice fields until December of 2018. The most damaging insect pest in California is the rice water weevil (*L. oryzophilus*) whose larvae account for 10-25% yield loss annually through extensive root pruning.[2] While current chemical controls used in California target the adult weevil, CAP targets weevil larvae, reducing the need for carefully timed applications. Furthermore, CAP is comparatively less toxic to non-target organisms, including crayfish and pollinators, than currently used insecticides such as λ-cyhalothrin (trade name Warrior®) and clothianidin (trade name Belay®).[3-5] However, CAP is highly toxic to aquatic invertebrate species and though it is reportedly non-mobile in soil (product label reports CAP to remain 1 – 3 inches from the point of application) it was recently detected in 72% of water samples collected along the central California coast.[6-8] The environmental fate of CAP under California rice field conditions should be investigated to ensure water quality for both endemic species and human consumers upon tailwater release into the Sacramento River.

CAP is a neutral species at environmentally relevant pH (pk_a = 10.88) with low water solubility (1.023 mg/L at 20˚C), low vapor pressure (6.3×10^{-12} Pa at 20˚C), and a moderate octanol-water partitioning coefficient (log K_{ow} = 2.77 at 20˚C). Air-water partitioning (characterized by the Henry's Law constant K_H) and soil-water partitioning (characterized by the partitioning coefficient K_d) are the primary chemodynamic processes in a flooded rice field. The USEPA calculated a Henry's Law constant for CAP of 3.1×10^{-15} atm·m^3·mol^{-1} from the registrant's experimentally derived solubility and vapor pressure at 20 ˚C and Freundlich sorption coefficients ranged between 1.09 – 2.30 L·kg^{-1} on Chinese soils at room temperature.[6, 9] However, these values were derived at a single temperature under conditions that do not reflect those of rice fields in the Sacramento Valley.

This investigation aims to characterize the primary processes driving CAP air-water and soil-water partitioning under simulated California rice field conditions and to both identify the factors impacting those processes and to inform safe and economical farming practices prior to use. To accomplish this, K_H was calculated as a function of temperature and soil sorption and desorption were measured at 15, 25 and 35 °C on three rice field soils from the Sacramento Valley. The effects of increased salinity and pre-flood application of CAP on soil sorption were also investigated to derive sorption parameters relevant to its use in California.

Methods

Henry's Law Constant. K_H was calculated, rather than experimentally derived, due to the extremely low reported value (3.1×10^{-15} atm·m^3·mol^{-1}, 20 ˚C) and to mathematically define its variation based upon temperature.[6] K_H was calculated using vapor pressure and water solubilities derived at 15, 25 and 35 °C by methods developed by Sepassi et al. and Lee et al., respectively.

Soil-Water Partitioning. Soil was collected from three rice fields in the Sacramento Valley near Davis (Sacramento silty clay loam classified as a fine, smectic, thermic, cumulic Vertic Endoaquoll) and Richvale (Esquon Neerdobe clay series classified as fine, smectic, thermic Xeric Epiaquerts); soil collection and preparation were previously described by Mulligan et al.[10-11] Soil pH, texture, fraction of

Table 1. Soil Properties

Soil	pH	f_{oc}	f_{om}	CEC (meq/100g)	% Sand	% Silt	% Clay
Davis	6.81	0.0160	0.0394	37.9	11	42	47
Richvale (Unburned)	4.46	0.0120	0.0282	6.54	42	34	24
Richvale (Burned)	4.44	0.0184	0.0393	6.25	39	35	26

organic carbon (f_{oc}), fraction of organic matter (f_{om}), and cation exchange capacity (CEC) (Table 1) were characterized by the UCD Analytical Laboratory (methods available at anlab.ucdavis.edu).[12]

Sorption and desorption isotherms were derived using a batch equilibrium method.[13] Briefly, 5 g of soil was weighed into a 50 mL light safe polypropylene centrifuge tube to which 10 g of 0.01 M $CaCl_{2(aq)}$ was added for a final soil to solution ratio of 1:2 (w/w), the optimal ratio determined in preliminary studies. Samples were equilibrated on a MaxQ 6000 temperature-controlled shaker (200 RPM) (Thermo Scientific, Waltham, MA) overnight prior to spiking to initial concentrations of 0.02, 0.04, 0.08, 0.2, 0.4 or 0.8 $\mu g \cdot g^{-1}$ CAP in the aqueous phase. Four replicates of each spike level and three negative controls were prepared for each experiment. Preliminary hydrolytic controls showed that CAP was stable and did not sorb to centrifuge tubes or PTFE filters throughout the experiment (less than 4 % loss). Samples were shaken (200 RPM, 24 h) and centrifuged (3000 RPM, 1587g, 15 min) before the aqueous phase was collected for liquid-liquid extraction and replaced with fresh 0.01 M $CaCl_{2(aq)}$ solution for desorption experiments. Desorption experiments were shaken (200 RPM, 48 h) prior to centrifugation (3000 RPM, 1587g, 15 min) and liquid-liquid extraction of the aqueous phase. The experiment was repeated for each soil at 15, 25 and 35°C (± 1°C) using 0.01M $CaCl_{2(aq)}$. Additionally, sorption was assessed using 0.1 M and 0.2 M mixtures of aqueous NaCl, $CaCl_2$, $MgSO_4$ and Na_2SO_4 (10:1:2:1 mole ratio) at 25 ± 1°C to simulate California rice field aqueous salt compositions.[14]

Desorption after application directly to the soil was investigated on each soil at 25 ±1°C. Again, 5 g quantities of soil were weighed into 50 mL light safe polypropylene tubes. CAP in methanol was added drop-wise to the surface of the soil for initial CAP concentrations of 0.04, 0.08, 0.16, 0.4, 0.8 and 1.6 $\mu g \cdot g^{-1}$. Samples were left uncapped for 1 h to allow the methanol to evaporate before capping and shaking the tubes to ensure even CAP distribution. Aqueous 0.01 M $CaCl_2$ was then added for a soil solution ratio of 1:2 (w/w) and the samples were shaken and processed as above.

All aqueous phase extracts were stored at 4 °C prior to analysis by high pressure liquid chromatography tandem mass spectrometry (HPLC-MS/MS). The concentration of CAP sorbed to the soil was calculated from the concentration of CAP measured in the aqueous phase and the results were used to calculate the soil-water partitioning coefficient (K_d) and organic carbon normalized soil-water partitioning coefficient

(K_{oc}). Additionally, sorption and desorption isotherms were fit to the log transformed Freundlich equation.

Results and Discussion

Henry's Law Constant. The Henry's law constant of a compound can be determined from its vapor pressure and aqueous solubility. Constants greater than 10^{-5} atm·m^3·mol^{-1} indicate that a compound is volatile from water while those less than 10^{-7} atm·m^3·mol^{-1} indicate non-volatility.[15] CAP has a very low vapor pressure (6.3×10^{-12} Pa, 20 °C), low aqueous solubility (1.023 mg·L^{-1}, 20 °C) and reported calculated Henry's law constant of 3.1×10^{-15} atm·m^3·mol^{-1} at 20 °C.[6] The K_H calculated in this work was 3.54×10^{-16} atm·m^3·mol^{-1} at 20 °C, in agreement with the value reported by the EPA that CAP can be considered non-volatile from water at 20°C.

Temperature influences K_H via its impact on both the vapor pressure and water solubility of the compound. Through calculation of both vapor pressure and water solubility as a function of temperature, K_H was determined at temperatures relevant to California rice fields; calculated K_H for CAP at 15, 25, and 35°C are presented in Table 2. A van't Hoff plot (Figure 2) was constructed using the values from Table 2 in order to characterize the effect of temperature on K_H through determination of $\Delta_{vap}H$.

Table 2. Calculated Henry's Law Constants

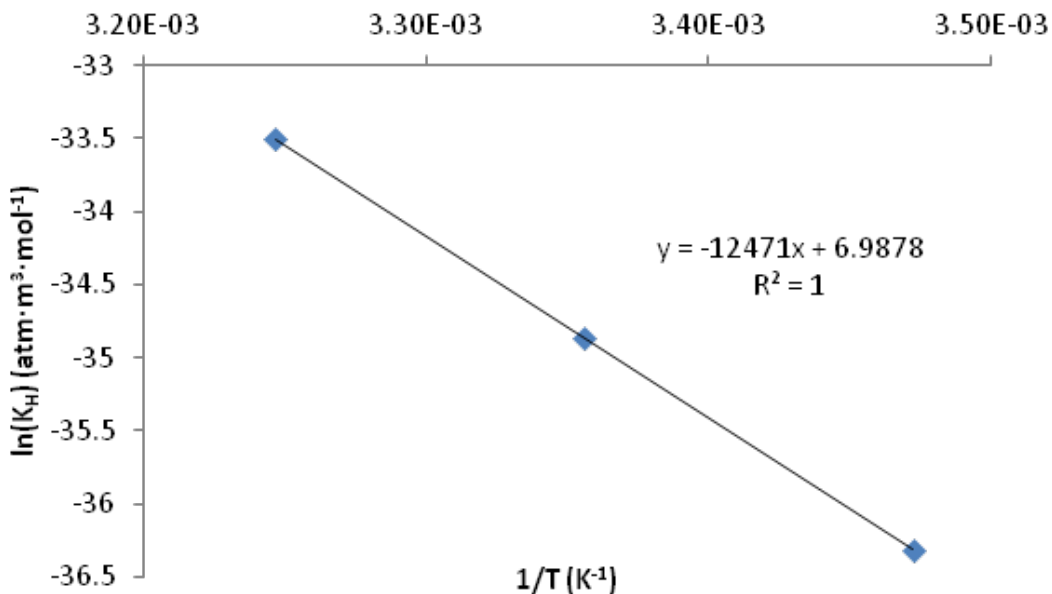| Temperature (°C)	K_H (atm·m^3·mol^{-1})
15	1.69×10^{-16}
25	7.24×10^{-16}
35	2.81×10^{-15}

Figure 2. Van't hoff plot for the determination of $\Delta_{vap}H$ from calculated Henry's Law constants.

The value of $\Delta_{vap}H$ calculated from the slope of the van't Hoff plot was 103.68 kJ·mol^{-1}, indicating that the excess enthalpy of vaporization is greater than the excess enthalpy of CAP in the liquid phase and that temperature will have a larger impact on the volatility, rather than solubility, of CAP. When $\Delta_{vap}H$ is 100 kJ·mol^{-1}, the K_H of a compound can be expected to change by factor of 4.1 per 10°C temperature increase.[16] K_H of CAP increased by an average factor of 4.25 per 10 °C temperature increase and by a factor of 79 over the total temperature range (5 – 35 °C). These results demonstrate that while temperature fluctuations cause considerable changes to the air-water partitioning of CAP that should be accounted for when determining its overall environmental fate, volatilization remains an insignificant means of CAP dissipation from California rice fields.

Soil Sorption. K_{oc}, K_F , and N for the sorption and desorption of CAP to rice field soils at 15, 25, and 35°C are presented in Table 3. Log(K_F) ranged from 0.61 – 0.95 and log(K_{oc}) ranged from 2.59 – 2.96; indicating low sorption affinity of CAP to soil. Richvale (Burned) log(K_F) were found to be significantly greater than the other soils (P < 0.0001), which could be attributed to the black carbon present after burning versus tilling the rice straw after harvest. Previous research showed that the amendment of 2% rice straw ash increased the Langmuir sorption maximum of 3-chlorophenol to Taiwanese soils by approximately 242% and that adding 0.5% red gum (*Eucalyptus* spp.) biochar into Chinese rice paddy soils increased the log(K_F) of CAP from 0.18 to 2.29.[17-18] A significant increase in sorption was seen between 15 and 35 °C (P = 0.0326) while no significant change was observed between sorption at 25 °C and both 15 and 35 °C. Therefore the soil-water partitioning of CAP could be significantly impacted by early growing season temperature fluctuations, however as the temperature stabilizes to daily fluctuations between 18 – 22 °C it is not expected to impact the sorption of CAP to California rice field soils.[19-20]

Table 3. Fruendlich parameters K_F (g/g), N, and R^2 for the sorption and desorption of CAP to California rice field soils (n=4).

Soil	Temperature (°C)	Log(K_{oc}) ± SE (g·g^{-1})	Sorption			Desorption			TII
			Log(K_F) ± SE	N ± SE	R^2	Log(K_F) ± SE	N ± SE	R^2	
	15	2.59 ± 0.01	0.66 ± 0.03	0.91 ± 0.02	0.990	1.45 ± 0.13	0.86 ± 0.05	0.944	0.05
Davis	25	2.80 ± 0.02	0.73 ± 0.04	0.84 ± 0.02	0.988	0.97 ± 0.26	0.61 ± 0.09	0.688	0.28
	35	2.69 ± 0.02	0.61 ± 0.04	0.86 ± 0.02	0.982	0.91 ± 0.07	0.83 ± 0.04	0.961	0.04
	15	2.93 ± 0.01	0.73 ± 0.04	0.85 ± 0.02	0.987	0.91 ± 0.10	0.77 ± 0.05	0.927	0.09
Richvale (Unburned)	25	2.59 ± 0.03	0.63 ± 0.02	0.94 ± 0.02	0.994	0.67 ± 0.04	0.81 ± 0.02	0.985	0.14
	35	2.86 ± 0.02	0.76 ± 0.04	0.91 ± 0.02	0.987	0.82 ± 0.06	0.81 ± 0.03	0.969	0.10
	15	2.79 ± 0.01	0.79 ± 0.05	0.86 ± 0.03	0.979	1.06 ± 0.11	0.79 ± 0.05	0.931	0.08
Richvale (Burned)	25	2.93 ± 0.03	0.95 ± 0.03	0.88 ± 0.02	0.991	1.00 ± 0.08	0.75 ± 0.04	0.953	0.15
	35	2.96 ± 0.04	0.92 ± 0.05	0.87 ± 0.03	0.982	1.20 ± 0.08	0.83 ± 0.03	0.965	0.04

Log (K_F) ranged from 0.63 – 1.06 for the sorption of CAP as a function of salinity (Table 4). An overall increase in sorption was observed as salinity increased with significantly greater log(K_F) measured once salt concentrations reached 0.2 M (P < 0.0001). This trend is consistent with the salting out effect observed for many neutral organic compounds wherein aqueous solubility decreases as salinity is increased resulting in an overall increase in sorption.[21-23] However, soil properties that impact sorption, such as conformational changes in humic substances and swelling or collapsing of the interstitial layers of clays, are also liable to change with aqueous salinity.[24-25] In this study log(K_F) differed significantly between all soil treatments when salinity was altered (P < 0.0001), however only the Richvale (Burned) soil was significantly different to the others when only temperature was altered. Enhancement in the effect of the soil treatments supports the argument that salinity is affecting soil properties relevant to the sorption of CAP. Interestingly, the Davis soil is characterized by higher clay content than the Richvale soils (47% versus 24 – 26%, Table 1) and an enhancement in the sorption of CAP to the Davis soil was not observed as strongly in response to increased salinity. While cation exchange on clays is not expected to influence the sorption of CAP (CAP is a neutral molecule at environmentally relevant pH) it is possible that the number of sorption sites on the surface of the Davis soil is diminished by the collapsing of clays at elevated salinities. However, further work specifically investigating the changes in these soils' structural properties in response to salinity changes should be done to prove this hypothesis. The deleterious effect of elevated salinity on rice yield in California has been well documented previously, and field water may be released without waiting for the mandatory hold time in the event that salinity exceeds 2.0 dS·m^{-1}.[14, 26] While overall sorption of CAP to rice field soils was moderately low, these results indicate that the quantity of CAP mobilized into the Sacramento River during an emergency release could vary significantly based upon changes to soil sorption caused by salinization.

Table 4. Fruendlich parameters K_F (g/g), N, and R^2 for the sorption of CAP to California rice field soils at 25°C with varying aqueous phase salinity (n=4).

Soil	Salinity (M)	Log(K_F) ± SE	N ± SE	R^2
	0.01	0.73 ± 0.04	0.84 ± 0.02	0.988
Davis	0.1	0.85 ± 0.03	0.97 ± 0.01	0.995
	0.2	0.83 ± 0.02	0.92 ± 0.01	0.995
	0.01	0.63 ± 0.02	0.94 ± 0.02	0.994
Richvale (Unburned)	0.1	0.89 ± 0.02	0.99 ± 0.01	0.996
	0.2	1.03 ± 0.03	1.04 ± 0.02	0.994
	0.01	0.95 ± 0.03	0.88 ± 0.02	0.991
Richvale (Burned)	0.1	1.03 ± 0.02	0.99 ± 0.01	0.998
	0.2	1.06 ± 0.03	0.98 ± 0.02	0.995

Because CAP is registered for pre-flood application to the soil surface, sorption was also investigated by applying CAP to the soil prior to the introduction of the aqueous phase. A significant increase in log(K_F) was observed, ranging between 0.88 – 1.24 and 0.63 – 0.95 for soil and aqueous applications respectively (P < 0.0001; Table 5). Increased contact time with soil has been shown to decrease desorption and extractability of organic compounds from soils; furthermore, evidence of the formation of non-desorbable pesticide residues was observed after 1 day of pesticide-soil contact.[27-28] In this study, an increase in the sorption of CAP was observed after only one hour of contact time with the soil prior to the addition of aqueous phase. Previous work observed a time dependent decrease in N and hypothesized that organic molecules were able to penetrate into the less accessible condensed regions of soil organic matter overtime.[29] An increase of N was observed when CAP was applied to soil rather than the aqueous phase that could indicate the sorption of CAP was increased due to the formation aggregates between CAP molecules on the soil rather than through penetration further into soil organic matter. However, this assessment is speculative as Freundlich isotherms alone cannot be used to determine sorption mechanisms.[30]

Table 5. Fruendlich parameters K_F (g/g), N, and R^2 for the desorption of CAP from California rice field soils at 25°C after application to the soil or aqueous phase (n=4).

Soil	Application	Log(K_F) ± SE	N ± SE	R^2
Davis	Soil	0.88 ± 0.032	0.98 ± 0.01	0.997
	Aqueous	0.73 ± 0.04	0.84 ± 0.02	0.988
Richvale (Unburned)	Soil	1.24 ± 0.03	1.10 ± 0.01	0.996
	Aqueous	0.63 ± 0.02	0.94 ± 0.02	0.994
Richvale (Burned)	Soil	1.14 ± 0.03	1.00 ± 0.01	0.996
	Aqueous	0.95 ± 0.03	0.88 ± 0.02	0.991

Desorption. Log(K_F), presented in Table 3, ranged from 0.67 – 1.45. While temperature did not significantly affect desorption, desorption log(K_F) were significantly different between soil treatments (P < 0.0001) and were observed to correlate with an increase in f_{om}. A decrease in desorption of CAP from soils correlated with f_{om} could be attributed to irreversible changes made to the structure of soil organic matter upon the initial sorption of CAP. Previous research implicated that pore deformation in soil organic matter could be a mechanism for increased hysteresis, or irreversible sorption, to soils.[31] The extent of sorption hysteresis was quantified using the thermodynamic index of irreversibility (TII) described by equation 10:[32]

$$TII = 1 - \frac{N_{desorb}}{N_{sorb}} \tag{10}$$

where N_{sorb} and N_{desorb} are the Freundlich exponents for sorption and desorption isotherms respectively. TII values near zero indicate that sorption is a reversible process while values approaching 1 indicate that the process is irreversible. Although K_F was not significantly impacted by temperature, calculated

sorption hysteresis on all soils was inexplicably greater at 25 °C than at 15 or 35 °C; evidence that the irreversibility of sorption to rice field soils may increase as the temperature stabilizes to fluctuations between 18 – 22 °C as previously described. However, in these experiments TII was 0.04 – 0.28, suggesting that overall sorption of CAP to these soils at all temperatures was reversible and that CAP has potential to mobilize into the Sacramento River with tailwater.

Pesticides in Flooded Applications Model (PFAM). The partitioning of CAP in a California rice field was simulated using PFAM along with the parameters generated by this work. Soil-water partitioning was modeled using the lowest and highest $\log(K_{oc})$ measured across all soil and temperature treatments (2.59 and 2.96, respectively; Table 3) and air-water partitioning was modeled using the Henry's law constant supplied by USEPA (3.1×10^{-15} atm·m^3·mol^{-1}) along with $\Delta_{vap}H$ (103.68 kJ·mol^{-1}) from this work. The simulated partitioning of CAP reached apparent equilibrium after 20 days and the average mass percentage ($\pm$SE) of CAP in the air, water, and soil compartments over the next 100 simulated days was 1.68 ± 0.11, 21.74 ± 0.10, and 76.58 ± 0.18 % and 0.97 ± 0.05, 11.45 ± 0.11, and 87.58 ± 0.05 %, for low and high $\log(K_{oc})$ simulations respectively. While the majority of CAP remained sorbed, an appreciable amount is predicted to mobilize into the aqueous phase as was expected based on the results obtained from batch equilibrium experiments. Though the K_H used in PFAM (3.1×10^{-15} atm·m^3·mol^{-1}) and determined in this work were significantly different, volatilization remained an insignificant transportation process of CAP from the modeled rice field. These results further support experimental evidence in this work, which suggest CAP will minimally sorb reversibly to rice field soil and is therefore likely to desorb and mobilize within an aqueous environment.

Objective III. Fate Modeling of Thiobencarb in Aquatic Systems Downstream from Rice Fields

Introduction

Thiobencarb (TB, Figure 1), the active ingredient of Abolish and Bolero, is a systemic pre-emergence carbamate herbicide used to control annual grasses and broadleaf weeds.[1] Approximately 84,000 acres of rice were treated with a total of 289,000 pounds of TB in California during 2013.[2] Abolish, an emulsifiable herbicide, can be applied directly to soil both pre-flood and after draining. Bolero, a granular herbicide, is applied to field water post-flood. In order to comply with the California MCL of 70 ppb and secondary MCL of 1 ppb in surface waters determined by the Office of Environmental Health and Hazard Assessment mandatory water hold times for treated fields of 30 days and 19 days for Bolero and Abolish respectively have been established. [3,4] Even with the implementation of hold times TB has been detected in Sacramento surface waters above the secondary MCL; [5] requiring that the environmental fate and regulations associated with TB be revisited.
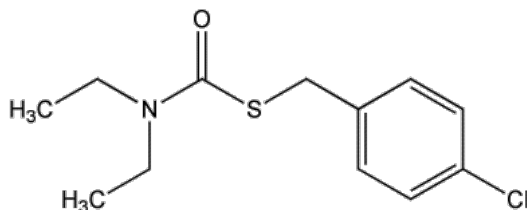

Figure 1. Structure of thiobencarb.

TB has moderate water solubility (30 µg/mL) and low vapor pressure (1.5×10^{-5} torr @ 20˚C) with a moderately high octanol-water partitioning coefficient (log K_{ow} = 3.4). Additionally, TB is acutely toxic to aquatic organisms and has been shown to bioconcentrate in some species of fish, clams, and shrimp.[1,6,7] Based on these properties TB is likely to adsorb to soils or remain partially in the aqueous phase depending on the soil properties at the site of application.

Results and Discussion

A method for the estimation of TB concentrations in the Calusa Basin Drain and Sacramento River was developed previously (see 2016 RRB report). Briefly, the Pesticides in Flooded Applications Model (PFAM) and the One Dimensional Transport with Inflow and Storage model (OTIS) were used in tandem to model the fate of TB in a rice field and nearby surface waters sequentially. While the combined model was capable of predicting TB concentrations in the Calusa Basin Drain, the concentration of TB in the Sacramento River could not be reliably estimated due to limitations inherent to the provided environmental monitoring data (Figures 2 & 3). Further validation of the model, necessary to extend its application to the prediction of TB concentrations at different locations or for different water flow conditions, is not possible without additional monitoring data.
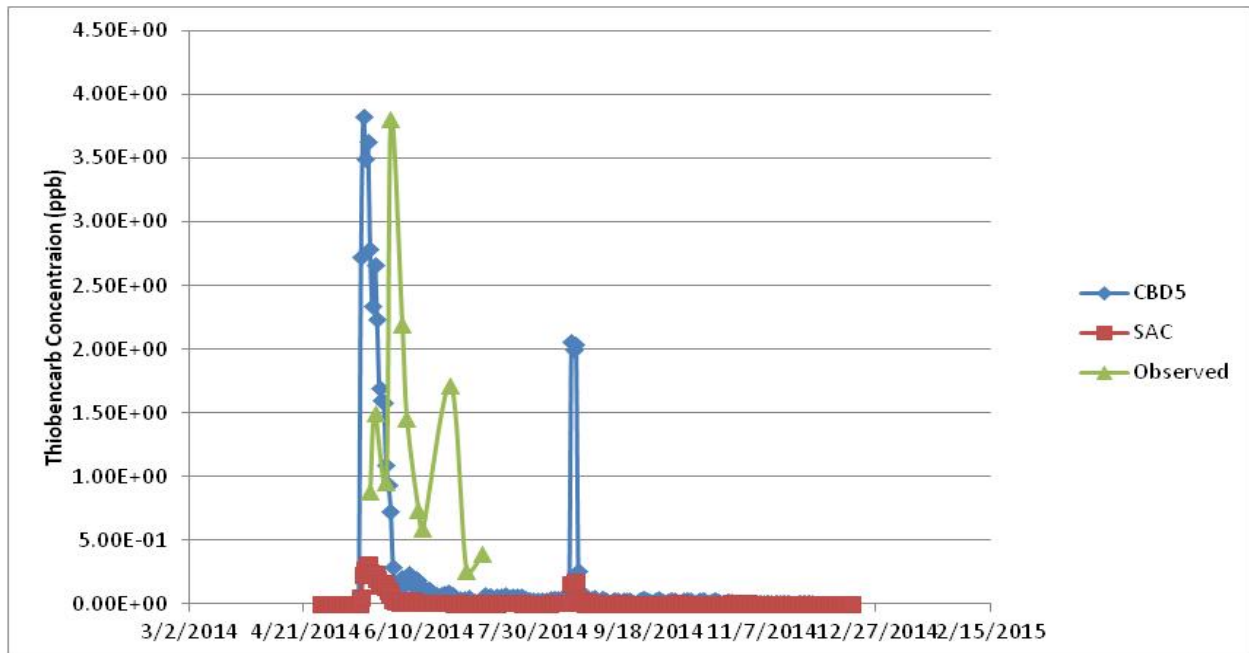

Figure 2. Predicted thobencarb concentrations and monitoring data collected at CBD5 for 2014.
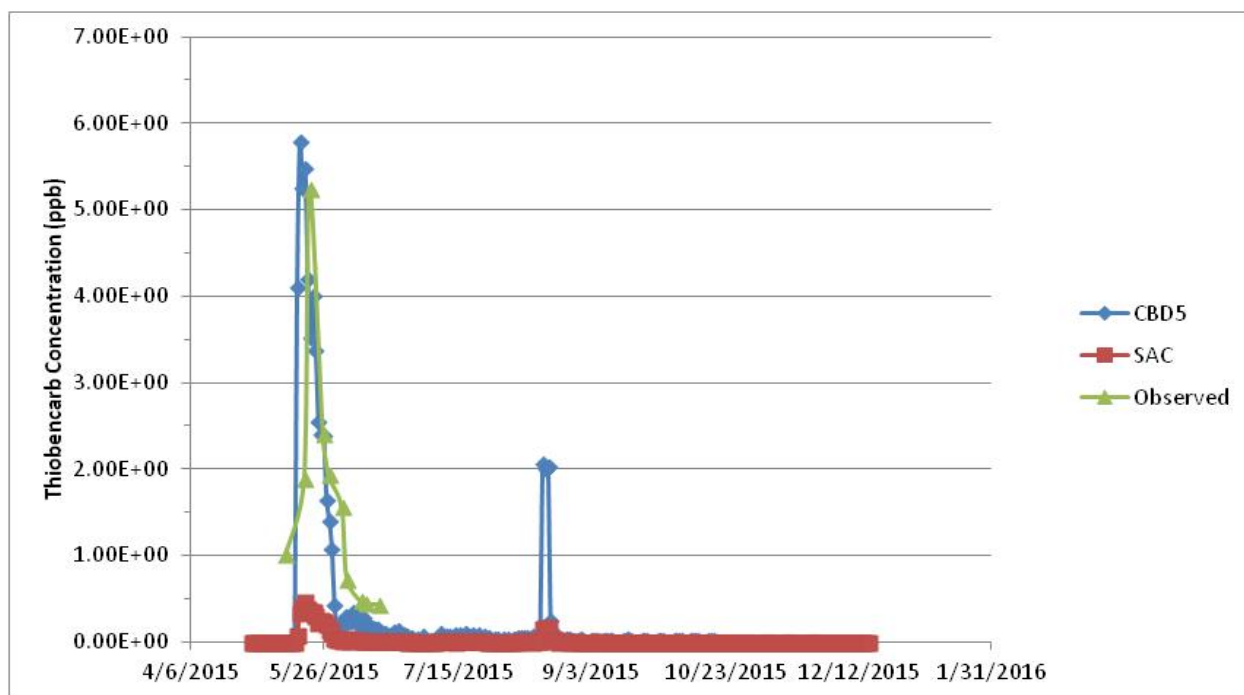
Figure 3. Predicted thobencarb concentration and monitoring data collected at CBD5 for 2015.

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SUMMARY OF 2017 RESEARCH (major accomplishments) BY OBJECTIVE:

Objective I. Aqueous photolysis is expected to play a significant role in the fate of aqueous BH, especially due to indirect processes. Light scattering in the water column is expected to significantly decrease the photolysis rate by as much as a factor of 2. A water holding period (20 d) was estimated based on experimental data using the Pesticides in Flooded Applications Model (PFAM). The majority of BH and its parent are expected to partition into the benthic sediments, where BH in particular appears to remain for a long period of time (> 100 d). The potential for long-term toxicity effects from sediments exposed to BH should be investigated further.

Objective II. Due to its calculated Henry's law constant volatilization is not expected to play a part in the dissipation of CAP from application sites. Soil-water partitioning experiments, corroborated by modeling results, indicate that CAP sorbs weakly to soil from water with some dependence on environmental factors such as temperature, salinity, and soil properties (detailed above). Further research should be conducted to characterize the environmental fate of CAP under simulated California rice field conditions under two categories: 1) photolysis on soil surfaces under dry and flooded conditions, and 2) aerobic and anaerobic soil microbial degradation.

Objective III. The model fits the data well for both years at the Colusa Basin Drain; however without additional monitoring data the model cannot be further validated to extend its application beyond the Calusa Basin Drain. Any future work would necessitate the collection of monitoring data at additional locations under varying flow conditions.

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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 contributing processes are investigated: volatilization to air, sorption (bonding) to soils, and degradation by either sunlight or soil microbes.

2. For Butte, photolysis in rice field water occurred rather rapidly and was sensitized by dissolved organic carbon. A water holding period of 20 days was also estimated using experimental fate data and the Pesticides in Flooded Applications Model (PFAM). This corresponds well with the recommended water holding time by the USEPA. Based on the model results, long term toxicity may be an issue for BH and its parent in rice field soil as soil dissipation of both compounds is slow.

3. For Coragen, calculation of Henry's law constant as a function of temperature has shown that volatilization is not expected to be a significant contributor to field dissipation, even at elevated temperatures. Furthermore, soil-water partitioning experiments showed that the sorption of Coragen to soils is a weak and reversible process impacted by environmental factors such as temperature, salinity, and soil properties. These results, corroborated by the Pesticides in Flooded Applications Model (PFAM), indicate that Coragen could mobilize into the Sacramento River with rice field tail water.

4. For thiobencarb (TB), a model capable of predicting TB concentrations downstream from rice fields based on application practices and water flow was developed in 2016 using the Pesticides in Flooded Applications Model (PFAM) and the One Dimensional Transport with Inflow and Storage Model (OTIS). Further validation or extension of the model's application

would first require the collection of additional monitoring data at additional locations under varying water flow conditions.