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Dissipation of Benzobicyclon and Benzobicyclon Hydrolysate in a Louisiana Rice Field

Xavier Poole

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DISSIPATION OF BENZOBICYCLON AND BENZOBICYCLON HYDROLYSATE IN A LOUISIANA RICE FIELD

A Thesis

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science

in

The Department of Environmental Sciences

by
Xavier Poole
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Abstract

Pesticide resistance in rice fields is an ongoing issue that has resulted in the development and use of pesticides with new modes of action. Benzobicyclon is the first registered hydroxyphenylpyruvate(HPPD)-inhibiting pesticide in the United States and has gained attention as a resistance management strategy to control weed pests in rice fields. Understanding the environmental fate and dissipation mechanisms of benzobicyclon is important due to the unique rotation of rice and crayfish in Louisiana on the same fields. Benzobicyclon persistence into the crayfish growing seasons may lead to unintended consequences for crayfish growth and production, assuming there is toxicity to crawfish. Multiple studies have investigated the dissipation of benzobicyclon in lab settings, but no published works have reported the dissipation of the pesticide in a field setting throughout a rice growing season. The environmental fate of benzobicyclon was tested in field studies spanning two rice growing seasons. Benzobicyclon and the principal degradation product, benzobicyclon hydrolysate, behaved as expected based upon their physical and chemical properties. Benzobicyclon partitioning favored sediment while the metabolite favored water with a slow partitioning of the metabolite into the water column as the parent degraded in sediment. Published literature on the dissipation mechanisms of benzobicyclon rarely mentions the dissipation of the pesticide by hydroxyl radicals. Hydroxyl radicals are an important mechanism in pollutant degradation but are rarely considered with other dissipation mechanisms. The hydroxyl radical rate constant of benzobicyclon hydrolysate was calculated and its influence modeled in an EXAMS2 simulation. A significant difference between benzobicyclon hydrolysate dissipation with and without the hydroxyl radical rate constant was observed in these simulations, with simulations including degradation by hydroxyl radicals more closely matching observed field behavior.

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1. Introduction

1.1. Background of the Study

Pesticides are substances used to control pests. There is a variety of pesticides to control a variety of pests. Pesticides are placed into different categories based on their target organism, for example, herbicides control weed pests, insecticides to control insect pests, and rodenticides to control mice and other rodent pests. Not all pesticides within a category elicit the same physiological change in its target organism. The physiological change a pesticide induces in pests is called the mode of action. The herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) mimics the compound auxin which is a growth hormone in plants. Exposure to 2,4-D results in uncontrollable growth and plant death. Atrazine binds to plastoquinone receptors in chloroplasts inhibiting photosynthesis. Both 2,4-D and atrazine control similar broadleaf weeds while using different modes of action.

Pesticide use has resulted in several issues for the world and these issues are still growing. The main issue associated with pesticide use is pesticide resistance. Pest species are developing resistance to pesticides. Continuous use of pesticides has artificially selected for pest populations that are largely resistant to the pesticide used against them. For example, glyphosate is a widely used herbicide and there are currently 38 weed species that are known to be resistant to glyphosate (45). Pollution and impacts on human health are other issues associated with pesticide use. Pollution from pesticides is associated with declines in non-target organisms and decreased water quality. Neonicotinoids are insecticides that have been linked to declines in honeybee populations due to the insecticide showing a high affinity for pollen and nectar in plants. Runoff from pesticide treated fields can impact the water quality of ground and surface water sources. Toxic responses to pesticides are a well known issue for the general public. Health impacts of pesticides to humans is a popular political and social issue when discussing pesticide use.

To counter the issues surrounding pesticide use it is important to understand the environmental fate of pesticides to determine any potential hazards and understand what environments or situations a certain pesticide would best be suited for. Learning the physical and chemical properties of a pesticide, the properties of the site being treated with the pesticide, and the mechanisms of dissipation for the pesticide are important when determining the environmental fate.

Benzobicyclon is a paddy-bleaching herbicide that hydrolyzes into its primary metabolite and active form, benzobicyclon hydrolysate. The pesticide was developed by SDS Biotech K.K and recently received federal section 3 registration and state registration in California (1). First registered for use in Japan in 2001, it has recently gained attention for use in Louisiana to control local weed species such as jungle rice, ducksalad, and certain species of perineal grasses. Rice weeds are highly competitive with rice and can lead to reductions in crop yields and quality. Benzobicyclon has been shown to control different weeds at different application rates. For example, benzobicyclon controlled the rice weed ducksalad with an efficiency of 93% at the highest application rate, while other tested weeds such as yellow nutsedge, barnyard grass, and false pimpernel were controlled with 50% efficacy at the highest application rate (2). This pesticide efficacy study was done with only one application of the pesticide.

The efficacy of a pesticide is mainly related to its properties and environmental behavior. Studies have been conducted to assess the primary mechanisms and kinetics of benzobicyclon hydrolysis and photolysis under varying environmental conditions. Hydrolysis and photolysis have been shown to be major modes of dissipation in water for benzobicyclon and its principal degradation product, benzobicyclon hydrolysate, respectively (4,5). Other studies have been conducted on benzobicyclon translocation into rice and its toxicity to various rice species. Previous work has shown minimal uptake of benzobicyclon by rice however, another study

demonstrated toxicity to certain *indica* rice cultivars (1,2,7,26). Louisiana rice production is unique in that rice fields rotate rice and crayfish production on the same fields in alternating seasons, leaving fields flooded for several months. Thus, there is concern with the use of any pesticide whose residues could persist into subsequent seasons and impact crayfish production. While there have been studies investigating pesticide efficacy and reactions involving benzobicyclon, there is currently no published work reporting the dissipation of benzobicyclon in the field. Controlled laboratory studies have been conducted on the dissipation of the pesticide, but no field studies have been reported for the parent compound or its principal degradant, benzobicyclon hydrolysate.

A primary reason for interest in benzobicyclon use is its application in the growing issue of weed resistance to pesticides. Pesticides sometimes lose efficacy over successive seasons of use due to pests that adapted a resistance to the compounds. Rice weed pesticide resistance is a fairly common issue, especially for pesticides classes with modes of action at a single enzyme target. The first documented case of weedy rice pesticide resistance came from Arkansas in 2002 with resistance to imidazolinone herbicides (6). Crop rotation, pesticide cycling, introducing new pesticides, and creating an integrated pest management program are some of the common practices implemented to prevent pesticide resistance. Finding pesticides with different modes of action has driven benzobicyclon investigations in the United States as benzobicyclon is set to be the first 4-hydroxyphenylpyruvate enzyme-inhibiting pesticide to be commercially available in this country (6). Benzobicyclon inhibits the 4-hydroxyphenylpyruvate dioxygenase (HPPD) enzyme in weeds, leading to chlorophyll depletion and cell death (3). HPPD in eukaryotic organisms leads to the production of acetyl CoA, tocopherols, and plastoquinones which are important for plant growth as well as photosynthesis. In mammals, HPPD is a key enzyme in the

catabolism of tyrosine and inhibition of HPPD can lead to elevated blood tyrosine concentrations (14).

Based on reported laboratory-measured physical and chemical properties, it was hypothesized the parent compound, benzobicyclon, would be found in higher concentrations in the sediment and the primary metabolite, benzobicyclon hydrolysate, would be found in greater concentrations in water. A key question was the persistence of benzobicyclon hydrolysate, as laboratory studies supporting its registration suggested it was persistent in water, potentially persistent in sediment and soil, and inconclusive about its persistence in field dissipation experiments (42). It was further hypothesized indirect photodegradation processes would contribute to its degradation (42). Recalcitrance of benzobicyclon hydrolysate would be amplified by sorption of benzobicyclon to sediments and leaching of adsorbed benzobicyclon as benzobicyclon hydrolysate back into the water column.

1.2. Objectives

This current study has several objectives intended to better characterize benzobicyclon dissipation:

- I. Measure the dissipation of benzobicyclon and benzobicyclon hydrolysate in sediment and water following application to experimental rice fields over two Louisiana rice growing seasons.
- II. Measure the hydroxyl radical rate constant of benzobicyclon hydrolysate.
- III. Use existing exposure models simulating pesticide partitioning and degradation in rice fields to estimate the significance of the hydroxyl radical rate constant to the dissipation of benzobicyclon hydrolysate.

2. Literature Review

2.1. Hydrolysis of Benzobicyclon

Understanding the dissipation of benzobicyclon in rice paddies requires an understanding of the rice paddy environment. Rice paddies are flooded for rice production therefore, hydrolysis is a major dissipation mechanism for pesticides susceptible to this process. It is generally accepted through observation and research studies, the hydrolysis of pesticides primarily follows a first-order kinetics (31). First-order kinetics depend mainly on the concentration and the hydrolysis rate constant of the compound. Hydrolysis can be categorized into neutral, acid-catalyzed, or base-catalyzed reactions. Different chemical classes of pesticides hydrolyze at different rates under neutral, basic, or acidic conditions. Esters, pyrethroids, amides, and carbamates are considered relatively stable under environmental conditions but they hydrolyze at accelerated rates under alkaline conditions. Triazine and sulfonylurea herbicides have shown increased hydrolysis rates under acidic conditions (31).

Flooding soils in rice production results in significant changes in the physicochemical and biological characteristics of the soil (31). Paddy soil types and temperature have also been observed to play significant roles in the hydrolysis of pesticides. Studies with the insecticide methyl parathion show hydrolysis is the only observed degradation mechanism in flooded laterite soil and soils high in iron and aluminum content (31). In acid sulphate soil, methyl parathion was observed to degrade by hydrolysis and nitro-group reduction. On average, pH has been shown to cycle daily in rice paddies within a range of 6-8 with pH higher at noon and lower at midnight from carbonate cycling due to photosynthesis and respiration (28). Fluctuations in diurnal hydrolysis rates can be attributed to changes in pH. Understanding if a pesticide is more susceptible to base or acid-catalyzed reactions can help determine when higher or lower hydrolysis rates are expected.

Dissolved organic matter (DOM) content in rice paddies ranges between 8-12% (28). The effect of DOM on abiotic hydrolysis was investigated with the pesticides chlorpyrifos, atrazine, diazinon, methyl-parathion, and simazine (30). The effect of DOM on the hydrolysis of chlorpyrifos was significant with hydrolysis rates diminishing by 32% in the presence of high concentrations of DOM (34.5 mg/L) (29). This is thought to be due to chlorpyrifos binding to organic matter. Rice paddies have been shown to have higher concentrations of dissolved organic matter than other fresh waterbodies, such as rivers and lakes (4). Chlorpyrifos and the other pesticides hydrolyzed at varying rates over a pH range of 4.5-8. Estimated half-lives for chlorpyrifos and other pesticides range from 1-2 days to over a year depending on the pesticide (29). The influence of water and soil pH was also investigated in this study however, only the pesticides in water showed significant changes in dissipation with changing pH. Adsorption to sediment is believed to be an inhibitor to hydrolysis.

The half-life for benzobicyclon hydrolysis was measured in controlled lab settings at several temperatures and the half-life of benzobicyclon was measured to be 16 hours at 25°C and pH 7 (5). The temperatures in southern Louisiana during the summer can range from 26-34°C on average. Benzobicyclon hydrolysate has an estimated aqueous solubility of 113 mg/L and a DT₅₀ of 88 to 113 days depending on soil profile and environmental conditions. The half-life of benzobicyclon has a reported negative correlation with temperature and pH (3). Benzobicyclon has shown to adsorb to sediment with higher affinity than benzobicyclon hydrolysate. Benzobicyclon has a reported mean K_{oc} of 15,908 while benzobicyclon hydrolysate has mean K_{oc} of 1,421 (15). The hydrolysis reaction has been proposed as a base-catalyzed 1,4 nucleophilic addition with a thiophenol leaving group (5).

In sediment-water systems there is a general assumption hydrolysis will not occur while the organic compound is in the sediment-sorbed state. Pesticides are believed to be in rapid

equilibrium between sediment and aqueous phases and hydrolysis occurs only through the aqueous phase (17). Lipophilic substances, like benzobicyclon, tend to adsorb strongly to organic matter and sediment. Studies have shown that compounds adsorbed to sediments hydrolyze, on average, at reduced rates; water and sediment hydrolysis rates were compared and hydrolysis of sediment-sorbed pesticides were roughly 10 times slower (17). Controlled studies of benzobicyclon hydrolysis in water have shown 100% conversion to benzobicyclon hydrolysate within 48 hours in controlled settings (5).

A study by Vebrosky et al. (2018) assessed the impact of sediment on benzobicyclon hydrolysis (41). Water-sediment mesocosms, composed of sediment collected from rice fields in Crowley, LA, seawater, and distilled water, tested sediment influence on dissipation. The study also determined differences in pesticide dissipation in trials with seawater and distilled water. Similar to the study by Williams et al. (2018) where 100% conversion of benzobicyclon was seen in 48 hours, water column concentrations of benzobicyclon dropped below detectable levels within 48 hours. Both the seawater and distilled water trials showed undetectable water column concentrations of benzobicyclon at 48 hours. Dissipation of benzobicyclon in sediment was slower than in the water column. Detectable levels of benzobicyclon in sediment were found through the entire trial period for both the seawater and distilled water trials. There were no discernable differences in benzobicyclon concentrations in sediment between the seawater and distilled water mesocosms. These data support the hypothesis that sediment does not significantly impact benzobicyclon hydrolysis in the water column however, sediment can act as a reservoir for benzobicyclon slowing benzobicyclon dissipation.

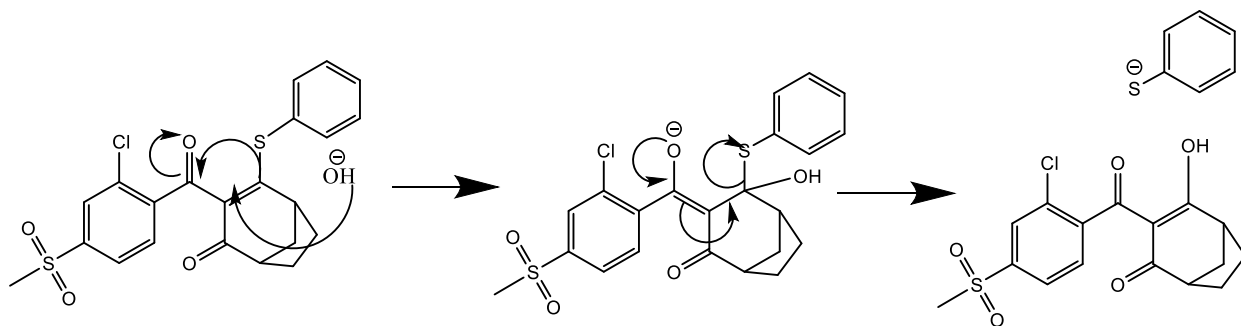


Figure 2.1. Redrawing of proposed transformation of Benzobicyclon to Benzobicyclon Hydrolylate via a base-catalyzed 1,4 nucleophilic addition mechanism (5).

Temperature and pH positively correlate with the hydrolysis rate of benzobicyclon.

Williams and Tjeerdema tested the effects of temperature and pH on benzobicyclon hydrolysis using temperatures ranging from 15°C to 35°C and pH ranging from 4 to 9 (year here).

Benzobicyclon hydrolysis under basic conditions was significantly faster while acidic scenarios were significantly slower. This finding supports benzobicyclon hydrolysis as a primarily base-catalyzed reaction. Dissolved organic matter (DOM) has been shown to negatively influence base-catalyzed hydrolysis rates (5). Above pH 4, acidic functional groups in DOM in the water are expected to deprotonate at carboxylic acid functional groups giving sediment an overall negative charge. The negative charge repels hydroxyl ions, potentially deterring hydrolysis. Field water from the Williams and Tjeerdema study in California was pH 8. Results from the field experiments were expected to mimic studies conducted with pH 9 water however, results are similar to pH 7 results. These findings support DOC potentially inhibiting base-catalyzed hydrolysis in rice fields. The pH of rice field water tested in the current Louisiana study is similar to California rice water pH described by Williams and Tjeerdema. Similar influences of DOC on benzobicyclon hydrolysis are expected in Louisiana.

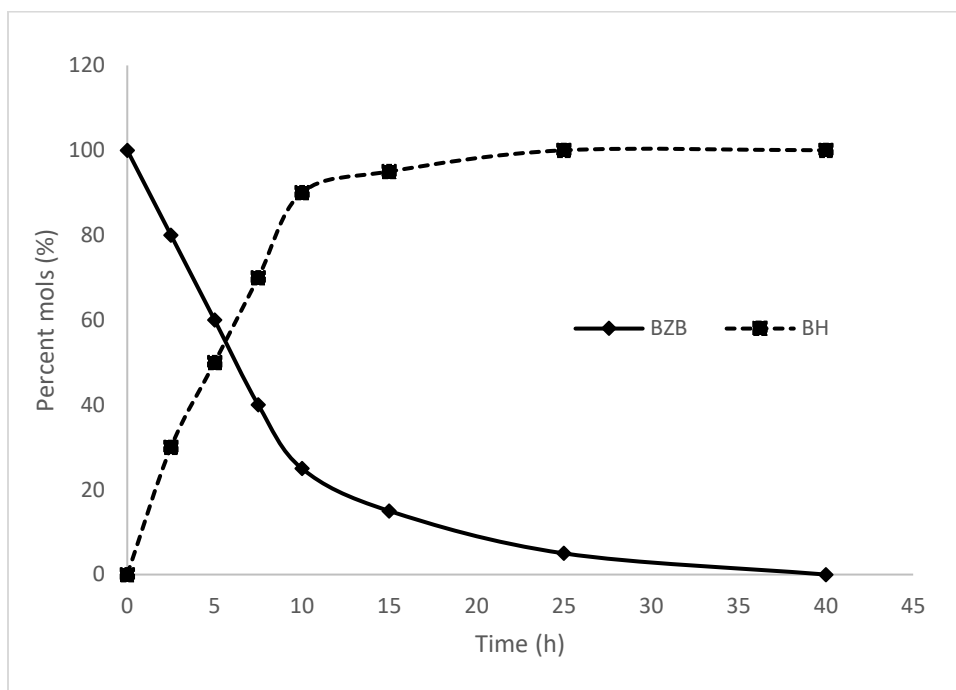


Figure 2.2. Conversion of benzobicyclon to benzobicyclon hydrolysate in pH 9 buffer at 35°C (5).

Other substances in water, such as dissolved clay species and metal species, could also potentially influence benzobicyclon hydrolysis (5). Montmorillonite, kaolinite and vermiculite are minerals found in clay. Studies performed to understand the effect of clay on the hydrolysis kinetics of pesticides showed the effects are not significant; when clay is saturated with water, the influence on hydrolysis is reduced further (17,18). Inhibition of hydrolysis due to dissolved metals is possible but unlikely according to current literature. Chelating compounds or nucleophiles can influence hydrolysis by bringing the reactants closer to each other for increased reaction or stabilize the leaving group to prevent reactions (18). In the case of benzobicyclon, the carbonyl oxygen and thiophenyl sulfur are poor ligand donors and the surrounding functional groups are bulky, preventing complexation. Furthermore, studies reported the catalysis of hydrolysis in basic conditions were observed more often than inhibition (5,7,19). Hydrolysis rates of benzobicyclon decreased as temperature decreased. Half-lives ranged from 5-8 hours at

35°C to 28-38 hours at 15°C (5). Base and acid-catalyzed hydrolysis rates increased with temperature, showing an overall increase in hydrolysis due to temperature.

2.2. Sediment Dissipation of Benzobicyclon

Dissipation in sediments and soils typically occurs through anaerobic and aerobic respiration. Due to the periodic flooding of rice fields, pesticides are potentially exposed to both types of respiration. Temperature, pesticide degradation, and microbial activity have all shown positive correlations with each other for soil dissipation (3). Microbial activity in sediment also correlates with pesticide dissipation, increasing as temperatures increase but slowing when optimal temperatures are exceeded. Fluctuations in temperature could impact microbial activity and pesticide dissipation due to respiration. Studies in California have reported changes in pesticide dissipation along with microbial activity as temperatures change (20,21). The relationship between pesticide and microbial activity could be indirect as they are both impacted by temperature. Another study by Williams et al. looked into the dissipation of benzobicyclon hydrolysate in sediment. Sediment samples taken from rice fields in California were used in microcosms under aerobic and anaerobic conditions. The unaltered and aerobic samples showed faster rates of degradation than autoclaved and anaerobic samples. The results of this study support the impact of microbial activity on the degradation of benzobicyclon hydrolysate. The metabolites of benzobicyclon hydrolysate formed from soil dissipation were not characterized, however potential metabolites were modeled from the dissipation of sulcultrione, a structurally similar triketone compound (3).

Pesticide applications have been shown to influence soil chemistry, microbial diversity, and abundance in sediments and soils. A study analyzing the impact of the herbicide butachlor on microbial populations, respiration, nitrogen fixation and nitrification found increased growth rates of anaerobic hydrolytic fermentative bacteria, sulfate-reducing bacteria and denitrifying

bacteria in the presence of butachlor. The changes in microbial growth rates and soil chemistry varied with the concentration of butachlor and the days after treatment (34). These studies were not performed with Louisiana rice fields, but give some insight into how microbes, sediment, and temperature interact with pesticides and methods to potentially study benzobicyclon degradation by Louisiana rice field microbes. Other potential studies analyzing DOM, pH, temperature and sediment composition in the water and sediment in Louisiana rice fields could characterize how the pesticide partitions and dissipates.

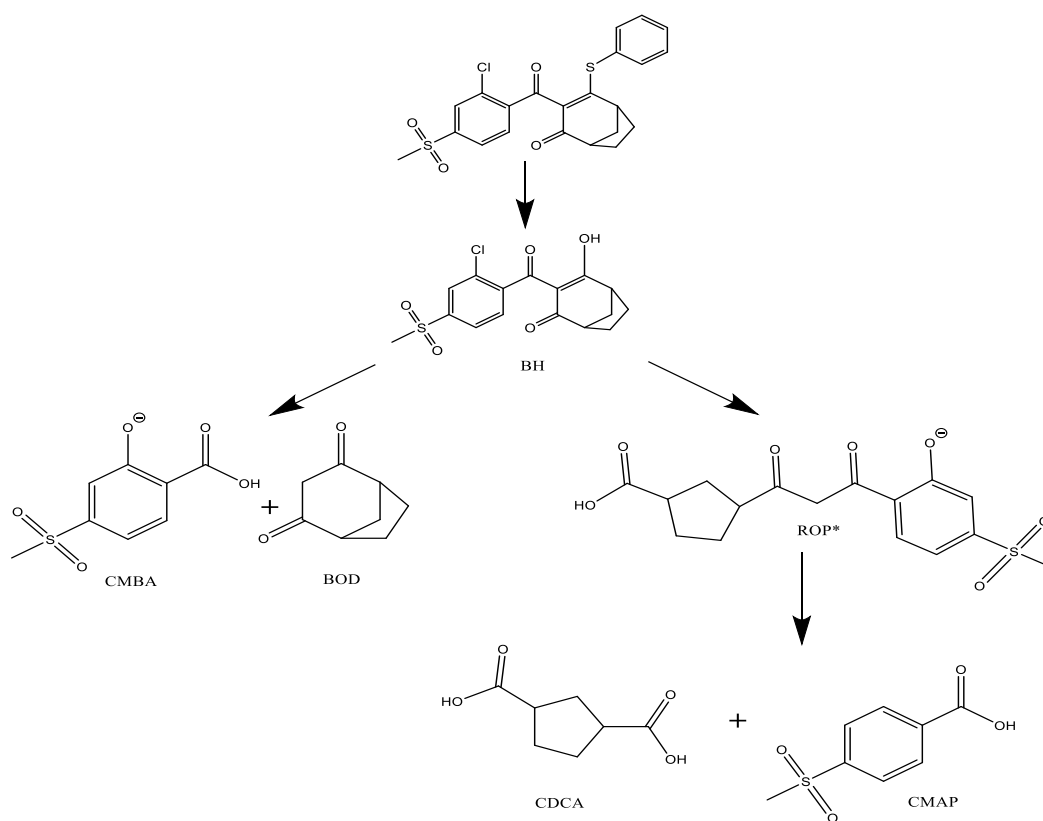


Figure 2.3. BH formation and hypothesized degradation pathways in soil based on previous research with a similar herbicide, sulcotrione (from Williams) (3).

2.3. Photolysis of Benzobicyclon Hydrolysat

Chemical degradation by direct and indirect photolysis is an important degradation route in rice paddies chemistry. The water in a rice paddy is shallow, varying in depths from 3-12 cm,

and well-lit, allowing for light penetration through the water column and onto the sediment-water interfaces. Direct photolysis occurs when compounds absorb light energy. The wavelength of natural sunlight reaching the earth is around 290 nm therefore, pesticides must be able to absorb that and higher wavelengths to undergo direct photolysis. Benzobicyclon and benzobicyclon hydrolysate absorb radiation between 250 and 400 nm indicating they are capable of degrading by direct photolysis (41). Indirect photolysis in rice paddies can occur through formation and reactions with hydroxyl, carbonate radicals, and singlet oxygen. These reactive species are formed from a variety of sources such as humic and fulvic substances from soil as well as certain amino acids. All of these have been shown to produce oxidants and reductants in paddy water (33). In some cases, compounds commonly found in paddy water have been shown to accelerate photolysis rates of pesticides. A study investigating the photolysis of isoprothiolane showed the fungicide dissipated at accelerated rates in the presence of riboflavin, a vitamin commonly found in green vegetables and grains (32). Photolysis studies of benzobicyclon hydrolysate have shown multiple potential photolysis products that varied with the ionic state of benzobicyclon hydrolysate. Benzobicyclon hydrolysate has been shown to be relatively stable to hydrolysis but able to degrade via photolysis. Benzobicyclon hydrolysate can produce various metabolites from photolysis, the metabolites formed depending upon the ionic state of the hydrolysate (4).

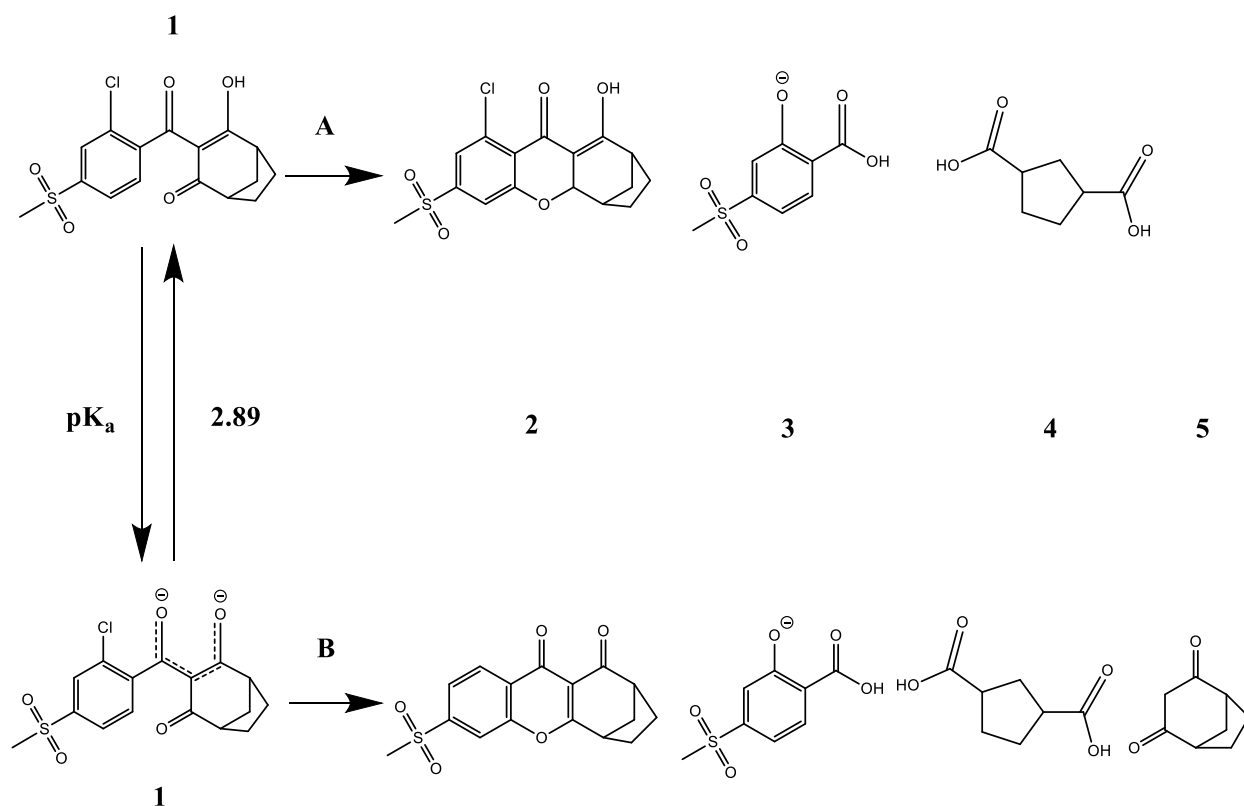


Figure 2.4. Detected photolysis products for both Benzobicyclon-Hydrolysate species: (A) neutral and (B) anionic from Williams et al, 2017.

The toxicity of these metabolites has not been extensively investigated. Compounds similar to two of the metabolites formed from benzobicyclon hydrolysate photolysis were studied for their effects on certain species of algae, protozoa, and bacteria. Toxic effects were seen only in the algae from one of the metabolites (22). The half-life of benzobicyclon hydrolysate in rice field water varied from 11-80 days depending on the time of year/light intensity. The 80-day half-life was determined under natural sunlight between the months of August and September, outside of the typical Louisiana rice season (4).

As previously discussed, dissolved organic matter has been shown to correlate positively with photolysis of benzobicyclon hydrolysate (4). In a study by Williams et al. (2018) rice field water was analyzed for its DOM content; results showed rice field water contained higher

concentrations of DOM than Sacramento River water and high purity water (4). These studies were performed in California and the natural sunlight assays were conducted in the time of the year that would be the end of rice season in Louisiana. Performing dissipation studies under natural sunlight in a Louisiana rice field environment and during rice season is necessary to understand if benzobicyclon acts similarly under Louisiana environmental conditions compared to California.

A study researched the photolysis of benzobicyclon and benzobicyclon hydrolysate in irradiated water-sediment mesocosms (44). Water-sediment mesocosms were created using seawater and distilled water. Mesocosms were exposed to artificial light simulating natural sunlight and the other trials were kept in complete darkness. Half-lives of benzobicyclon hydrolysate in the mesocosms varied between seawater and distilled water trials. Distilled water half-lives averaged 35 hours while seawater half-lives averaged 25 hours. Photolysis of benzobicyclon hydrolysate solely in the aqueous phase was also studied. In this portion of the study, distilled water, seawater, filtered and unfiltered rice water trials were conducted. Seawater showed the fastest dissipation rates with half-lives averaging 3.4 hours. Dissipation in unfiltered rice water was faster than filtered rice water with average half-lives of 34 hours and 38 hours respectively. Benzobicyclon hydrolysate half-lives were slowest in distilled water with an average half-life of 78.1 hours. Filtered rice water likely contains less DOM and other substances that produce reactive species for indirect photolytic processes. This leads to slower degradation rates of benzobicyclon hydrolysate. The low half-lives seen in the seawater trials are likely due to the influence of ions on benzobicyclon hydrolysate along with indirect photolysis and direct photolysis. Ion interactions with benzobicyclon may be more reactive than DOM and other components in filtered rice water due to how much faster benzobicyclon hydrolysate dissipates in seawater.

2.4. Hydroxyl Radical Rate Constants

Degradation by hydroxyl radicals is an indirect photolysis reaction. Hydroxyl radicals act as strong oxidants in the degradation of organic substances (11). Studies have provided evidence that hydroxyl radicals are formed by the photolysis of organic matter, nitrite, nitrate as well as in waters containing sufficient metal concentrations through ligand-to metal charge-transfer reactions (35). The direct photolysis of dissolved organic matter is another route of hydroxyl radical formation (35). Aqueous nitrate photolysis has been shown to occur at wavelengths equal to or greater than 295 nm. Nitrate reacts with UV radiation forming nitrite and singlet oxygen. Nitrite can also undergo photolysis forming singlet oxygen and nitrous oxide. The singlet oxygen then reacts with water forming hydroxide and hydroxyl radicals (36).

Metal substances such as iron can produce hydroxyl radicals in a wide variety of environments via the Fenton reaction (37). Iron (Fe^{2+}) is oxidized by hydrogen peroxide forming hydrogen peroxide and hydroxyl radicals. Oxidized iron is reduced back to Fe^{2+} and reused in indirect photolysis reactions (37). Various ores such as magnetite, goethite, and hematite have been shown to work as catalysts for Fenton reactions. The better catalyst, magnetite, contains a combination of Fe^{2+} and Fe^{3+} oxidative states. Fe^{2+} has been shown to be more reactive in hydroxyl radical formation processes than Fe^{3+} (37). Ores containing both oxidative states of iron however have an overall higher hydroxyl radical production rate.

DOM acts similarly to nitrates and iron, absorbing light energy to indirectly photodegrade organic compounds and inorganic compounds (i.e. water via production of hydroxyl radicals) (38). The pathways described for nitrates, iron Fenton reactions, and DOM are simplistic pathways of hydroxyl radical formation as there are several intermediate species such

as singlet oxygen, reactive oxygen species, carbon dioxide radicals, and chromophoric dissolved organic matter that are key to producing hydroxyl radicals (39). The combination of hydroxyl radical formation and reaction processes allow for a steady-state concentration of hydroxyl radicals in aquatic systems. Various studies have assessed the steady-state concentration of hydroxyl radicals in freshwater sources and they range between 10^{-17} - 10^{-15} M, with higher concentrations in more eutrophic water bodies and lower concentrations in clear oligotrophic lakes. Hydroxyl radical steady-state concentrations vary with the size of the photic zone, depth, and concentrations of its precursors (38). Deeper and darker waters contain lower levels of hydroxyl radicals than shallow well-lit water.

Degradation by hydroxyl radicals is studied for use in aquatic remediation due to the high reactivity of hydroxyl radicals with organic contaminants (8,9). Crude oil constituents, such as DBT (dibenzothiophene) and some of its derivatives, have been studied to understand their susceptibility to hydroxyl radical dissipation in aquatic systems (8). This study measured the hydroxyl radical rate constant by competition kinetics, likely the best means to characterize the hydroxyl radical rate constant of benzobicyclon hydrolysate. Pesticide degradation by hydroxyl radicals produced in natural waters is an important dissipation mechanism, significantly impacting the overall dissipation pathway. For example, degradation by hydroxyl radicals is estimated to account for 15% of the degradation profile of pesticides under certain conditions (9). Shallow, well-lit waterbodies are expected to show the highest rates of hydroxyl radical degradation due to higher levels of hydroxyl radical production. Contaminants in any clear waterbody show some level of hydroxyl radical degradation.

Assessments on the mechanisms of hydroxyl radical dissipation with other dissipation processes have rarely been conducted (9). Studies simulating the dissipation of pesticides using computer modeling software that included dissipation by hydroxyl radical successfully predicted

partitioning and dissipation of compounds as compared to actual field data. EXAMS2 modeling of bensulfuron methyl and azimsulfuron dissipation and partitioning in rice fields showed similar results to field data when the hydroxyl radical rate constant was included in the model (23).

These studies support the importance of the hydroxyl radical rate constant in how contaminants will degrade in aquatic systems (12). In order to build a complete degradation profile for benzobicyclon in water, the various modes of degradation of the pesticide must be characterized.

Hydroxyl radical dissipation is an important contributor to aquatic dissipation, therefore measuring the rate constant for benzobicyclon hydrolysate is important to properly conduct an exposure assessment. There is currently no rate constant value available in literature as its measurement is not a required property in support of pesticide registration with the US EPA.

3. Materials and Methods

Benzobicyclon (99.3%) and benzobicyclon hydrolysate (99.6%) were received as a generous gift from Gowan Company, LLC. 2,4-Dichlorophenoxyacetic acid (98.3%) was purchased from Chem Service. Catalase from bovine liver to quench residual hydrogen peroxide (10,000-40,000 units/mg protein) and benzoic acid (99.5%) were purchased from Sigma-Aldrich (St. Louis, MO). Hydrochloric acid (37%), 0.45 μm PTFE syringe filters, and sodium phosphate dibasic were purchased from Fisher Scientific (Hampton, NH). All solutions were prepared with HPLC-grade water and acetonitrile from VWR (Radnor, PA).

3.1. Hydroxyl Radical Rate Constant Measurement

The hydroxyl radical rate constant was measured for benzobicyclon hydrolysate via competition kinetics in distilled water at pH 7 following the method of Sarajampour et al., 2017 (8). Acetophenone and benzoic acid, compounds with known hydroxyl radicals rate constants were used as the competitors (reference compounds) for this study. Equimolar concentrations (0.03M) of the hydrolysate and benzoic acid or acetophenone as the reference compound were dissolved in phosphate buffer (20 mM) and placed into borosilicate glass vials. Hydroxyl radicals were generated from the irradiation of hydrogen peroxide (H_2O_2). The concentrations of H_2O_2 varied in each vial at 0 mM, 0.5 mM, 1 mM, 3mM, 5 mM, 10 mM, and 20 mM. Triplicates of each mixture were irradiated at 65 W/m^2 for 30 min using an Atlas SUNTEST XXL++ Environmental Exposure Chamber. The aqueous samples were analyzed for residuals of the hydrolysate and competitor by HPLC using an Agilent 1260 Infinity HPLC with a ZORBAX C-8 Eclipse Plus Analytical 4.6 x 150 mm 5 μm column using a water, formic acid, and acetonitrile gradient mobile phase. The analytes were measured using photodiode array detection at 280 nm for analysis of benzobicyclon hydrolysate, acetophenone, and benzoic acid (5,7,19). Several controls were used to ensure only hydroxyl radical dissipation was occurring during this study or

quantify the impact of other dissipation mechanisms. The first control was not irradiated and contained benzobicyclon hydrolysate and one of the reference compounds. This control was analyzed at the beginning and the end of the HPLC sequence to determine if degradation of the hydrolysate or the reference compound was occurring while the compounds were in each other's presence. The first control was used as the baseline for quantifying degradation rates of the other samples. The second control was irradiated and contained the hydrolysate, the reference compound, and hydrogen peroxide at 20mM in an amber vial to understand if any reactions were occurring between hydrogen peroxide and the other compounds in the sample. The third control contained the hydrolysate and reference compound in a clear vial. The third control contained only the hydrolysate and reference compound and was irradiated to test if direct photolysis reactions were occurring. Quality assurance studies were conducted to ensure the method was conducted properly and the results were reproducible. The quality of the method was tested by calculating the hydroxyl radical rate constant of a pesticide with a known rate constant. The rate constant for 2,4-D was calculated using benzoic acid as the reference compound and the calculated rate constant was within the range of rate constant values for 2,4-D in literature.

3.2. Field Dissipation

The dissipation of benzobicyclon was measured in conjunction with field tests to assess the potential for injury to various rice cultivars at higher application rates. Thus, benzobicyclon was applied once at three times the normal application (736 g/ai) by handheld boom sprayers to rice fields in Crowley, Louisiana during the summer rice seasons of 2018 and 2019.

Benzobicyclon was applied to one 18 x 420 ft plot each season. The same plot was not used for both seasons. The first sampling period occurred from April 2018 to July 2018. Sampling for the 2019 rice season began in June 2019 and ended in August 2019. The sampling periods began at different times due to cooler weather preventing the rice plots from being setup earlier in 2019.

Specific sampling dates are reported in Appendix Table 1. Water and sediment samples were collected periodically over the 75-day period from the benzobicyclon-treated rice fields.

Two water samples and three sediment samples were collected on each sampling day. Samples were collected from the seed bed, not collected from the deeper burrow pits surrounding the seed bed in the rice plots. Approximately 500 ml of water was collected in amber bottles, attached to a pole above the seed bed surrounding the rice shoots. The amber bottles were then stored in labeled Ziploc bags. 1000 g of sediment was collected using a stainless-steel sampling scoop directly from approximately the top two inches of the seed bed and placed into labeled Ziploc bags. Sediment samples were collected from three separate locations within the rice paddy and two locations for water samples. No two sediment samples were pulled from the same disturbed location from a previous sampling date. Background sediment and water samples were collected immediately before application of benzobicyclon to the paddies. Water samples were collected one-third of the distance from the center of the paddy to both ends of the plot. Samples were frozen overnight at the sampling site immediately after collection, then transported to the lab for analysis. Background sediment samples were characterized by AGVISE (Appendix Table 2) for soil physical properties.

3.3. Laboratory Analysis

For analysis of benzobicyclon and its degradation product in sediment, 50 g of sediment was measured into a 250 ml Erlenmeyer flask and mixed with 100 ml of 70:30 ACN and 0.1% Formic Acid in ACN for 2 hours on a table-top shaker. The mixed samples were centrifuged, and the supernatant was filtered through 0.45 μm PTFE syringe filters into 2 ml borosilicate glass vials from Agilent Technologies (Santa Clara, CA). Water samples were thawed and filtered through 0.45 μm PTFE syringe filters into 2 ml borosilicate glass vials. Residues of both benzobicyclon and its hydrolysate in the extracts were quantified on an Agilent 1260 Infinity

High-Performance Liquid Chromatograph with a ZORBAX C-8 Eclipse Plus Analytical 4.6 x 150 mm 5 µm column using a water, formic acid, and acetonitrile gradient mobile phase. The analytes were measured using photodiode array detection at 280 nm for analysis of benzobicyclon hydrolysate and 340 nm for analysis of benzobicyclon. Untreated sediment and water collected from the rice paddy in Crowley, LA were spiked at 1000 ppb, 500 ppb, 100 ppb, 50 ppb, and 25 ppb with benzobicyclon and benzobicyclon hydrolysate for recovery experiments. Standard curves of benzobicyclon and benzobicyclon hydrolysate consisting of 1000 ppb, 500 ppb, 100 ppb, 50 ppb, and 25 ppb standards were used to quantify the parent and metabolite in each sample set. A standard curve was prepared for each day a sample was analyzed to account for instrument variability.

3.4. EXAMS2 Modeling of Benzobicyclon

Pesticide dissipation simulations in paddies were conducted from batch files using the exposure analysis modeling system (EXAMS2), version 2.98. This model is used to simulate chemical movements through different environments to understand their environmental fate. The environmental and chemical variables used in this simulation are displayed in Table A.4 of the appendix. The model was represented as a two compartment system comprised of a water column and benthic sediment. Simulations showed the conversion of benzobicyclon into the primary metabolite, benzobicyclon hydrolysate, and the dissipation of both compounds in water and benthic sediment. Benzobicyclon hydrolysate is the only verified product of benzobicyclon degradation in aquatic systems. As such, the model assumed a 1:1 conversion of benzobicyclon to benzobicyclon hydrolysate via hydrolysis in sediment and water. EXAMS2 also assumed the applied pesticide was spread uniformly throughout the paddy and partitioning and sorption to sediment was assumed to occur immediately after application. Benzobicyclon hydrolysate undergoes photolysis and bacterial biolysis in water and sediment while hydroxyl radical

degradation in the model occurred only in the water column. To determine the influence of hydroxyl radicals on benzobicyclon degradation, simulations were conducted with and without the hydroxyl radical rate constant while other dissipation mechanisms occurred simultaneously. The rate at which a chemical degrades by indirect photolysis in this model is determined by the steady state concentration of hydroxyl radicals, OXRAD in EXAMS2, and the hydroxyl radical rate constant of the compound. The hydroxyl radical rate constant is shown as the variable KOX in the EXAMS2 model.

3.5. Statistical Analysis of Data

Benzobicyclon and benzobicyclon hydrolysate concentrations measured in sediment and water samples for each sampling day were averaged with the replicate samples of each specific day. The standard error of the sediment and water samples was calculated for each sampling day. Standard error was also calculated for the hydroxyl radical rate constant for both the benzoic acid and acetophenone trials. One-way ANOVA tests ($\alpha = 0.05$) were conducted comparing average sediment and water concentrations on each sampling day between the two sampling seasons. One-way ANOVA tests ($\alpha = 0.05$) were conducted for the calculated hydroxyl radical rate constants, comparing the benzoic acid trials to the acetophenone trials. One-way ANOVA ($\alpha = 0.05$) were conducted for the EXAMS2 simulations comparing the models with and without the hydroxyl radical rate constant.

4. Results and Discussion

4.1. Hydroxyl Radical Rate Constant Measurement

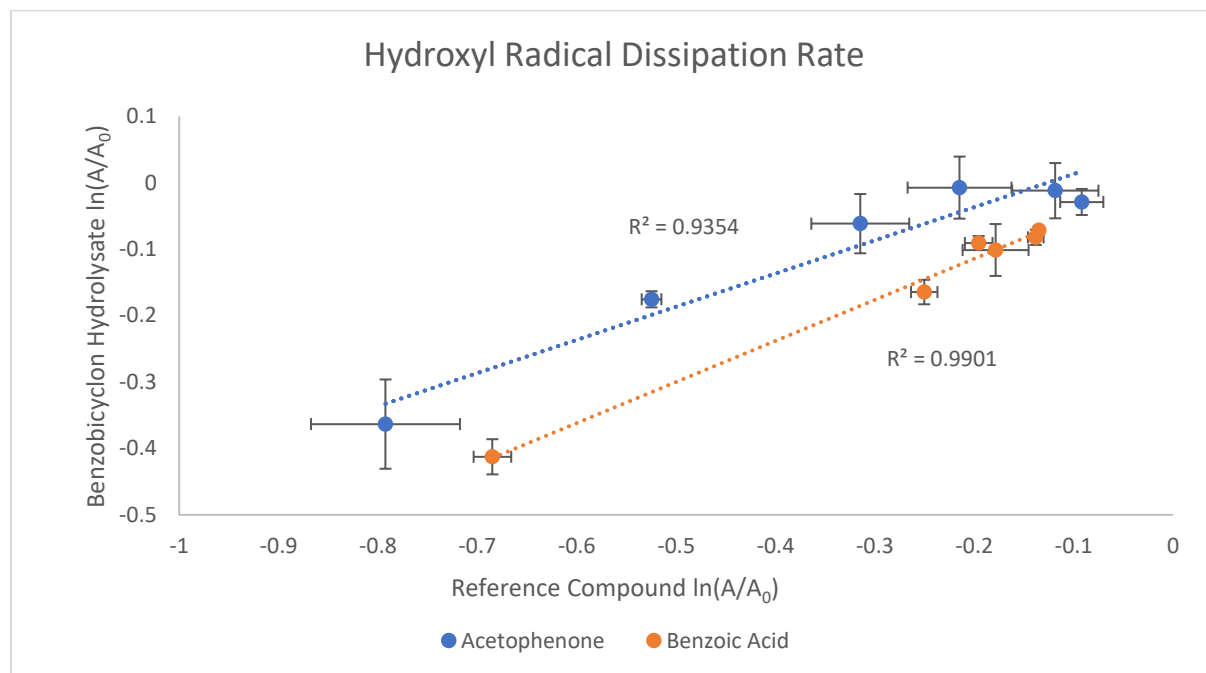


Figure 4.1. Average dissipation rates of benzobicyclon hydrolysate and reference compounds: benzoic acid (orange) and acetophenone (blue) \pm standard error (n = 3).

Table 4.1. Average hydroxyl radical rate constant of benzobicyclon hydrolysate ($\times 10^{13}$) \pm standard error ($\times 10^{13}$) calculated using competition kinetics.

Reference Compound	BH Calculated Rate Constant ($\times 10^{13}$)($M^{-1}h^{-1}$)
Acetophenone	1.0 \pm 0.082
Benzoic Acid	0.73 \pm 0.014

The hydroxyl radical rate constants characterized for benzobicyclon hydrolysate with two separate reference compounds are within a range of approximately 30% of one another, typical of the variability observed for other compounds such as 2,4-D, bensulfuron, chlorpyrifos reported in the literature, using this method (9). To further test this, the rate constant of a chemical with a known hydroxyl radical rate constant, 2-4,D, was measured against benzoic acid

as a reference compound generating a value of $1.1 \times 10^{13} \text{ M}^{-1}\text{h}^{-1}$. Hydroxyl radical rate constants for 2-4, D found in the literature ranged from 5.76×10^{12} to $1.8 \times 10^{13} \text{ M}^{-1}\text{h}^{-1}$ (43,44). Thus the rate constant for 2-4, D measured in this experiment is similar to those in literature. A study that used a similar competition kinetics method to measure hydroxyl radical rate constants calculated a similar hydroxyl radical rate constant for 2-4, D (9). The rate constant calculated in this study was $8.4 \times 10^{12} \text{ M}^{-1}\text{h}^{-1}$. One-way ANOVA ($\alpha = 0.05$) comparing the two calculated rate constant trials shows the two rate constants are not statistically different from one another ($p = 0.55$). There was not a defined hydroxyl radical rate constant for benzobicyclon hydrolysate found in the literature review. However, the accuracy of the method and data from other studies showing similar rate constant measurements with different methods support the hydroxyl radical rate constants measured for benzobicyclon hydrolysate in this study.

4.2. Field Dissipation of Benzobicyclon and Benzobicyclon Hydrolysate in Louisiana Rice Fields

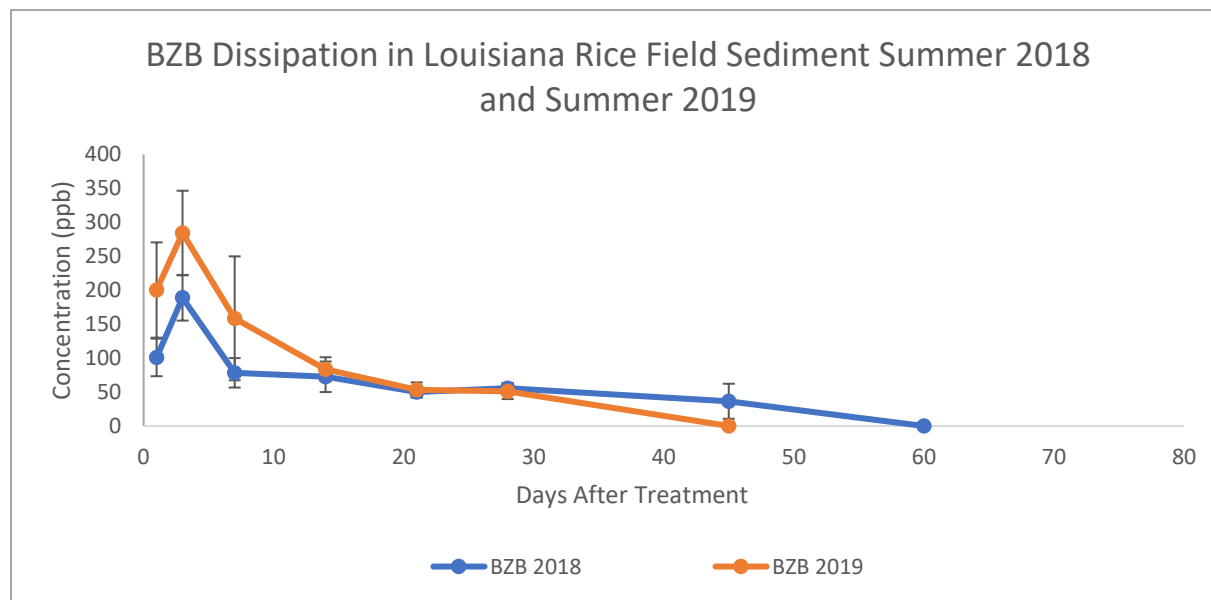


Figure 4.2. Dissipation of Benzobicyclon in sediment over two sampling seasons. Error bars represent standard error (\pm SE).

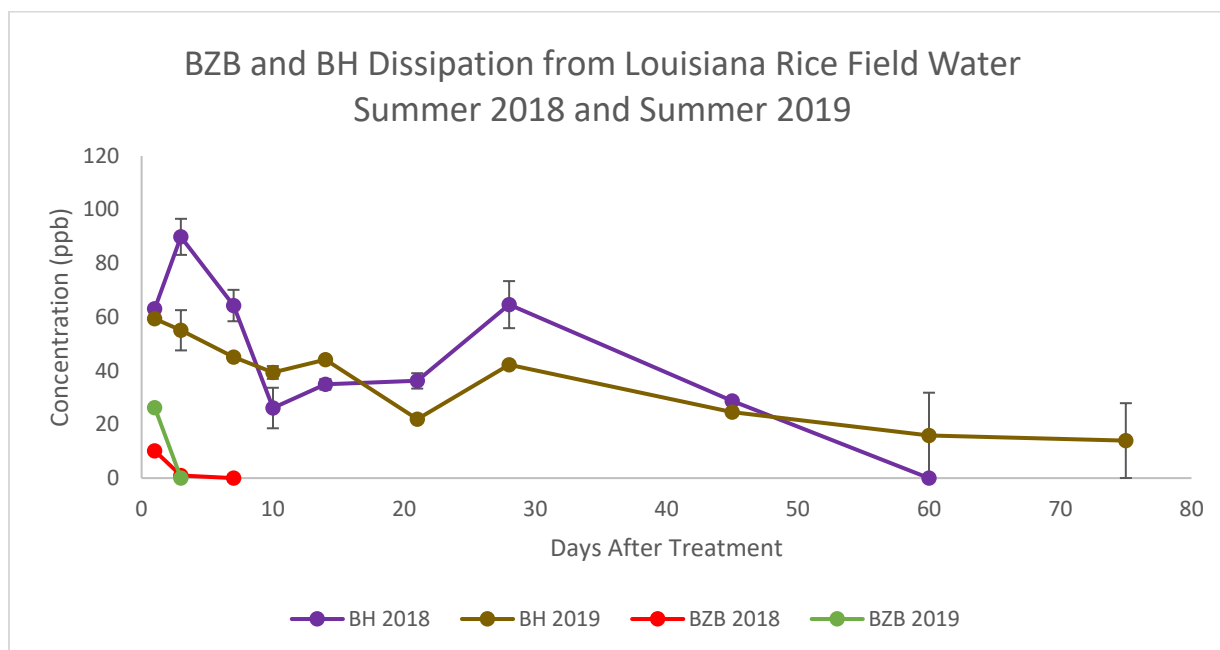


Figure 4.3 Dissipation of Benzobicyclon and Benzobicyclon Hydrolysate from water over two sampling seasons. Error bars represent standard error (\pm SE).

Sediment and water recoveries conducted for benzobicyclon and benzobicyclon hydrolysate averaged 90% or higher for both sediment and water samples (Appendix Table A.4). These data show the extraction method was effective and the concentrations calculated for both compounds were an accurate representation of the residue levels in the samples. The results over the two sampling seasons are presented in Figure 4.1 and Figure 4.2 showing the dissipation of benzobicyclon and benzobicyclon hydrolysate in sediment and water. The average concentration in replicate samples at each time for benzobicyclon and benzobicyclon hydrolysate was used to represent the total concentration in the rice paddy sediment and water on that specific date. The error bars represent the standard error of the concentrations between replicates.

One-way ANOVA ($\alpha = 0.05$) indicated there was no significant difference between the dissipation of benzobicyclon in sediment ($p=0.49$) or the hydrolysate in water ($p=0.69$) between the sampling seasons. Benzobicyclon hydrolysate was detected in water throughout the 2019

season whereas in 2018 it was not detected in any sample after Day 45. The error bars represent the standard error of the average concentrations on each sampling day.

Benzobicyclon was measured at higher concentrations in sediment than in water samples for both sampling seasons and the parent concentrations in water dropped below detectable levels within 7 days. Benzobicyclon hydrolysate was consistently found at higher concentrations in water and was detected only sporadically in sediment samples over both sampling seasons. The exact reason for the unusual detection of the hydrolysate in sediment may be due desorption of the hydrolysate from sediment after sample collection, extraction of pore water in the sample, or extraction from residual plant material in the sediment sample. Future studies could investigate benzobicyclon hydrolysate behavior in sediment. The hydrolysate dissipated slowly between 45 to 75 days with detectable concentrations up to the last sampling date. These data are consistent with the reported physical and chemical properties of benzobicyclon and the hydrolysate (1,4,5,15). Benzobicyclon has a reported aqueous solubility limit of 0.051 mg/L and K_{oc} values ranging from 4,249 to 16,235 L/kg_{oc}, explaining its rapid dissipation from water into sediment following application. In contrast, the hydrolysate has considerably higher aqueous solubility (133 mg/L) and lower soil absorptivity (K_{oc} values ranging from 90 to 771 L/kg_{oc}). These values suggest as benzobicyclon in sediment is degraded by hydrolysis, the hydrolysate will partition back into the water where it is degraded by photolytic processes and microbial degradation.

Benzobicyclon concentrations in sediment peaked at 3 days after treatment in both seasons, followed by rapid dissipation that slowed as concentrations fell below 100 ppb. The shift in dissipation rate occurred within the same time frame for both sampling seasons, 7-14 days after treatment. The decrease in the dissipation rate of benzobicyclon could be due to hydrolysis being the major dissipation mechanism for benzobicyclon in this environment. The

rapid dissipation of benzobicyclon in sediment in the first week does not result in a substantial increase in hydrolysate concentrations in sediment or water, suggesting other degradation mechanisms to other products may be acting on sediment-bound benzobicyclon outside of hydrolysis. Additionally the hydrolysate may also be degraded by multiple mechanisms as it is formed. Benzobicyclon fell below detectable levels within 45-60 days. however other published works suggest that in aquatic environments, hydrolysis is the dominate dissipation mechanism for benzobicyclon with little mention of other mechanisms being significant, and no other degradation products identified. It appears this assessment was based solely upon laboratory data and not field data (4,42). Redistribution of the pesticide after application is a likely reason for the peak concentration of benzobicyclon in sediment within the first 7 days. The pesticide was applied to the water column and sorption to sediment is not instantaneous. In the first 7 days after treatment the pesticide moved towards equilibrium between the sediment and water phases.

Benzobicyclon hydrolysate dissipated slowly in water from its peak during both seasons, presumably due to photodegradation and/or microbial degradation processes. Interestingly, concentrations increased significantly between the 21st and 28th day after treatment after falling steadily during the first 21 days from its peak concentrations at approximately 3 days after application. This increase in hydrolysate concentration does not coincide with any significant dissipation in the parent compound in sediments. While a delay of benzobicyclon hydrolysate leaching into the water column due to sediment binding was possible, the most likely explanation for this increase is due to additional resuspension of sediment from the burrow pit due to the addition of water to the paddy system. This occurred each season of the investigation and the increases in hydrolysate concentrations roughly corresponded with the additions of water. The resuspension of bottom sediment containing the parent compound into the water column would

likely result in increased partitioning from sediment into water with concomitant increases in hydrolysate in the water.

Benzobicyclon hydrolysate was not detected in sediment samples from the 2018 season however it was detected sporadically in samples for the 2019 season. These residues were most likely associated with pore water rather than the sediment itself. Benzobicyclon hydrolysate was detected in the pore water removed from the sediment by centrifugation on selected archived 2019 samples suggesting this is indeed the case.

Benzobicyclon hydrolysate was reported to be stable to hydrolysis in water therefore photolysis, metabolism, and radical degradation are other mechanisms possibly responsible for degrading benzobicyclon hydrolysate throughout the water column and sediment. Williams et al (2018) reported a photolysis half-life in river water of 320 hours compared to 91 hours in a rice field environment. The shorter half-life in rice field water was thought to be due to indirect photolysis reactions. Rice fields have higher concentrations of dissolved organic matter, forming higher concentrations of free radicals to degrade the hydrolysate thus, direct and indirect photolytic processes are most likely the major dissipation mechanisms for the hydrolysate. Microbial degradation is also a possible pathway for dissipation of the hydrolysate. Experiments conducted at 25 and 35 °C in sterile and non-sterile soil under aerobic and anaerobic conditions resulted in half-lives ranging from 3 months under aerobic conditions to approximately a year under anaerobic conditions (3). Aerobic and anaerobic aquatic metabolism studies on the hydrolysate conducted by the pesticide registrant in support of its registration on two soils (Arkansas and California) reported half-lives similar to those above. Dissipation was greater under aerobic conditions with respective DT_{50} values of 151 days and 319 days in California soil and Arkansas soil. Degradation was slower under anaerobic conditions with respective DT_{50} values of 195 days and 529 days (15).

4.3. Environmental Influences on Benzobicyclon Dissipation

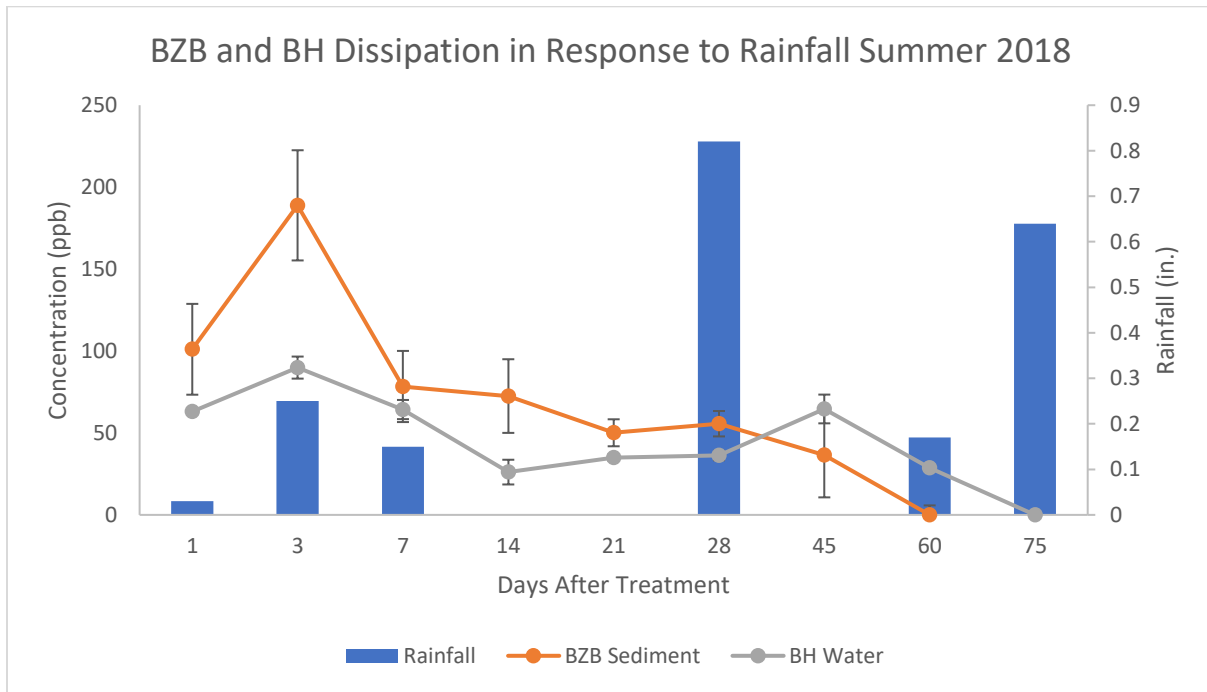


Figure 4.4 Rainfall over benzobicyclon treated rice paddies in Summer 2018.

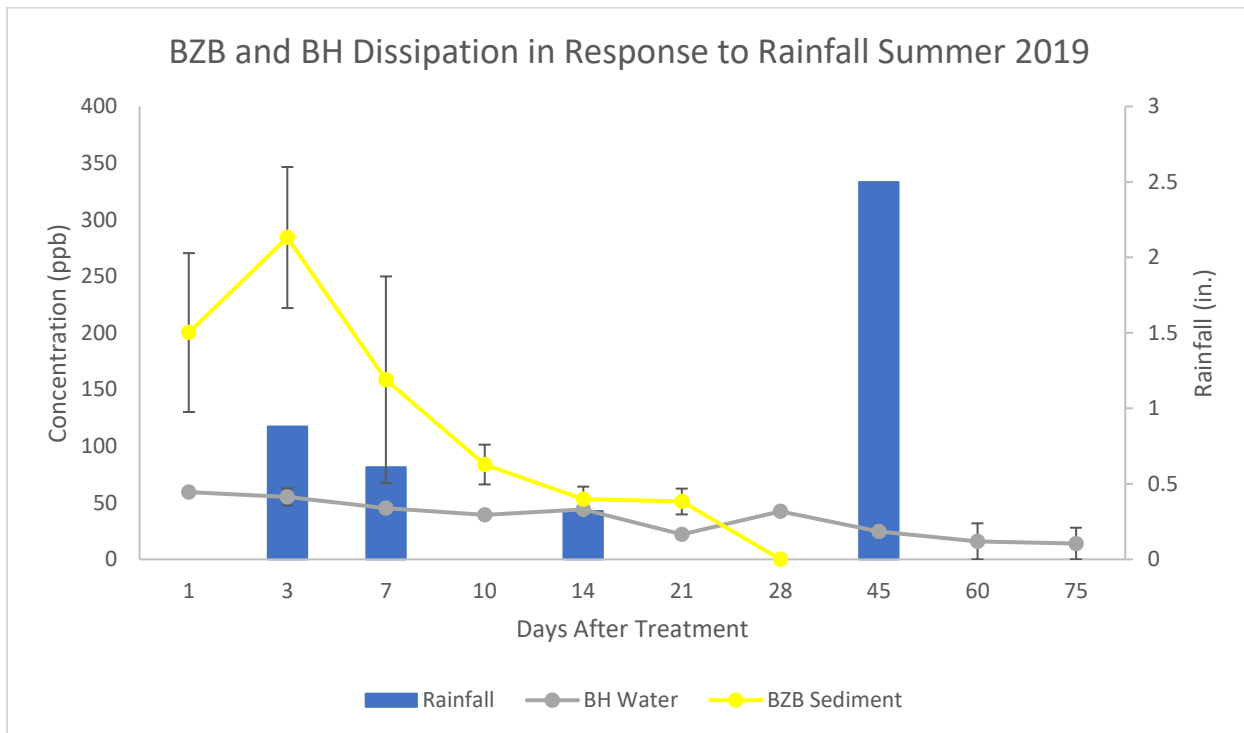


Figure 4.5 Rainfall over benzobicyclon treated rice paddies in Summer 2019.

Rainfall in the southeastern states is a regular occurrence during the spring and summer months during the rice growing season. Thunderstorm events can be highly localized geographically and drop large volumes of rain over relatively short periods of time. A large rainfall event could conceivably influence chemical levels in the rice paddy by increasing the water level or by disturbing the bottom sediment resulting in chemical precipitation from the sorbed state. In order to account for these environmental variables, rainfall events were recorded using the closest weather station; a weather station was not located at the immediate site. Recorded rainfall events all occurred before or during sampling on a specific date. Weather data for the beginning of the summer rice growing season of 2018 was not recorded, therefore archived weather data from the National Oceanic and Atmospheric Administration (NOAA) was used. Local hourly climatological data was collected from the nearest NOAA weather station at the Abbeville Chris Crusta Memorial Airport in Abbeville, Louisiana, approximately 20 miles from the rice field site. Rainfall over the past two summers occurred mainly in the beginning and end of both sampling seasons. The summer of 2019 received 0.88 inches of rain on the 3rd day while the summer of 2018 received 0.2 inches of rain on the 3rd day each season. These levels of rainfall did not likely significantly impact chemical residue levels. Larger amounts of rainfall occurred later in each season, near the time when the parent and hydrolysate had dissipated to levels near the detection limit. Given the highly localized nature of rainfall associated with thunderstorm activity, weather stations juxtaposed to the field sites would have provided the most accurate record of rainfall as well as an indication if rainfall truly impacted levels observed in the field.

Other factors could also impact residue levels. Differences in sediment composition change how the pesticide partitions into sediment, influencing the differences between the peak

concentrations for each season. The sediment composition for the 2019 rice plot was a silty clay while the 2018 plot was a silty loam sediment. Sediments higher in clay content have a higher affinity for organic matter due to the electrically charged nature of clay particles; unit layers function to attract and adsorb organic material (40). Therefore, adsorption to sediments high in clay and organic matter is likely for pesticides including benzobicyclon. Sediment characterization results for the 2018 and 2019 rice paddies show that the rice paddy in 2019 contained a slightly higher organic matter content (Appendix Table A.2.).

Plant uptake of pesticide residue from water could also be a factor in loss. This was unlikely soon after application as the rice had only recently germinated and not emerged yet from the water. Later in the sampling period, by approximately day 30-45, the rice had grown much taller and the biomass in the field could have played a role impacting dissipation. Residue levels in plant biomass were not measured in this investigation, however they could be beneficial in future work to better understand exactly the benzobicyclon behavior in the rice paddy. Benzobicyclon hydrolysate movement into target weeds is important for the mode of action for this pesticide, thus information on its ability to translocate in plant biomass would be beneficial. Sampling rice for the parent compound, benzobicyclon, would likely be unnecessary due to minimal translocation into rice and rice straw (1). Further work may also be necessary to better understand the dissipation of sediment-bound benzobicyclon. It is reported to stable under aerobic soil conditions and could possibly be present in soils in subsequent years after use (3,15).

4.4. EXAMS2 Modeling the Impact of Hydroxyl radicals on Benzobicyclon Dissipation

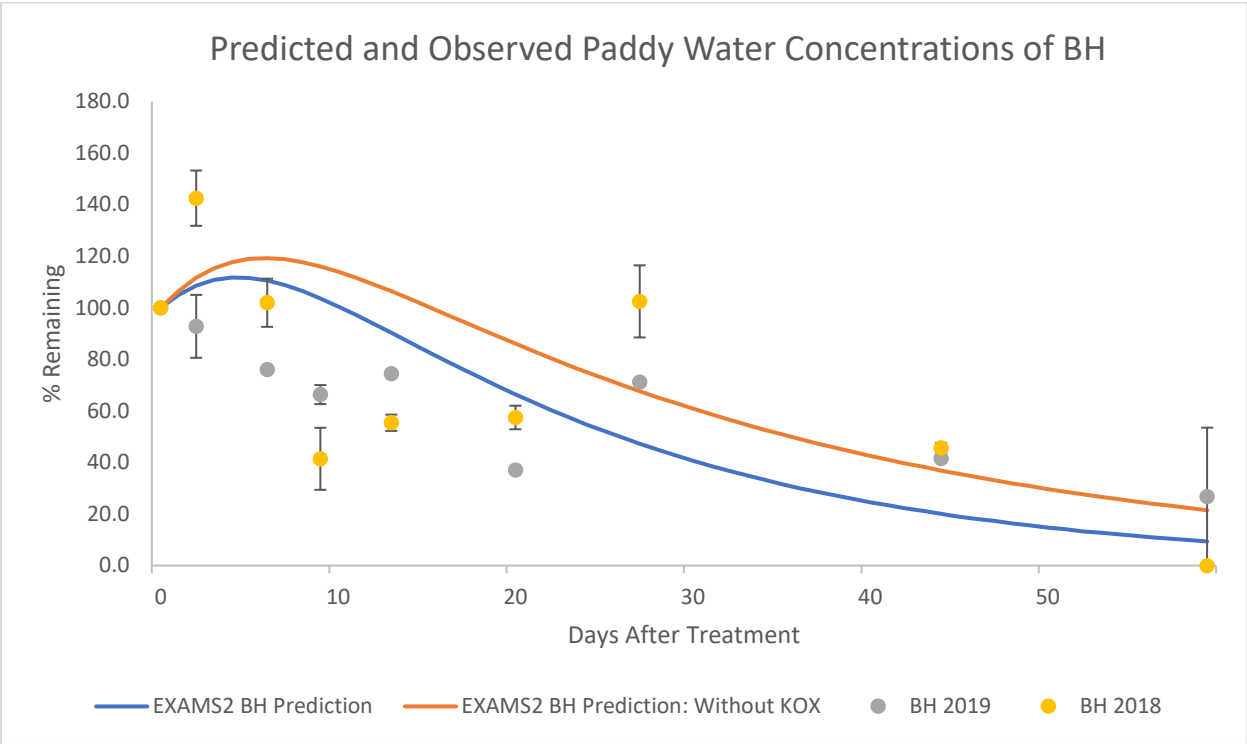


Figure 4.6. Predicted and observed paddy water concentrations of benzobicyclon hydrolysate (BH).

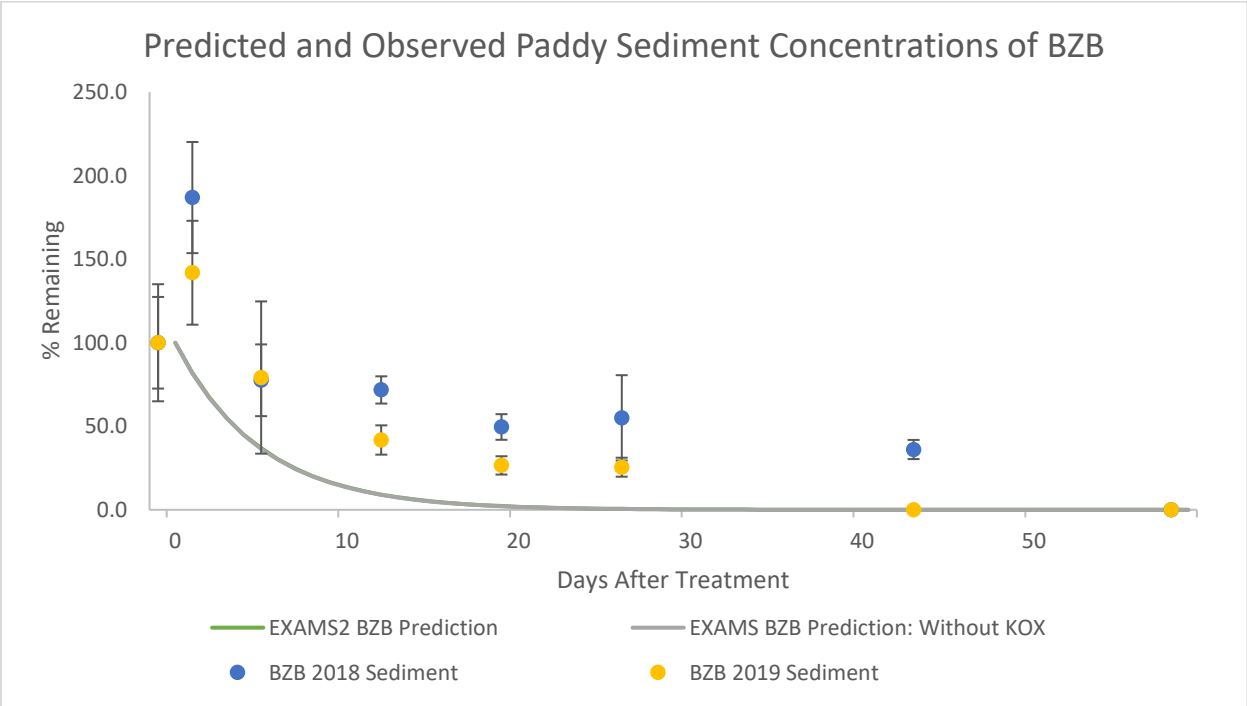


Figure 4.7. Predicted and observed paddy sediment concentrations of benzobicyclon (BZB).

It is not simple to differentiate the contribution of indirect photolysis processes from direct photolysis processes occurring in a field situation based only on sample analysis. However, the environmental exposure model EXAMS2 provides a means of computationally separating these processes on the basis of their individual kinetic rates. The direct photolysis contribution is acquired from a photodegradation study in buffered distilled water as conducted by the pesticide registrant. While a similar study in a natural water may account for some indirect photolysis processes in addition to direct processes, use of the measured hydroxyl radical rate constant, along with the corresponding steady-state concentrations of hydroxyl radicals, allows for analysis of the direct contribution of the process of radical oxidation to the chemical's dissipation. EXAMS2 modeling of benzobicyclon hydrolysate dissipation showed a significant difference ($p = 0.015$) between dissipation of benzobicyclon hydrolysate with and without hydroxyl radical dissipation. Radical oxidation represented 35% of benzobicyclon hydrolysate dissipation, while direct photolysis represented roughly 60% of the dissipation of the compound. The remaining 5% was comprised of benthic, bacterial biodegradation and volatilization. Field data showed periods of increasing benzobicyclon hydrolysate concentrations after day 10; this was not seen in the model. The increases in benzobicyclon hydrolysate concentrations in the water column was hypothesized to be due to leaching of the metabolite from sediment as sediment-sorbed benzobicyclon dissipates. These simulations did not account for the addition of water re-suspending benzobicyclon from benthic sediment that hydrolyzed and potentially increased hydrolysate concentrations.

EXAMS2 requires dissipation rate constants specify which mechanism, hydrolysis, direct/indirect photolysis, and biolysis for example, were acting on the compound of interest in each phase. Dissipation rate constants for hydrolysis of benzobicyclon collected from the literature described the overall dissipation of benzobicyclon in the aqueous phase (5).

Benzobicyclon is known to dissipate primarily by hydrolysis therefore, these rate constants were used under the assumption that hydrolysis is the only mechanism degrading benzobicyclon. Rate constants for sediment dissipation of benzobicyclon from literature were used in the simulation (42). These sediment dissipation constants followed the same assumption that hydrolysis is the only mechanism degrading the pesticide. For the purpose of this study, dissipation of benzobicyclon hydrolysate in sediment was assumed to occur completely by biolysis due to the compound being relatively stable to hydrolysis, and photodegradation was not be expected in sediment. Environmental variables in water such as water depth, dissolved oxygen content, hydroxyl radical steady state concentration, and weather conditions were kept constant. Paddy water depths were not monitored during the field studies therefore dilution and concentration events could have influenced trends in benzobicyclon hydrolysate dissipation in the water column. Hydroxyl radical steady state concentrations are known to vary with environmental conditions over time but have also been shown to be relatively higher in agricultural field water than in other surface waters (38).

The simulation and field data followed a similar dissipation trend in the first 21 days after treatment although there is some variation in absolute concentrations. Benzobicyclon hydrolysate reached peak concentrations on day 3 while the simulation peak concentration was found on day 7. From days 28 to 45, benzobicyclon concentrations in the field were identical to the scenario without the KOX. The dissipation rate from day 28 to day 60 (0.01 day^{-1}) was slower than the dissipation rate from day 1 to day 21 (0.4 day^{-1}) therefore a change in the dissipation processes acting on benzobicyclon hydrolysate over the sampling season is likely.

5. Conclusions

In this study, all primary objectives were met. Hydroxyl radical rate constants were calculated for benzobicyclon hydrolysate using competition kinetics against the reference compounds acetophenone and benzoic acid with calculated rate constants of 1.0×10^{13} and $0.73 \times 10^{13} \text{ M}^{-1}\text{h}^{-1}$ respectively. These calculated rate constants were used to model dissipation of benzobicyclon and benzobicyclon hydrolysate in a rice paddy. The model showed a significant difference in benzobicyclon hydrolysate dissipation with and without dissipation by hydroxyl radicals. In comparison to the field data, the model simulation including degradation by hydroxyl radicals of benzobicyclon hydrolysate more closely resembled field data than the simulation without degradation by hydroxyl radicals.

The field data for benzobicyclon and benzobicyclon hydrolysate was collected from two sampling studies conducted in Crowley, LA rice paddies. The pesticide and primary metabolite behaved in the field as expected based on their chemical properties and showed similar patterns to dissipation seen in other studies (1,3,4,6,42). The pro-herbicide, benzobicyclon, showed a higher affinity for sediment while benzobicyclon hydrolysate favored water. Detection of benzobicyclon in water fell below detectable levels within 7 days while benzobicyclon hydrolysate in sediment was sporadic, not uniform between replicates; it was only detected in Summer 2019 samples. The study was conducted over two consecutive rice seasons and overall, both seasons showed similar results regarding benzobicyclon and benzobicyclon hydrolysate partitioning and dissipation. Benzobicyclon concentrations dropped below detectable levels between 30 to 45 days post application while benzobicyclon hydrolysate was detected in water samples between 45 days and the last sampling date of the study.

Rice paddy sediment was shown to act as a reservoir for benzobicyclon as hypothesized in this study. Benzobicyclon falls below detectable levels quickly in the water column and dissipates slowly from sediment. Slow leaching of benzobicyclon from sediment to the water

column as benzobicyclon hydrolysate prolongs recalcitrance of pesticide efficacy in a rice paddy. The calculated half-life of 13.8 days for benzobicyclon in sediment in this study is similar to previous studies investigating dissipation of benzobicyclon in sediment (1,15). The half-life of benzobicyclon hydrolysate was calculated at 33.9 days with no comparable values in the literature. Recalcitrance of benzobicyclon hydrolysate in water into the succeeding crayfish season is not likely as it had fallen below detectable levels by the time the field was drained for harvest, even at an application rate three times the normal field application rate.

Future research could investigate the fate of this pesticide at rates and application times that align more with commercial use of the pesticide and also during actual use in commercial fields. Understanding the efficacy of the pesticide can give insight into what rates and how many applications are necessary to control pests effectively. This study could be conducted again with the same rates and conditions but monitoring of water levels and other environmental factors could give better insight into trends seen in the dissipation of benzobicyclon. Changes in DOM content, suspended metals, ions, and other substances in the water and sediment may lead to changes in the dissipation mechanisms acting on benzobicyclon.

Appendix

Table A.1. Sampling dates for the Summer 2018 and 2019.

Sampling Dates		
Year	2018	2019
Day 1	18-Apr	4-Jun
Day 3	20-Apr	6-Jun
Day 7	24-Apr	10-Jun
Day 10	27-Apr	14-Jun
Day 14	1-May	18-Jun
Day 21	8-May	25-Jun
Day 28	16-May	2-Jul
Day 45	30-May	16-Jul
Day 60	15-Jun	30-Jul
Day 75	3-Jul	14-Aug

Table A.2. Sediment characterization of rice field sediments from Summer 2018 and 2018 rice paddies.

Sediment Characterization		
Properties	2018	2019
Texture Class	Silt Loam	Silty Clay
% Moisture at 1/3 Bar	30.3	38.9
% Moisture at 15 Bar	11.4	21.8
% Organic Matter	2.3	3.7
% Total Nitrogen	0.109	0.17
Olsen Phosphorus (ppm)	13	18
Soluble Salts (mmhos/cm)	0.28	0.3
Cation Exchange Capacity (meq/100 g)	9.1	16.1
Cations:		
Potassium (ppm)	87	120
Calcium (ppm)	1011	1764
Magnesium (ppm)	312	486
Sodium (ppm)	109	100
Hydrogen (ppm)	24.6	25

Table A.3. Physical and Chemical Properties of Benzobicyclon and Benzobicyclon Hydrolysate.

Physical and Chemical Properties			
Properties		BZB	BH
Molar Mass (g/mol)		447	355
Solubility (mg/L)		0.051	133
K _{oc}		15,908	1,421
Log K _{ow}		3.1	1.51
Hydrolysis half-life (days)		0.65	388
Aqueous Photolysis half-life (days)		N/A	12.9
Soil photolysis half-life (days)		776	N/A
Aerobic aqueous metabolism half-life (days)		0.99	234.95
Anaerobic aqueous metabolism half-life (days)		0.9	361.8
Aquatic field water dissipation half-life (days)		0.943	N/A
Aquatic field sediment dissipation half-life (days)		17	N/A

Table A.4. Environmental and chemical input variables.

Environment:		Rice Paddy			
set kount:	2	set dsp(1,*):	3.80E-06	set pOH(1,*):	6
set type(1):	L	set oxrad(*):	1.20E-16	set pOH(2,*):	8
set type(2):	B	set dfac(1,*):	1.19	set ph(2,*):	6
set area(1):	1000	set dfac(2,*):	2	set froc(*,*):	0.012
set area(2):	1000	set jturb(1):	1	set sused(1,*):	5
set depth(1):	0.1	set iturb(1):	2	set doc(*,*):	1
set depth(2):	0.01	set xstur(1):	1025		
set vol(1):	100	set charl(1):	0.055		
set vol(2):	10	set ph(1,*):	8		
Chemical 1:		Benzobicyclon			
set mwt(1):	447	set koc(1):	15908	set quant(*,1,1):	1
set sol(*,1):	5.10E-02	set knh(1,1,1):	4.31E-02	set lamax(1,1):	300
set vap(1):	4.20E-07	set kbh(1,1,1):	0	set kbacs(*,*,*):	0
set henry(1):	4.06E-03	set knh(2,1,1):	3.30E-02	set kbacw(*,*,*):	0
set kox(1,*,*):	0.00E+00	set kdp(1,1):	0		
Chemical 2:		Benzobicyclon Hydrolysate			
set mwt(1):	355	set kox(2,*,*):	0	set kdp(1,1):	3.70E-03
set sol(*,1):	133	set koc(1):	299	set quant(*,1,1):	1

(Table Cont'd)

Environment:		Rice Paddy			
set vapr(1):	5.87E-11	set	0	set lamax(1,1):	300
set henry(1):	7.11E-08	knh(1,1,1):	0	set kbacs(*,*,*):	1.60E-04
set kox(1,*,*):	9.1E+12	set	0	set	1.60E-04
		knh(2,1,1):		kbacw(*,*,*):	
		set			
		kbh(*,1,1):			

Table A.5. Average Sediment and Water Recoveries of Benzobicyclon and Benzobicyclon Hydrolysate with standard error (n=3).

	BZB (% Recovery)		BH (% Recovery)	
	Sediment	Water	Sediment	Water
1000 ppb	97.42±0.32	98.56±0.37	97.78±0.97	99.14±1.7
500 ppb	97.35±1.5	96.41±0.35	95.47±1.1	96.82±2.9
100 ppb	92.35±3.0	97.17±1.4	92.15±1.6	94.56±5.0
50 ppb	91.48±1.7	94.62±3.1	97.52±2.3	92.34±1.5
25 ppb	94.00±1.6	92.15±4.1	89.63±4.9	89.75±4.5

Table A.6. Predicted dissipation of BZB in sediment and BH in water from EXAMS2 simulations.

DAT	Without KOX (kg)		With KOX (kg)	
	BZB in Sediment	BH in Water	BZB in Sediment	BH in Water
0	0	0	0	0
1	3.27E-02	7.66E-03	3.27E-02	7.53E-03
2	2.67E-02	8.15E-03	2.67E-02	7.90E-03
3	2.18E-02	8.55E-03	2.18E-02	8.17E-03
4	1.79E-02	8.83E-03	1.79E-02	8.34E-03
5	1.46E-02	9.01E-03	1.46E-02	8.41E-03
6	1.19E-02	9.11E-03	1.19E-02	8.40E-03
7	9.77E-03	9.13E-03	9.77E-03	8.32E-03
8	7.99E-03	9.10E-03	7.99E-03	8.19E-03
9	6.53E-03	9.01E-03	6.53E-03	8.01E-03
10	5.34E-03	8.88E-03	5.34E-03	7.80E-03
11	4.37E-03	8.73E-03	4.37E-03	7.57E-03
12	3.57E-03	8.55E-03	3.57E-03	7.32E-03
13	2.92E-03	8.35E-03	2.92E-03	7.06E-03
14	2.39E-03	8.15E-03	2.39E-03	6.80E-03
15	1.95E-03	7.93E-03	1.95E-03	6.53E-03
16	1.60E-03	7.71E-03	1.60E-03	6.26E-03
17	1.31E-03	7.48E-03	1.31E-03	6.00E-03
18	1.07E-03	7.26E-03	1.07E-03	5.74E-03
19	8.74E-04	7.03E-03	8.74E-04	5.49E-03

(Table Cont'd)

DAT	Without KOX (kg)		With KOX (kg)	
	BZB in Sediment	BH in Water	BZB in Sediment	BH in Water
20	7.15E-04	6.81E-03	7.15E-04	5.24E-03
21	5.84E-04	6.59E-03	5.84E-04	5.00E-03
22	4.78E-04	6.37E-03	4.78E-04	4.77E-03
23	3.91E-04	6.16E-03	3.91E-04	4.54E-03
24	3.20E-04	5.95E-03	3.20E-04	4.33E-03
25	2.61E-04	5.75E-03	2.61E-04	4.12E-03
26	2.14E-04	5.56E-03	2.14E-04	3.93E-03
27	1.75E-04	5.37E-03	1.75E-04	3.74E-03
28	1.43E-04	5.18E-03	1.43E-04	3.56E-03
29	1.17E-04	5.00E-03	1.17E-04	3.39E-03
30	9.56E-05	4.83E-03	9.56E-05	3.22E-03
31	7.81E-05	4.66E-03	7.81E-05	3.06E-03
32	6.39E-05	4.50E-03	6.39E-05	2.91E-03
33	5.23E-05	4.34E-03	5.23E-05	2.77E-03
34	4.27E-05	4.19E-03	4.27E-05	2.64E-03
35	3.49E-05	4.04E-03	3.49E-05	2.51E-03
36	2.86E-05	3.90E-03	2.86E-05	2.38E-03
37	2.34E-05	3.76E-03	2.34E-05	2.26E-03
38	1.91E-05	3.63E-03	1.91E-05	2.15E-03
39	1.56E-05	3.50E-03	1.56E-05	2.05E-03
40	1.28E-05	3.38E-03	1.28E-05	1.95E-03
41	1.04E-05	3.26E-03	1.04E-05	1.85E-03
42	8.54E-06	3.14E-03	8.54E-06	1.76E-03
43	6.99E-06	3.03E-03	6.99E-06	1.67E-03
44	5.71E-06	2.93E-03	5.71E-06	1.59E-03
45	4.67E-06	2.82E-03	4.67E-06	1.51E-03
46	3.82E-06	2.72E-03	3.82E-06	1.43E-03
47	3.12E-06	2.63E-03	3.12E-06	1.36E-03
48	2.56E-06	2.53E-03	2.56E-06	1.30E-03
49	2.09E-06	2.44E-03	2.09E-06	1.23E-03
50	1.71E-06	2.36E-03	1.71E-06	1.17E-03
51	1.40E-06	2.27E-03	1.40E-06	1.11E-03
52	1.14E-06	2.19E-03	1.14E-06	1.06E-03
53	9.34E-07	2.12E-03	9.34E-07	1.00E-03
54	7.64E-07	2.04E-03	7.64E-07	9.55E-04
55	6.25E-07	1.97E-03	6.25E-07	9.07E-04
56	5.11E-07	1.90E-03	5.11E-07	8.62E-04
57	4.18E-07	1.83E-03	4.18E-07	8.19E-04
58	3.42E-07	1.77E-03	3.42E-07	7.79E-04
59	2.79E-07	1.71E-03	2.79E-07	7.40E-04
60	2.29E-07	1.64E-03	2.29E-07	7.03E-04

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