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Analysis of the Photodegradation of the Pro-Herbicide
Benzobicyclon Hydrolysate Using a Seawater Gradient and Constituent Ions

by

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Baton Rouge, Louisiana

Abstract

Benzobicyclon (BZB) is a pro-herbicide recently approved for application on rice in California and undergoing research in anticipation of registration in southern states including Louisiana. BZB rapidly hydrolyzes in flooded fields to generate the active ingredient of the herbicide (BUTTE®), benzobicyclon hydrolysate (BH). Previous research has shown BH preferentially partitions into rice field water, while BZB is adsorbed in sediments. BH undergoes photolysis and its half-life varies depending on the characteristics of the water. Previous investigation by this author has shown that small amounts of iron, magnesium, and copper are in part responsible for the rapid degradation of BH in seawater when the ions are isolated from other confounding variables. While there is little risk for the herbicide to be transported from treated systems to non-target ecosystems because of spray drift, there is risk of contamination to ecosystems when flooded fields are drained. The fate of BH is also a concern in coastal watersheds, as are its fates in estuarine and marine systems. The objective of the current study is to determine if the exacerbating effects of seawater exist when Benzobicyclon Hydrolysate is irradiated across a gradient of salinities and to determine if environmentally relevant concentrations of seawater's constituent ions result in the same rapid degradation seen previously. This was done to analyze the impact that brackish water may have on the partitioning and degradation of BZB in marine and estuarine systems receiving rice tail-waters. It was found that as salinity increased from 0 ppt to 35 ppt, the half-life of BH decreased exponentially from 84.1 ± 2.6 hours to 3.5 ± 0.07 hours. Additionally, it was found that, when isolated from other ions, magnesium ions most influenced this degradation. The half-life of BH in the presence of magnesium was 5.85 ± 0.12 hours. The half-lives in the presence of copper, iron, and zinc were 126.4 ± 2.24 hours, 146.5 ± 4.5 hours, and 87.23 ± 2.7 hours, respectively. The results of this investigation should provide information used for the more accurate assessment of risk to aquatic ecosystems.

Introduction

Pesticides are a class of chemicals used to control pests in a variety of settings. They can be broken into three major categories—herbicides, fungicides, and insecticides (Aktar et al., 2009). Herbicides are used to treat crops for unwanted or harmful plants or weeds. The use of both chemical and synthetic pesticides has increased since the introduction of dichlorodiphenyltrichloroethane (DDT) during the first half of the 20th century, resulting in dependable food supplies for the ever-increasing global population. Prior to DDT, pesticide use was often biological or by application of toxic metals such as arsenic and lead. In fact, early writing by the Greek author Homer describes the use of sulfur on crops by ancient Grecians, and the utilization of hellebore (*Veratrum alba*) by the ancient Romans (Crosby, 1998). Pesticides have benefited humans by increasing of crop health and yield by decreasing the risk of crop loss and harm due to pests and diseases. However, they have unfortunately harmed both terrestrial and aquatic ecosystems as a side effect (Rathore et al., 2012). The last two decades have shown an increase in herbicide-resistant weed species, particularly in herbicides commonly used in rice fields (McKnight et al., 2018). Increasing levels of herbicide resistance have required the development of novel pesticides with new modes of action as well as changes in chemical formulation and in application practices.

Benzobicyclon (BZB) (Trade name: BUTTE ®) is a pro-herbicide recently approved for application on rice in California; it is undergoing research in anticipation of registration in southern states including Louisiana (Vebrosky, 2018). In a pro-herbicide, the parent compound is not the active ingredient. Instead, the herbicide degrades to form the active ingredient. In the case of BZB, the chemical is applied to rice fields in a granular form and rapidly hydrolyzes once fields are flooded to produce the active ingredient, benzobicyclon hydrolysate (BH) (Sun et al.,

2016). Previous research has shown BH preferentially partitions into rice field water, while BZB is adsorbed to sediments (Vebrosky). This herbicide is used to control weed species that compete with rice crops in fields for water and nutrients (McKnight et al., 2018; Smith, 1988). BZB has a different mode of action compared to other currently registered rice herbicides. It bleaches the target pest plants by inhibiting the enzyme 4-hydroxyphenylpyruvate dioxygenase (4-HPPD) (McKnight et al.). Benzobicyclon shows broad-spectrum activity against annual grass, sedge, and broadleaf weeds without causing phytotoxic injury to transplanted or direct-seeded rice (Komatsubara et al., 2009).

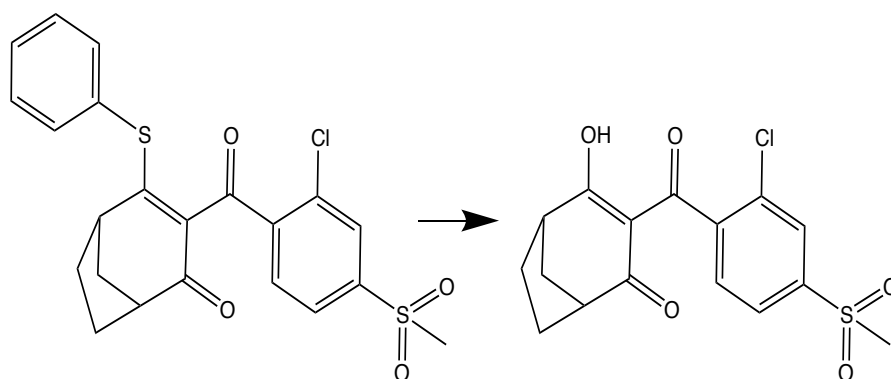


Figure 1: BZB hydrolysis to BH

Benzobicyclon hydrolytate undergoes photodegradation and its half-life varies depending on the characteristics of the water applied to the field. Many chemical compounds have the potential to absorb energy from ultraviolet (UV) and visible light dependent on their physical and chemical properties. This addition of light energy transforms chemicals from a stable ground state to an unstable form that breaks down readily (Hage et al, 2011). Hydroxyl radicals ($\bullet\text{OH}$) are considered an oxidant and can be generated by a photochemical reaction of chemical constituents in natural waters. The hydroxyl radicals act as scavengers to dissolved organic matter and ions in water; indirect photolysis and photodegradation may occur and generate $\bullet\text{OH}$, which may further react with other chemicals (Crosby, 1972). Hydroxyl radicals formed

photochemically often react with organic pollutants, but can also react with inorganics chemicals (Crosby, 1998). Photodegradation occurs because of both direct and indirect photolysis. Direct photolysis is due to chemical absorption of light energy at wavelengths greater than 290 but typically less than 400 nm (USEPA, 2008). Indirect photolysis occurs in a few different ways. One example is the transfer of light energy from a natural water constituent to the chemical resulting in its oxidation. Photolysis typically occurs because of a combination of both direct and indirect factors (Crosby, 1998; Rathore et al., 2012; USEPA, 1998).

Seawater is composed of various anions and cations that interact with chemicals and organisms that inhabit saline waters. By definition, [surface] seawater consists of 11 major ions: chloride (Cl^-), sulfate (SO_4^-), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), strontium (Sr^{2+}), fluorine (F^-), bromine (Br^-), bicarbonate (HCO_3^-), and boric acid ($\text{B}(\text{OH})_3^-$) (Stumm et al., 1981). Seawater also contains trace amounts of transition metals such as iron, zinc, copper, and manganese (Stumm et al., 1981). Salinity has been reported to impact bioaccumulation factors, half-lives ($t_{1/2}$), degradation rates, degradation product formation, as well as overall degradation (Crosby, 1998; Saranjampour et al., 2017; Vebrosky et al., 2018). Salinity has also been shown to influence the bioavailability of chemicals, metals, and ions in waters (Crosby, 1998). In distilled water, BH has a reported half-life of 77 hours. Its half-life is 34 hours in rice water and 3.4 hours in 25 ppt seawater (Vebrosky, 2018).

Benzobicyclon has been in use on rice crops in Asian countries such as Japan and Korea for almost two decades. There, its behavior has been studied both in fields and simulated field conditions (Komatsubara et al., 2009). The herbicide's behavior in American rice fields, particularly in California and Louisiana, is currently undergoing monitoring and study. Louisiana

State University, for example, has been testing benzobicyclon at the H. Rouse Caffey Rice Research Station in Crowley, LA since 2015 (Gould, 2016 A, B; McKnight et al., 2018)

Gaps in knowledge exist on how this pesticide (or any) may interact within an ecosystem due to registration studies not accounting for environmental parameters in a particular environment (Vebrosky, 2018). While all pesticides undergo field and laboratory testing prior to registration, the behavior of the pesticide may vary dependent upon field characteristics (i.e., soil type, water and soil pH, salinity). In addition to local variability, current regulation does not account for important variables that may be important to a particular pesticide in a particular location. For example, chemicals can exhibit dramatically different behavior in aqueous systems as a function of salinity, however this is not considered in current studies (Vebrosky, 2018). This variability of behavior could be very important in environments such as the rice fields of southern Louisiana.

South Louisiana is currently experiencing land loss, coastal erosion and saltwater intrusion. Natural drivers of saltwater intrusion include storm surges from hurricanes, fluctuations in climate, sea level rise, and subsidence; anthropogenic causes of saltwater intrusion are land drainage, exhaustion of coastal freshwater aquifers, water diversions, hydraulic structures, and land-use changes within watersheds (White and Kaplan, 2018).

Anthropogenically exacerbated climate-driven causes of saltwater intrusion are often interconnected, which can cause exacerbating effects. Hurricanes of higher intensity bring more powerful storm surges. These factors acting in concert with sea level rise and local subsidence can drive inundation far more than either driver alone (Yang et al. 2014). Areas in South Louisiana can be impacted by saltwater surge from hurricanes and could face saltwater intrusion as coastal lands subside (Gambrell, 2005). Rice farmers are already seeing higher levels of salt

in water used for irrigation during periods of drought (Schultz, 2006). Additionally, canals and bayous that were once used as surface sources for freshwater irrigation are disappearing due to a myriad of factors that include coastal land loss (Linscombe, 2012).

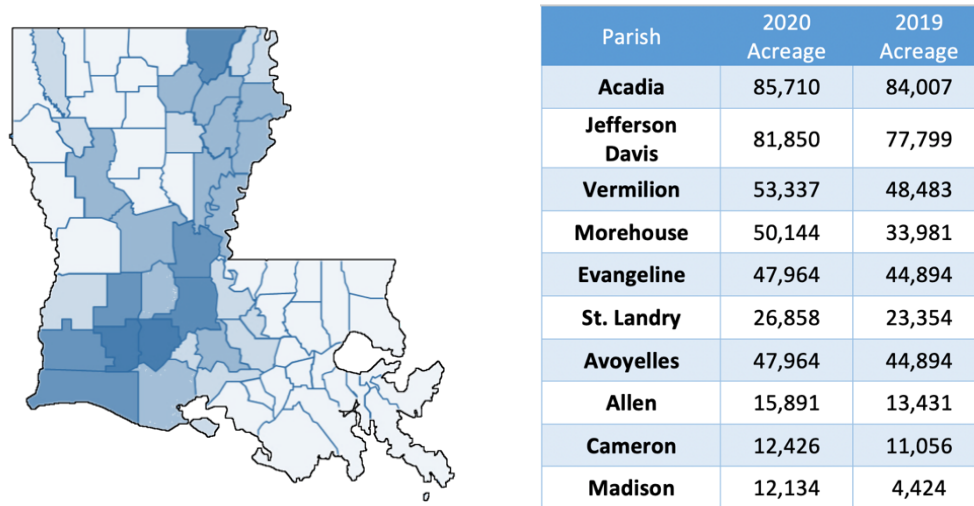


Figure 2 and Table 1: Parishes where rice is grown in Louisiana. The darkest shade indicates greater than 81,000 acres of cultivation, the lightest represents less than 1,800 acres. (Schultz, 2018)

Acreage devoted to rice farming in recent years has been increasing (Figure 2 and Table 1), and these expansions could be harmed by saltwater intrusion. As climate changes, saltwater is shifting landward into regions that previously have not experienced or adapted to salinity, leading to novel transitions in many arenas including agriculture (Tully et al., 2019). Increasing temperatures, salinity changes, saltwater intrusion, and land loss or coastal erosion resulting from human impacts and climate change will impact agricultural lands, water sources, water salinity and pH, the amount of available freshwater for use on crops, and the tolerance of crops grown in regions based upon temperatures and underlying conditions. With environmental variations in ecosystems, the use of pesticides has the potential to continue to increase crop health and high yields to maintain a sustainable future only if pesticides are suitable for the changing environments (Rathore et al., 2012).

Previous experimentation by this author and others has also shown that iron, magnesium, and copper are in part responsible for the rapid degradation of BH in seawater when the water is isolated from other confounding variables. These ions can interact with chemicals that enter water and influence the degradation, product formation, and overall behavior of pesticides (Vebrosky, 2018).

The objective of the current study is to determine what salinity or salinities of seawater could be responsible for the rapid degradation of BH in estuarine environments. Additionally, the research seeks to discover which major ions in seawater are responsible for the rapid photolysis of benzobicyclon hydrolysate in irradiated solutions.

Methods

Ion solutions

The solutions in this experiment fall into three categories: deionized water, artificial seawater, and individual seawater ions. Instant Ocean (Blacksburg, VA) was mixed into distilled water to prepare artificial seawater (ASW) and salinity was monitored using a YSI Model 30 salinity, conductivity, and temperature meter (Yellow Springs, OH). ASW with salinities of 2.5, 5, 10, 15, 20, 25, 30, and 35 parts per thousand (PPT) were used to make up the seawater gradient.

The environmentally relevant concentrations of Fe^{3+} , Mg^{2+} , Cu^{2+} , and Zn^{2+} were calculated in g/L from g/Kg and -log of molarity data (Stumm et al., 1981). These concentrations and the calculations of the masses needed to generate the appropriate concentration of solutions are shown in Table 2.

Table 2: The calculation of environmentally relevant concentrations of the ions of interest isolated from seawater.

Ion	Molar Mass (g)	- log M	M (mol/L)	Compound	Mass Compound (g/mol)	mg / L
Fe ³⁺	55.84	-7.5	3.16-08	FeCl ₃	162.20	0.0051
Cu ²⁺	63.54	-8.1	7.94-09	CuCl ₂	134.45	0.0011
Zn ²⁺	65.38	-4.9	1.26-05	ZnCl ₂	136.29	1.7157
Ion	Molar Mass (g)	g/kg SW	M (mol/L)	Compound	Mass Compound (g/mol)	g / L
Mg ²⁺	24.31	1.29	0.055	MgCl ₂	95.21	5.1915

Solutions were made using deionized water and a chloride salt of the ion in question (FeCl₃, for example). Salts were sourced from Fisher Chemical, Mallinckrodt Pharmaceuticals, or Sigma-Aldrich. Ion solutions were made in one-liter batches, autoclaved, and stored at 15° Celsius.

Experimental Set Up

To expose benzobicyclon hydrolysate to artificial sunlight, 2 mL Borosilicate glass vials containing 1 mL of distilled water (unbuffered, but previous research has showed that buffering of water has no impact on the degradation rate of BH), artificial sea water, or a solution of one of seawater's constituent ions were spiked with benzobicyclon hydrolysate at 1 ppm and were irradiated in an ATLAS SUNTEST XXL+ environmental chamber fitted with a daylight filter with a light intensity of 40 W/m² for several different time periods ranging from 1 hour to 96 hours. Calibration curves were prepared to quantify benzobicyclon hydrolysate in irradiated solutions at concentrations of 0.05 ppm, 0.1 ppm, 0.25 ppm, 0.5 ppm, and 1.0 ppm BH.

Chemical Analysis

All trials were conducted in triplicate. At each time point, three vials were sampled to determine the residual concentration of benzobicyclon hydrolysate. The 1 mL samples were analyzed directly on an Agilent 1260 Infinity HPLC (Agilent Technologies). The method included a gradient mobile phase comprised of water, 0.1% formic acid in water, and 0.1% formic acid in acetonitrile (ACN) using a ZORBAX C-8 Eclipse Plus Analytical 4.6 x 150 mm 5 μm column, and a 20 μL injection volume. The gradient of solvents over time is shown below.

Table 3: The gradient mobile phase used for analysis.

Time (minutes)	0.1% Formic Acid in Acetonitrile	0.1 % Formic Acid in H2O	Flow (mL/min)	Pressure (bar)
2.00	15	85	0.9	500
13.00	70	30	0.9	500
17.00	70	30	0.9	500
21.00	15	85	0.9	500
23.00	15	85	0/9	500

The 280 nm wavelength and 12-minute retention time were monitored with a photodiode array. Samples of the ion solution were removed from the environmental chamber for analysis at 0, 1, 2, 4, and 24, hours and then every 24 hours after until BH had gone through approximately one-half life.

Data Analysis

Calibration curves were used to determine the residual concentration of benzobicyclon hydrolysate from curve areas generated by the HPLC. A pseudo-first order rate constant was calculated from these residual concentrations using the following formula:

$$\ln \frac{C}{C_0} = -kt$$

In this formula, k is the rate constant, C is the concentration, C_0 is the initial concentration, and t is time. These rate constants were calculated for each time point for each salinity or ion solution and plotted against time, yielding a line with the slope equal to the rate constant for the degradation of BH in the ion of interest, k^*

Estimated half-life of BH in each condition was calculated by dividing the natural logarithm of 2 by the rate constant for the degradation of BH. The half-life time was estimated by

$$\begin{aligned} t_{1/2} &= \ln 2 / k * \\ &= 0.693 / k * \end{aligned}$$

To generate standard errors of the half-lives for comparison to one another and to generate replicates for a one-way ANOVA, a bootstrap analysis was conducted in R. The triplet residual concentrations of BH under each ion or salinity condition at each timepoint were bootstrapped. Bootstrapping is the process of sampling with replacement to generate many averages for a small set of data. An example bootstrap sample may be A, A and B sampled from a set of A, B, and C. These data were bootstrapped 1,000 times. After bootstrapping, the many replicates of the data were used to generate many k^* values that were used to calculate many half-lives with the logarithm function. These 1,000 half-lives were averaged together to generate a final estimate of the half-life of BH under each condition. The bootstrap estimate of the standard

error of the half-life time is the standard deviation of the 1,000 estimated half-life times from bootstrapping.

Results and Discussion

The results of the degradation of BH across the salinity gradient are shown below.

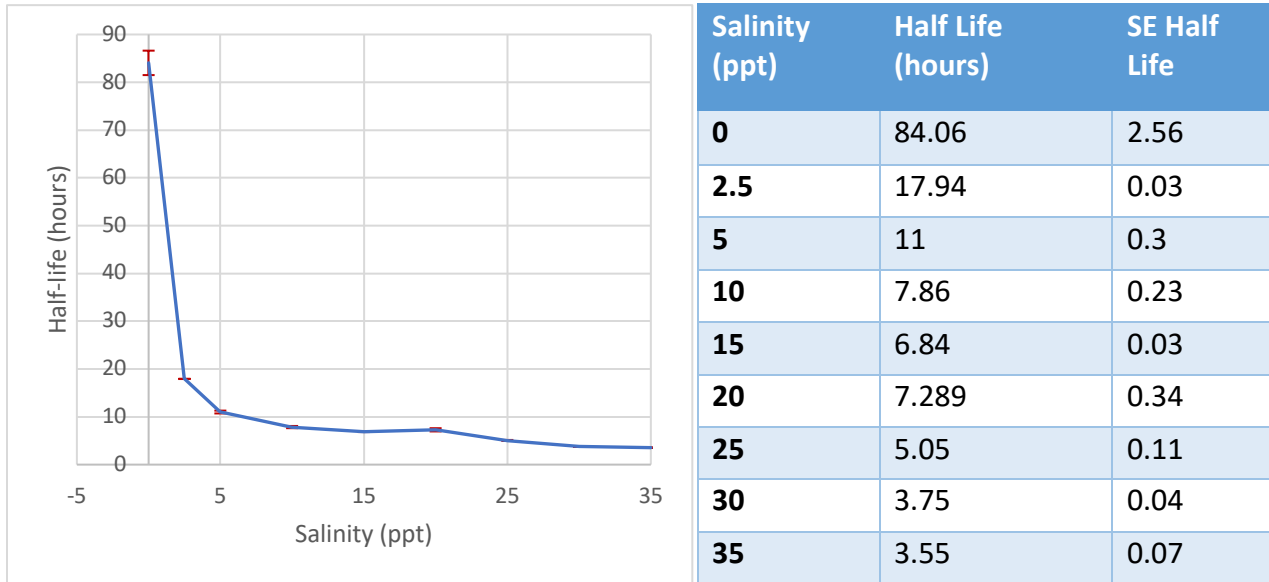


Figure 3 and Table 4: Variation of half-life with salinity from 0 ppt to 35 ppt. Half-lives differ among the nine salinity conditions in the gradient ($F_{8,8991} = 855694.2$, $p < 0.0001$, Figure 3). As salinity increases, half-life decreases exponentially. The error bars (in red) representing the standard error of half-life are shown in the figure and on the right (Table 3).

The degradation of BH in various isolated ion solutions is shown below.

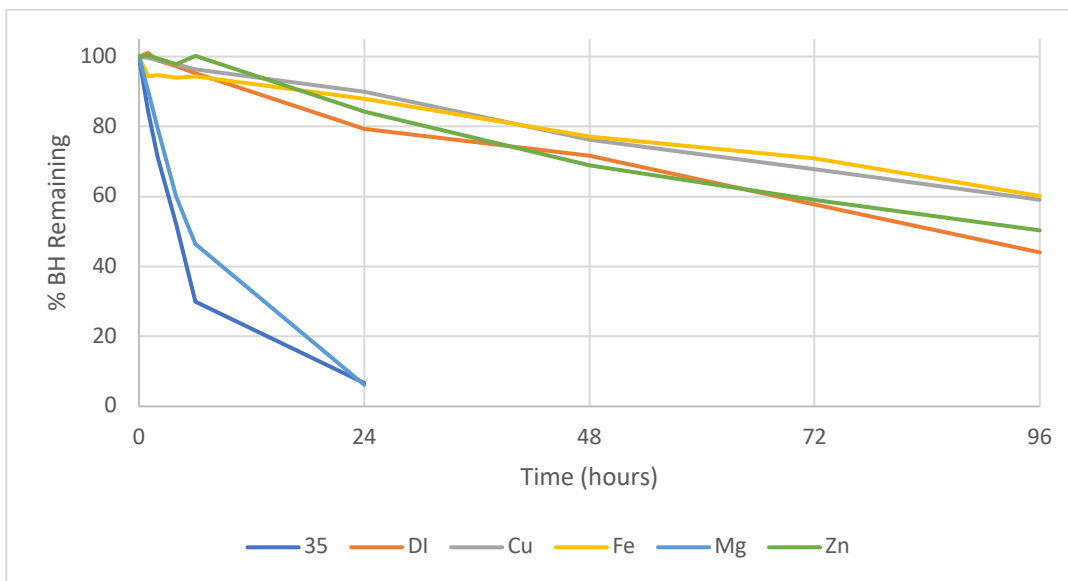


Figure 4: the photodegradation of BH in 35 ppt artificial sea water, magnesium solution, deionized water, copper solution, iron solution, and zinc solution. The degradation was much more expedient in artificial seawater and in the presence of magnesium than in the presence of any other ions.

The half-life of BH in the presence of various ions isolated from seawater is shown below.

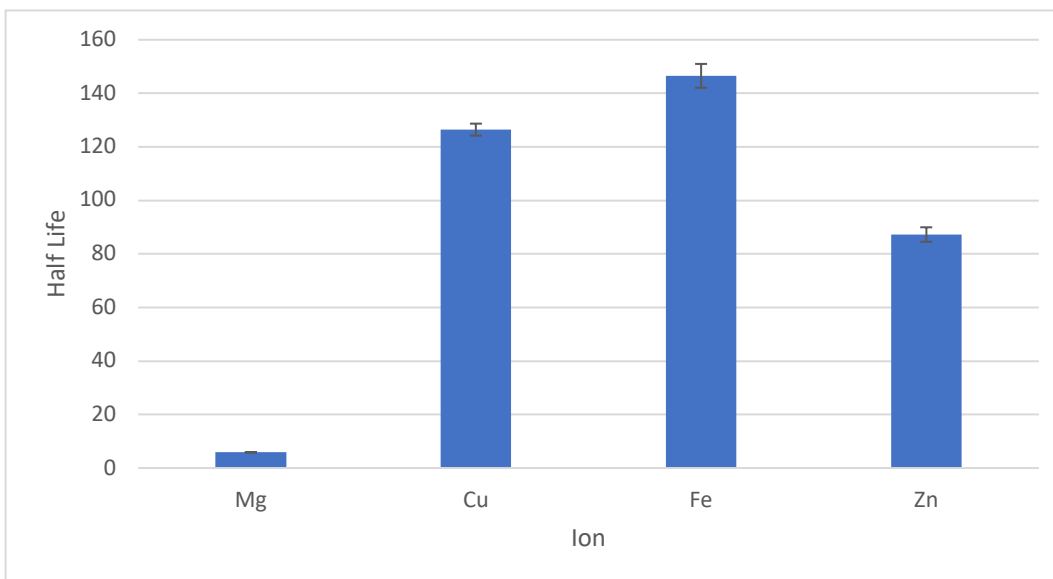


Figure 5: Half-life of BH differs significantly in the presence of four ions isolated from seawater: copper, iron, magnesium, and zinc. ($F_{3,3996} = 480071.6$, $p < 0.0001$, Figure 5). Half-life was shortest in the presence of magnesium and longest in the presence of iron.

As salinity increased from 0 ppt to 35 ppt, the half-life of BZB decreased exponentially from 84.1 ± 2.6 hours to 3.5 ± 0.07 hours (Figure 3 and Table 4). Additionally, it was found that, when isolated from other ions, magnesium ions influenced this degradation (Figure 4). The half-life of BH in the presence of magnesium was 5.85 ± 0.12 hours. The half-lives in the presence of copper, iron, and zinc were 126.4 ± 2.24 hours, 146.5 ± 4.5 hours, and 87.23 ± 2.7 hours, respectively (Figure 5). These results show that the presence of magnesium ions could be, in large part, responsible for the rapid degradation of benzobicyclon hydrolysate in seawater.

One study by Karuppusamy et al. (2021) showed that calcium magnesium oxide (CaMgO_2) nanoflakes had strong photocatalytic activity on the degradation of methylene blue and p-nitrophenol in the presence of hydrogen peroxide under UV irradiation. Nanocomposites composed of silver, magnesium oxide and tantalum oxide ($\text{Ag@Mg}_4\text{Ta}_2\text{O}_9$) have been shown to act as a photocatalyst the degradation of the herbicide Atrazine (Alkayal et al., 2019). Additionally, magnesium ion and titanium dioxide were combined to form a catalyst ($\text{Mg}^{2+}\text{-TiO}_2$) that accelerated the degradation of dichlorvos, an organophosphate insecticide (Siva Rao et al., 2012). The structures of these four chemicals are not dissimilar from that of benzobicyclon hydrolysate. They all contain electrophilic functional groups and conjugated rings. Magnesium compounds may be reacting with these functional groups to enhance degradation. It is intriguing that magnesium is being used in multiple forms as a photocatalyst to degrade these other pesticides. However, since we do not know the photoproducts of benzobicyclon hydrolysate degradation, it is difficult to determine if magnesium is catalyzing the hydrolysate reaction in the same way it is acting on the other four compounds.

Climate change will have a myriad of effects on the environmental fate and behavior of chemical toxicants by altering physical, chemical, and biological drivers of partitioning between

the atmosphere, water, soil, sediment, and biota as well as degradation processes within each of these compartments. These could include air-surface exchange, deposition, and reaction rates (including but not limited to photolysis, biodegradation, and oxidation) (Noyes et al., 2009). Temperature and precipitation, as altered by climate change, are expected to have the largest influence on the partitioning of chemical toxicants (Noyes et al., 2009).

As stated previously, salinity has been reported to impact bioaccumulation factors, half-lives ($t_{1/2}$), degradation rates, degradation product formation, as well as overall degradation (Crosby, 1998; Saranjampour et al., 2017; Vebrosky et al., 2018). Salinity has also been shown to influence the bioavailability of chemicals, metals, and ions in waters (Crosby, 1998). As climate variation becomes more chaotic, Louisiana could have an increased risk of saltwater intrusion into areas that currently farm rice, resulting in an increase of the salinity of the water used to flood fields. Since benzobicyclon degrades much more quickly in seawater than it does in freshwater this addition of novel ions could exacerbate the effects the herbicide on non-target organisms since Louisiana rice fields are unique environments in which crops are rotated with other agricultural commodities such as crawfish. Rapid degradation could also decrease the efficacy of the herbicide, requiring more frequent application of the chemical to fields. Bailey (2004) examined residues of the pesticide isoproturon in soils over a two-decade period and found that from 1997–2001 warming soils caused pesticides to degrade too quickly and that concentrations fell too low to control weed growth 30 days earlier than in years before 1997. Additionally, increased water temperature was found to increase the photodegradation rate of several phenyl-urea pesticides (Benitez et al., 2006). Given the potential increase in the loss of applied pesticides due to enhanced volatility and degradation, a compensatory increase in pesticide applications may be necessary to be efficacious against target pests. It has also been

shown that for every 10 °C increase in temperature, the predicted half-life of pesticides in soils may decrease by 60% (Bloomfield et al., 2006).

Conclusion

In conclusion, this study was effective in determining that increasing salinity increases the photodegradation of benzobicyclon hydrolysate. Further, the aims of this study were met when it was determined that magnesium ions are, in part, responsible for this rapid degradation.

Future Research

This study raises more questions than it answers. It would be prudent to investigate what photoproducts are being formed by the photolysis of BH and how those photoproducts may be interacting with the environment. Confirmation of photoproduct structure may be able to explain why magnesium may be acting as a photocatalyst.

Experimentation with beryllium (an alkali earth metal in the same group as magnesium) may be able to further elucidate if the photolysis is caused by the chemical properties of magnesium. Additionally, removal of oxygen from the system by bubbling nitrogen through the ion solutions may be able to eliminate the role of oxygen in the photochemical reaction.

This research could also be expanded by studying the degradation of BH in water-sediment systems instead of water alone. These sediments would be sourced from Louisiana rice fields to examine the impacts of BH on target ecosystems or from Louisiana wetlands to examine the effects of BH runoff on non-target ecosystems. This could be accomplished in two ways: By using different ions at environmentally relevant concentrations with a single rice sediment or by utilizing multiple sediments in DI water.

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