Degradation of Thiamethoxam via Photocatalysis: Kinetics, Mineralization, and Toxicity

A Major Qualifying Project Report
Submitted to the Faculty of

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the
Degree of Bachelor of Science, Chemical Engineering

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April 25, 2013

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Acknowledgements

We would like to acknowledge Marie-Noelle Pons, Phillippe Arnoux, and Orfan Zahraa for their help and guidance while we were conducting our experiments in France. We would also like to acknowledge Terri Camesano and Robert Thompson for their help interpreting our data and developing our results. Lastly, we would like to thank Maroua Jguirim for helping us feel comfortable and welcome in France and at ENSIC.

Abstract

The goal of this project was to characterize the photocatalytic degradation of the pesticide thiamethoxam and the effects of the additives ammonium nitrate, humic acid, and river water on this degradation by measuring reaction kinetics, degree of mineralization, and toxicity. Experimental results were obtained for these methods via high performance liquid chromatography, total organic carbon (TOC) and total nitrogen (TN) analysis, and a lettuce test, respectively. Reaction rate coefficients were found to be approximately 0.0054 min^{-1}. Nearly all samples decreased in TOC and increased in TN after degradation. Base thiamethoxam was shown to increase in toxicity after degradation. Overall, humic acid was found to be the most efficient additive for this reaction.

Table of Contents

Table of Figures

Table of Tables

1.0 Introduction

With 4.5 billion pounds of pesticides being applied in the United States annually, the use of these chemicals, and the environmental impacts of doing so, are widespread (Weiss et. al, 2004). Once introduced to a field, pesticides can leach into groundwater or collect in runoff, affecting local drinking water and wildlife. As a result, many of the environmental impacts of these chemicals are currently being investigated. One such chemical under investigation is thiamethoxam, a relatively new pesticide, and the first second-generation neonicotinoid to enter the market. Thiamethoxam is widely used because of its efficacy at low doses, variety of application methods, and long half-life (Maienfisch et al, 2001). However, these characteristics also make thiamethoxam an environmental concern, particularly because of its high toxicity to honeybees, which can negatively impact the natural crop pollination process (Henry et al, 2012; Cresswell, 2011).

Due to the many hazardous side effects of pesticides in drinking water, scientists are currently investigating several degradation methods. One of the most promising groups of methods being studied is Advanced Oxidation Processes, or AOPs, which introduce hydroxyl radicals to the system that unselectively attack organic molecules, mineralizing them into water and carbon dioxide (Malato, 2002). Photocatalysis is an AOP that uses ultraviolet light and a catalyst to generate these radicals. Titanium dioxide is a particularly popular catalyst for this process, as it is relatively inexpensive and one of the most active materials available (Devipriya & Yesodharan, 2005). To increase the efficiency of the process, some scientists are investigating the use of additives that naturally occur in water which increase the production of hydroxyl radicals. These additives include substances such as humic acids, carbonates, and nitrates (Ukpebor, Halsall, 2011).

The photocatalytic degradations of several pesticides under various conditions have been extensively studied (Malato et. al, 2002; Konstantinou et. al, 2001; Oller et. al, 2006). However, due to its fairly recent introduction to the market, thiamethoxam's behavior during photocatalysis has been relatively under-studied. The purpose of this research was to address this gap by not only studying thiamethoxam's photocatalytic degradation via TiO_2, but also the effects of adding ammonium nitrate, humic acid, and natural river water to the solution. In these experiments, a

UV lamp and PC-500 TiO_2 bounded onto cellulose paper by SiO_2 were used to degrade 30 ppm thiamethoxam. Kinetics, mineralization, toxicity, and the effects of the three additives on this degradation were analyzed.

2.0 Background

As mentioned in the previous section, although thiamethoxam's photocatalytic degradation remains relatively understudied, the photocatalytic degradation of several other pesticides has been thoroughly examined. In this chapter, this research is reviewed by first placing thiamethoxam, a relatively new pesticide, in the context of other pesticides. Then, different methods currently used to treat pesticides are discussed, with emphasis placed on Advanced Oxidation Processes and how photocatalysis falls into this category. Finally, previous research on the photocatalytic degradation of other pesticides via TiO_2 is reviewed, including relevant studies that examined the effects of additives on this process.

2.1 Pesticides

There are over 20,000 different pesticides with around 900 different active ingredients available for purchase and use. According to Weiss, Amler, & Amler (2004), these pesticides are used as "insecticides, miticides, fumigants, woods preservatives, and plant growth regulators" among other uses (p. 1030). There are four main categories of active ingredients used in pesticides: 1) carbamates and organophosphates, 2) organochlorides, 3) pyrethroids, and 4) neonicotinoids. Carbamates and Organophosphates work by inhibiting acetylcholinesterase which then impairs the organisms' nervous system function. Organochlorides depolarize nerve membranes and therefore disrupt nervous system function. Pyrethroids change the permeability of organisms' membranes to sodium ions which ultimately impairs nervous system function (Weiss, et. al., 2004, p. 1031). Neonicotinoids, a type of pesticide derived from nicotine and the focus of this study, bind to the nicotinic acetylcholine receptors in insects, displacing tritiated imidacloprid, and killing the insect. It is effective on select insects including "aphids, whiteflies, thrips, leaf miners, beetles, and some lepidopteran species" (Nauen, et al., 2003, p. 56). The first neonicotinoids were made available in 1991, and they are used in many different applications, from seed treatment to stem applications (Zabar, Komel, Fabjan, Kralj, & Trebse, 2012, p. 293).

Pesticides are generally used in agriculture to produce larger crop yields with less human effort, but they are also used to reduce the risk and frequency of insect-borne diseases. According to Weiss et al. (2004), 4.5 billion pounds of chemicals are applied in the United States annually (p. 1030). 2.5 billion pounds of this total are herbicides and insecticides applied to only corn and soybean crops (Reimer & Propoky, 2012, p. 362). According to Reimer & Prokopy (2012), there

are three distinct groups of commercial pesticide applicators: industrial weed management, agricultural pest management, and aerial application, as well as private applicators (p. 363). Pesticides become an environmental issue when they enter surface waters, which can occur during the application process, disposal process, through soil leaching, or as condensation from the atmosphere (Ukpebor & Halsall, 2012, 656). Effort must be put into removing these contaminants from the environment as pesticides tend to be highly stable, bioaccumulative, and toxic to many species (Devipriya, Yesodharan, 2004; Ormad et al. 2007).

2.1.1 Thiamethoxam

Thiamethoxam was the first second-generation neonicotinoid. Synthesized in 1991, thiamethoxam is effective against both chewing and sucking insects, and was introduced to market in 1998 by Novartis Agribusiness, a precursor to the Swiss company, Syngenta Crop Protection (Maienfisch et al, 2001, "Discovery"). Thiamethoxam is highly stable, with an "estimated half-life at room temperature [of] 200-300 days" at pH 7 (Maienfisch et al, 2001, "Chemistry"). It also exhibits a "relatively high water solubility" of 4.1 g/L at room temperature, and is relatively non-toxic to birds, fish, and mammals. However, a study conducted by entomologist Mickaël Henry and colleagues and presented in the March 30, 2013 issue of *Science*, found that thiamethoxam may be toxic to bees. According to the *Chemical & Engineering News* article that followed the story, bees that had been exposed to "sublethal doses" of the pesticide were "twice as likely to die while foraging," suggesting that the pesticide "may contribute to colony collapse disorder" (Bomgardner, 2012). Because of the results of this study, France considered banning the pesticide in June of 2012, but decided more research was needed before passing the ban.

As shown in Figure 1, a molecule of thiamethoxam contains two organic rings and 5 nitrogen atoms. Thiamethoxam's complex structure makes it difficult to predict a mechanism for photocatalytic degradation (Kegley et al., 2010).

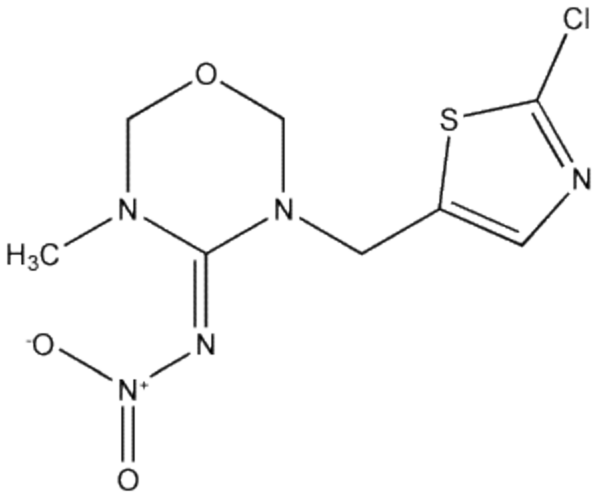

Figure 1: Molecular Structure of Thiamethoxam

2.2 Treatment Techniques

To ameliorate the water pollution resulting from pesticide use, different treatment techniques have been developed over the years. The goal of basic water treatment practices is to degrade or remove the majority of the contaminants. One of the industry standards for pesticide removal involves oxidizing the pesticides using chlorine, however, the intermediates and by-products generated by these reactions can sometimes be extremely harmful and carcinogenic. Water treatment plants will also introduce coagulants such as aluminum sulfate to floc out the pesticides. Furthermore, adsorption onto activated carbon is an option for those plants that are large enough to sustain the high cost of purchasing the carbon (Ormad, et al., 2007, p. 98).

2.2.1 Advanced Oxidation Processes (AOPs)

Other degradation techniques being investigated involve the employment of Advanced Oxidation Processes (AOPs), which are defined by Quiroz, Bandala and Martínez-Huitle as, "processes involving the generation of highly reactive oxidizing species able to attack and degrade organic substances" (2011, p. 685) By these processes, the pesticides are not only removed but may also be completely mineralized. Mineralization is the process of breaking down chemicals into carbon dioxide and water. There are four groups of AOPs: ozone/ozonation processes, electro chemical oxidation, heterogeneous photocatalysis, and homogeneous photocatalysis (Quiroz, et al., 2011).

In ozone processes, ozone is dissolved into the contaminated water, where it breaks down to produce free radicals that readily react with pesticides (Chen, Lin, Kuo, 2013). Because of this, ozone can degrade pesticides via two pathways: direct reactions between ozone and the molecule

or indirect reactions caused by the free radicals produced during the breakdown of ozone (Ormad, et al., 2007, p. 104). This method is not dissimilar to chlorination in theory, but ozonation does not create secondary pollutants when dissolved. However, it is often limited by the instability of ozone and the high cost of generating it.

Electrochemical oxidation uses an anode to oxidize water, allowing degradation of the pesticide at the anode, where hydroxyl radicals are adsorbed (Quiroz, et al., 2011). Because the anode is the primary surface for degradation, the anode material is very important, with its efficiency directly proportional to the efficiency of the degradation. The weaker the attraction is between the anode and hydroxyl radicals, the more efficiently the pesticides can degrade, as the organic compounds have more access to the highly reactive radicals. Direct electrochemical oxidation is effective in a wide range of treatment conditions and does not necessitate any further reagents for complete oxidation and mineralization. Electrochemical oxidation can also be coupled with oxidizing reagents such as hydrogen peroxide for a stronger effect.

Photocatalytic processes offer many advantages including fast reaction rates, cheap and readily available catalyst options, a lack of generated harmful polycyclised products, and effectiveness at very small concentrations of contaminant (Devipriya, Yesodharan, 2004). Heterogeneous photocatalysis involves a stationary catalyst, generally TiO_2, in the presence of UV light, wherein the irradiated catalyst produces an “electron/hole pair” that induces redox reactions in the water at the catalyst’s surface (Quiroz, et al., 2011). Homogenous photocatalysis involves the same generic process as heterogeneous photocatalysis, but in this case the catalyst is suspended into the water.

The most notable examples of homogeneous photocatalysis are Fenton and Fenton-like reactions. In Fenton reactions, combinations of ferrous salts and hydrogen peroxide or another hydroxyl radical generator are applied to a solution (Quiroz, et al., 2011). The reaction can take place with or without the presence of UV light. It has been found that homogenous photocatalysis is more efficient than heterogenous photocatalysis, but the filtering process to remove the catalyst offsets this efficiency with added cost (Devipriya, Yesodharan, 2004, 313). Also, scale up for such processes is much more difficult than that of heterogeneous processes because the light distribution within the tank is more complex and must be assessed. Heterogenous photocatalysis will be the main focus of this study.

2.3 Heterogeneous Photocatalysis

In heterogeneous photocatalysis, a stationary oxide-producing catalyst is irradiated with an energy source to create highly reactive free radical hydroxyls. This process begins with Reaction 1, as reviewed by Devipriya & Yesodharan (2004):

$$TiO_2 + hv \rightarrow e^- + h^+, \quad (1)$$

The catalyst often acts as a semi-conductor, which means that the particles contain voids which cannot conduct electricity, unlike metals (Linsebigler, et al., 1995, p.739). When the particles of the catalyst absorb sufficient energy from a light source, electrons will jump across these voids, from the ground state to an excited state, or in other words, from the valence band to the conduction band. As the electron jumps to the conduction band, it generates a reciprocal positive gap in the valence band, which can be seen in Reaction 2 (Linsebigler, et al., 1995). The irradiated electrons may travel to the surface of the particle, where they will interact with species adsorbed onto the particle. Charge is then transferred from the excited electrons and positively charged holes to substances adsorbed onto the surface of the catalyst. In the presence of water, hydroxyl groups will collect this charge, producing hydroxyl radicals. These hydroxyl radicals may leave the surface of the catalyst or remain adsorbed.

A proposed generation process for hydroxyl radicals is presented in Reactions 2-3b (Devipriya, Yesodharan, 2004).

$$(O_2)ads + e^- \rightarrow (O_2^{-\bullet})ads, \quad (2)$$

$$Ti(IV) - OH^- + h^+ \leftrightarrow Ti(IV) - {}^{\bullet}OH, \quad (3a)$$

$$Ti(IV) - OH_2 + h^+ \leftrightarrow Ti(IV) - {}^{\bullet}OH + H^+. \quad (3b)$$

Here, oxygen that has been adsorbed to the surface of the catalyst receives the electrons from the excited particles and is reduced to a superoxide radical. The now positively charged TiO_2 particles can oxidize water on their surfaces into hydroxyl radicals. This mechanism shows that the presence of molecular oxygen, O_2, is imperative in photocatalytic processes with TiO_2 (Devipriya, Yesodharan, 2004).

Figure 2 shows a visual representation of the photoactivation reaction and its products.

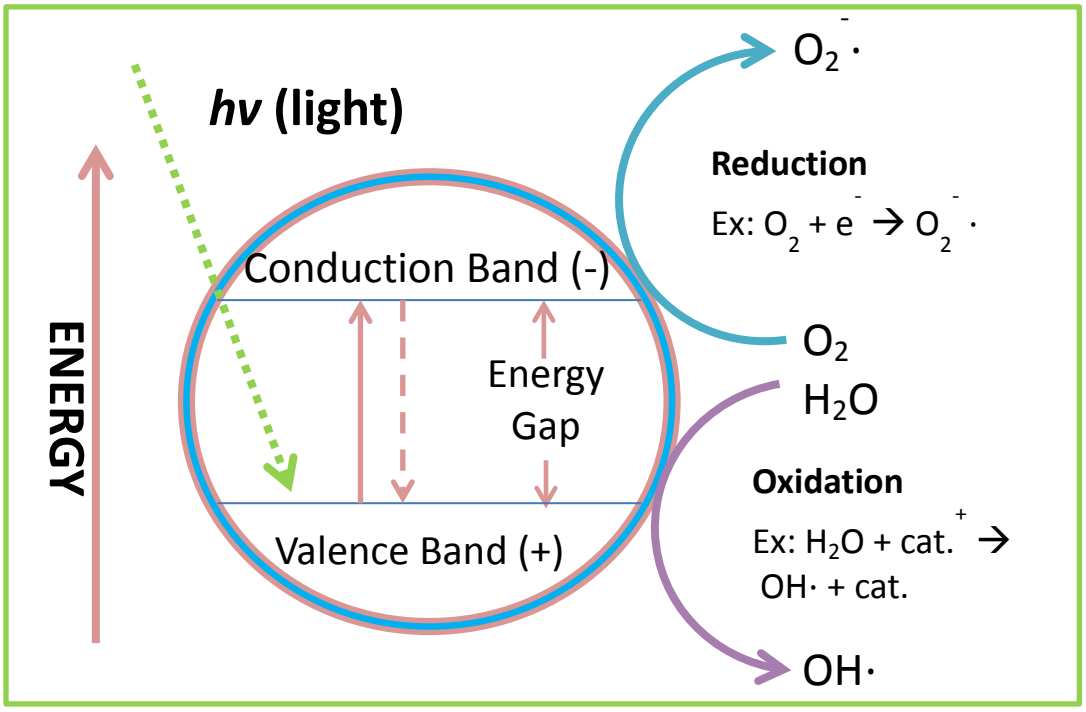

Figure 2: Photocatalysis Reaction Diagram, adapted from Photocatalysis (2005)

As hv (light) hits the particle, an electron jumps across the band gap to the conduction band, leaving a positively charged hole in its place, represented by the "energy gap". The electron can then be used to reduce an adsorbed compound, O_2 in Figure 2, while the hole can be used to oxidize an adsorbed compound, most commonly water or OH^-.

2.3.1 Photocatalysis via TiO_2

Photocatalysis via TiO_2 is a well-researched process. This is evidenced by the thousands of published studies "related to the degradation of toxic and hazardous substances in water" (Miguel et al, 2012). A large number of these studies focus on hazardous soluble pesticides, which can enter freshwater supplies via agricultural runoff. In particular, there is great interest in assessing the capabilities of solar processes to degrade and mineralize these toxic chemicals, which would greatly reduce the costs involved.

TiO_2 is an ideal catalyst for solar photocatalysis studies for several reasons. Most importantly, TiO_2 is active within the range of natural sunlight. It is also relatively cheap and has been proven to be the most active catalyst in many studies (Devipriya & Yesodharan, 2005). In addition, it is

relatively stable under harsh conditions, and can be used in fixed bed or suspension studies, making it adaptable to many types of experiments and reactors.

2.3.2 Transformation Products

Ideally, solar photolysis would be able to completely degrade and mineralize harmful chemicals in the environment, completely eliminating the need for human intervention. However, photolysis and photocatalysis, even in cases when complete degradation is possible, often lead to numerous sometimes toxic transformation products instead of mineralization. In fact, in some cases these procedures can leave the solution more toxic than it was originally. For example, in their paper, "Degradation and Detoxification of 4-nitrophenol by Advanced Oxidation Technologies and Bench-scale Constructed Wetlands," J.A Herrera-Melián and her colleagues found that smaller concentrations of the intermediates produced from photocatalysis of 4-nitrophenol, a pollutant produced by various manufacturing industries, were more toxic to duckweed than larger concentrations of the original pollutant (2012).

One of the main difficulties of studying photocatalytic degradation of pesticides arises from the fact that there are so many different transformation products created. While many attempts have been made to propose mechanisms and structures for some of these transformation products, the complex structures of the initial chemical as well as the complexity of the reactions makes this process difficult (Malato, S. et al, 2002). In addition, due to the differing structures of the multitude of pesticides studied, the transformation products discovered from one pesticide can be different from those of another. Further complicating the matter, the procedures and equipment used in photocatalytic studies tend to vary, which can also result in the observation of different degradation times and transformation products. According to Ukpebor and Halsall, the transformation products observed during their study of the pesticides fenitrothion and diazinon varied from those of other studies of the same pesticides (2011). In their paper, "Effects of Dissolved Water Constituents on the Photodegradation of Fenitrothion and Diazinon", they attributed these differences to differences in procedure used, such as different sources of light and variations in water composition.

2.4 Enhancing Photocatalysis: Coupling Reactions and Additives

Photocatalytic degradations, particularly the mineralization portions, can be incomplete and very slow. To remedy this, researchers recommend coupling photocatalytic reactions with other water treatment methods such as photo-Fenton and constructed wetlands (Herrera-Melián, J.A. et al, 2012). Photo-Fenton procedures tend to be faster and in some cases, more effective. However, this process is much more expensive. Unlike the TiO_2, the iron and hydrogen peroxide involved in photo-Fenton reactions must be replaced throughout the experiment. The amount of material needed will vary based on operating conditions and equipment, and may not be cost prohibitive in all cases. For example, in their paper, "Photocatalytic Treatment of Water-soluble Pesticides by Photo-Fenton and TiO_2 using Solar Energy," Malato and his colleagues argue that the amount of iron needed to degrade and mineralize the pesticides was so small, it could be discharged safely into the environment, eliminating any filtration costs (2002).

Yet another method to increase the effectiveness and efficiency of photocatalytic processes is to introduce naturally occurring oxidizers such as hydrogen peroxide (H_2O_2), nitrates (NO_3^-), carbonates (CO_3^{-2}), and dissolved organic content, or DOC. Adding these additives allows scientists to study photodegradation under more natural conditions, thus helping them analyze what really happens when pesticides and other such chemicals are introduced to the environment. These substances are naturally found in freshwater in small amounts, and are capable of producing OH radicals, which can speed up photodegradation. However, the particles of DOC can also have a shielding effect, slowing down the reaction (Ukpebor & Halsall, 2011). Therefore, it is important to filter larger particles out of solution to counteract any shielding.

3.0 Methodology

In the previous chapter, Advanced Oxidation Processes were reviewed as a potential method to degrade pesticides, with emphasis placed on heterogeneous photocatalytic reactions that used TiO_2. Previous research studying the accelerative effects of additives on this process was also reviewed. This research forms the basis for the experimental methods presented in this chapter. These methods include a discussion of solution preparations, reactor conditions and procedures, and an overview of the three types of studies conducted on the solutions: reaction kinetics, mineralization, and toxicity.

3.1 Solution Preparations

Base solutions of 30 ppm thiamethoxam were prepared from an original solution of 100 ppm thiamethoxam in ultrapurified water by diluting with additional ultrapurified water. For the ammonium nitrate solutions, solid ammonium nitrate was dissolved completely into the base solution before being placed in the reactor. For the humic acid solutions, humic acid, which is only partially soluble in water, was added and left to mix for about an hour. Filtered and unfiltered samples containing humic acid were tested in the reactor. To make the river water solution, the original solution was diluted with natural river water collected from the Meurthe River instead of ultrapurified water. The following table shows data on all of the solutions run through the reactor and the conditions under which they were tested.

Table 1: Summary of Test Conditions

Solution Description	**Reactor Conditions**	**Experiment Length (min)**
30 ppm thiamethoxam	Catalyst 1 + UV	390 510
30 ppm thiamethoxam	Catalyst 2 + UV	450 300 2805
30 ppm thiamethoxam	UV only	2885
30 ppm thiamethoxam	Catalyst 1 only	215
30 ppm thiamethoxam + 500 mg/L KNO_3	Catalyst 1 + UV	375 540
30 ppm thiamethoxam + 500 mg/L NH_4NO_3	Catalyst 1 + UV	460 465
30 ppm thiamethoxam + 500 mg/L NH_4NO_3	Catalyst 2 + UV	370 440
30 ppm thiamethoxam + 20 mg/L NH_4NO_3	Catalyst 2 + UV	460

		440
30 ppm thiamethoxam + 10 mg/L Humic Acid (unfiltered)	Catalyst 2 + UV	435 440 450 450
30 ppm thiamethoxam + 10 mg/L Humic Acid (filtered)	Catalyst 2 + UV	425
30 ppm thiamethoxam + river water	Catalyst 2 + UV	465 405 440 405

3.2 Reactor

The reactor used in this experiment was designed by researchers at École Nationale Supérieure des Industries Chimiques in Nancy, France. The main feature of this reactor was the reactor chamber. In this rectangular glass receptacle, the sample being tested was exposed to UV light and the TiO_2 catalyst simultaneously, thus causing the photocatalytic reaction to occur. This rectangular glass receptacle was open to the air, further facilitating the oxidation process, but allowing for significant evaporation, which impacted some of the degradation results. The receptacle contained a 48 cm glass slide with TiO_2 paper folded over it. The UV light was positioned directly above the reactor chamber for maximum exposure.

The reactor also contained a peristaltic pump that cycled the solution continuously through the reactor chamber, allowing for sustained exposure to the catalyst and UV light, and thus continuous degradation of the solution. To collect samples for periodic HPLC testing, a Florence flask open to the air served as a sampling reservoir, minimizing evaporation. Approximately 6 feet of connecting tubing were used to contain the circulating solution as it cycled between the reactor chamber, sampling reservoir, and the pump. A diagram of the system used is provided in Figure 3.

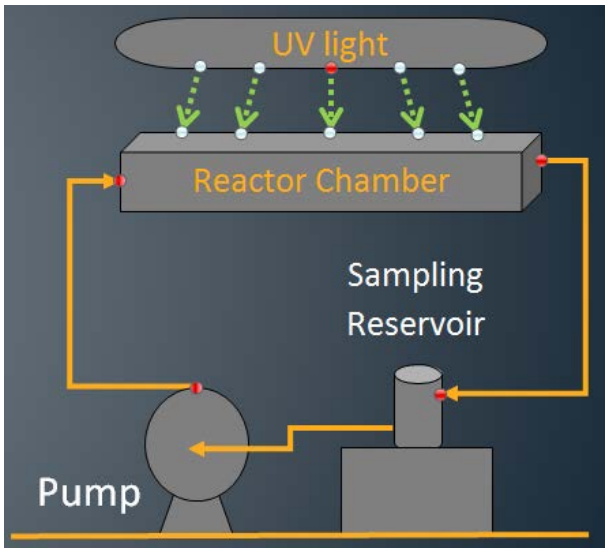

Figure 3: Schematic of Reactor System

3.3 Reactor Procedure

To prepare the reactor chamber, a piece of photocatalytic TiO_2 bound with SiO_2 paper was cut with scissors to slightly larger than the reactor chamber size, approximately 48 x 4 cm. The ends of the catalyst paper were wrapped around a clean glass plate. The paper and glass plate were then thoroughly rinsed using ultrapurified water to remove any loose pieces of catalyst which could later become dislodged, affecting the reaction and damaging the HPLC's column. Once thoroughly rinsed, the catalyst paper and glass plate were placed into the bottom of the reactor chamber.

The peristaltic pump was set to operate at Speed 2 which equates to approximately 255 mL/min. Solutions of approximately 250 mL per experiment were cycled for 60 minutes without UV light, allowing time for adsorption of the solution's constituents to the catalyst. After 60 minutes, the UV light was turned on and left on for the remainder of the experiment. The exceptions to this were the two experiments without catalyst and without UV light (Appendix B). The length of time that the solution was exposed to light varied depending on the rate of the reaction, allowing more time for slower reactions, so that the solution could more fully degrade. Shorter reactions were sampled for HPLC testing every 10-15 minutes, while longer reactions were sampled every 30-60 minutes. Sampling procedure is discussed in Section 3.4, Reactor Cleaning Procedure.

3.4 Reactor Cleaning Procedure

The reactor was cleaned shortly before each new experiment was conducted. To do this, ultrapurified water was pumped through the reactor twice for approximately 5 minutes with the catalyst installed but the light off, and then drained out. This procedure was conducted before each experiment for the first month. On the 31st of January, a test was conducted to ensure that all residual thiamethoxam was being removed between experiments. Ultrapurified water was added to the reactor and left to cycle in the presence of the catalyst and UV light for 130 minutes. Samples were taken every 10 minutes and run through the HPLC to determine the concentration of any residual thiamethoxam. Results from this test can be found in Appendix C. After this test, the cleaning procedure for the reactor changed. For every experiment after the 31st, ultrapurified water was pumped through the reactor once for approximately 10 minutes with the catalyst in place and the UV light on, and then drained out.

3.5 Kinetic Rate Testing

3.5.1 Sampling Procedure

2 mL samples were taken from the sampling reservoir of the reactor using a long-needled syringe. From these samples, approximately 50 microliters were injected into the HPLC via a smaller syringe for testing (see Section 3.5.2). After testing, the remainder of the thiamethoxam solution was added back into the reactor. The sampling syringe and the vial were rinsed once with ultrapurified water between samples. The vial was dried completely between samples using paper towels.

For the unfiltered humic acid and river water experiments, the samples were filtered through a 0.22 micron syringe filter before being placed in the vial. This was to ensure no particles of humic acid entered the HPLC. The filter and filter syringe were rinsed once with ultrapurified water between samples.

After the reactor had been run for the full duration of the experiment, the entire contents of the reactor were collected and stored in dark glass bottles in a refrigerator for further analyses.

3.5.2 High Performance Liquid Chromatography

High Performance Liquid Chromotagraphy (HPLC) is a useful and efficient means for separating components in a mixture. HPLC involves the interactions between three phases: a mobile phase, a stationary phase, and the sample to be separated, as with all chromatography. The mobile phase is passed through a separating column, often packed with some sort of granules or thin film (Umber, 2012) under very high pressure (up to 400 atm), rendering this method much more efficient than normal gravity-induced column chromatography (Clark, 2007). One of the benefits of HPLC is that the high pressure of the column also permits the use of smaller packing granules with increased surface area, which allow for increased interactions between the three phases as they pass through the column (Clark, 2007).

The HPLC column used in this research was run in reversed phase. Reversed phase HPLC features non-polar packing and a polar solvent, meaning that polar components are more attracted to the solvent and pass through the column more quickly than nonpolar materials. The retention time of components in a solution can vary depending on differences in system pressure and temperature, mobile phase feed rate, and the compositions of both the mobile and solid phases.

Many different types of detectors may be used to identify the separated materials leaving the column, but the most common is an UV-Vis spectrophotometer. This detector can identify the retention time of a material by producing a peak on a time line as the material passes by. The area under this peak corresponds to the material's concentration in the solution and can be correlated using calibration curves.

HPLC Procedure

The HPLC machine was prepared before each experiment. The mobile phase liquid was purged from the system using the automatic purge feature, to ensure that no air bubbles were trapped in the tubing. The mobile phase pumps were turned on and the pressure in the system was allowed to equilibrate. The pumps were set to pump at 0.150 mL/min of 1.5 volume % glacial acetic acid in ultrapurified water and 0.150 mL/min HPLC-grade acetonitrile. After they had equilibrated, the UV-Vis spectrophotometer was zeroed. Approximately 40 microliter samples were injected using a 50 microliter syringe, which was rinsed three times with acetonitrile between samples.

3.6 Mineralization Testing: Total Organic Carbon and Total Nitrogen

Often, the transformation products of photocatalytic reactions are difficult to track and characterize. Rather than measuring individual molecules of products, it is more common for scientists to measure total organic carbon (TOC) or total nitrogen (TN) of the sample instead. However, these mass balances can still fail to reach stoichiometric agreement. In particular, the degradation of these chemicals sometimes leads to the production of nitrogen gas, which escapes the system, leaving nitrogen unbalanced (Oller et al, 2006). Despite this, researchers have been attempting to improve transition product tracking indirectly by measuring NH_4^+ or NO^{3-} concentrations. However, balance of nitrogen still remains difficult for a number of photocatalytic processes.

3.6.1 Total Organic Carbon and Total Nitrogen Test Procedure

Approximately 40 mL of each degraded test solution were placed in a tall thin flask and affixed with a permeable cap. The bottles were labeled and processed with a Shimadzu VCH machine, where they were tested for inorganic carbon content by first exposing the solution to a strong acid and measuring the amount of CO_2 released using a CO_2 detector. After this, organic carbon was measured by burning the solution and measuring the CO_2 released with the same detector. Nitrogen was also detected by first combusting all nitrogen to form NO and NO_2. These compounds were then exposed to ozone, which allowed for nitrogen concentration detection by chemiluminescence.

3.7 Toxicity Test Procedure

Toxicity tests were performed according to the procedure presented by Cobb & Byberg (2012). Two circles of absorbent paper were placed in the bottom of short glass jars and filled with around 3 mL of each solution. Both original and degraded solutions were tested. Positive and negative controls were also included. The positive control contained Vittel mineral water and the negative control contained the same water with 5 g/L of NaCl. Twelve lettuce (*Lactuca sativa*) seeds were placed on the absorbent paper and the jar was covered with aluminum foil. Four small holes were made in the top of the foil to allow proper aeration and each covered glass jar was sealed in a plastic bag. The samples were left to germinate in the dark in a cabinet for 5

days. After 5 days, the samples were removed and measured. The entire length and the root portion of the sprout were recorded.

Relative toxicity was the main means by which the toxicity of each sample was compared. Degraded samples were compared not only to the positive and negative controls but also against their original solutions. Determining the change in relative toxicity for each solution helped identify clearly which solutions became more or less toxic after degradation. Toxicology calculations were made as presented by Equation 1.

$$RT = \frac{L_{Posit\_Control} - L_{Sample}}{L_{Posit\_Control} - L_{Negat\_Control}} \qquad \text{(Equation 1)}$$

In Equation 1, RT is the relative toxicity, L_{Sample} is the average length of seedlings in the samples, $L_{posit\_control}$ is average length of seedlings in the positive control sample, and $L_{negat\_control}$ is the average length of seedlings in the negative control.

4.0 Results and Discussion

Base solutions of 30 ppm thiamethoxam and solutions containing 30 ppm thiamethoxam as well as added nitrates, humic acid, and river water were degraded in a batch reactor in the presence of an immobilized TiO_2 catalyst and UV light. The data was examined to determine the kinetic rate coefficient for each experiment, and the solutions were tested for dissolved organic carbon and nitrogen content. Finally, toxicity of the degraded solutions was assessed using a lettuce test.

4.1 Kinetics Results

As expected, the thiamethoxam degradation reaction best fit a pseudo-first order rate law, which is typical for photocatalytic degradation of many pesticides (Devipriya & Yesodharan, 2004; Sur et al., 2005; Zabar et al., 2012). From the HPLC data collected during each experiment, the reaction rate coefficient for each reaction could be determined as the slope of the straight line on a plot of the natural log of concentration with respect to time. Figures 4 and 5 are examples of the graphs generated from the HPLC data, showing the concentration data from a degradation of base thiamethoxam. Kinetic data from the rest of the experiments can be found in Appendix D.

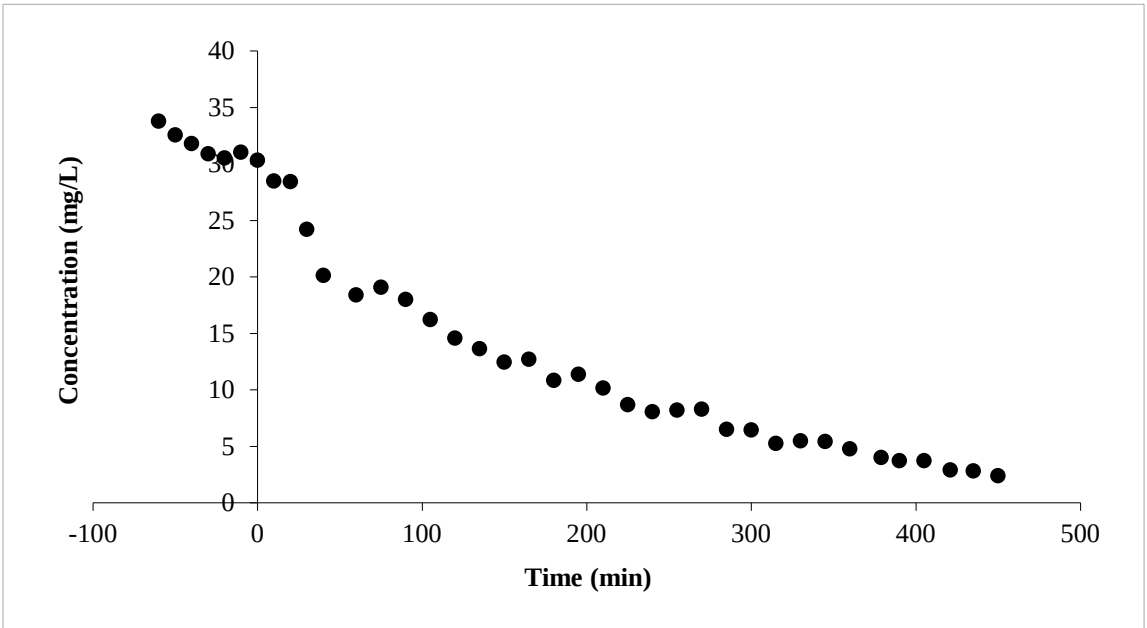

Figure 4: Concentration of 30 ppm Thiamethoxam vs. Time during Photocatalysis

In Figure 4, the time before zero represents the 60 minutes during which the UV light was off and the solution was allowed to adsorb to the catalyst. The decrease in concentration of

thiamethoxam during this time indicates that adsorption was occurring. In this example, the concentration of thiamethoxam was reduced to less than 3 ppm in 450 minutes.

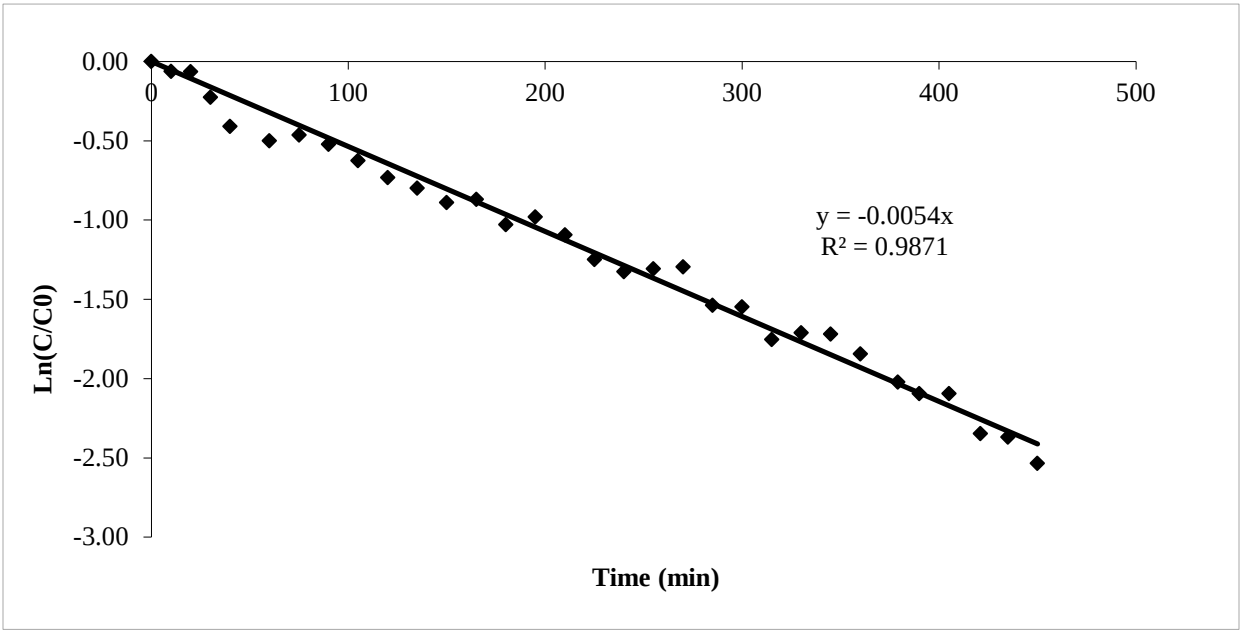

Figure 5: 1st Order Rate Coefficient Graph for the Photocatalytic Degradation of 30 ppm Thiamethoxam

Figure 5 shows the data from Figure 4, manipulated as a plot of the natural log of the concentration (C/C_0, where C_0 is the original concentration of thiamethoxam) versus time. Under these conditions, the concentration data forms a straight line, as is expected for a first order or pseudo first order equation. The rate coefficient for this experiment was found to be 0.0054 min^{-1}, as determined by the slope of the graph.

Average rate coefficients were determined for each different solution tested with the same piece of catalyst using the method described above. Figure 6 summarizes these rate coefficients. The base solution of 30 ppm thiamethoxam degraded with a first order rate coefficient of 0.0054 min^{-1}. There were then two solutions with additives that degraded slightly faster, the 500 mg/L ammonium nitrate and 10 mg/L humic acid, and two that degraded slightly slower, the 20mg/L ammonium nitrate and the solution made with river water.

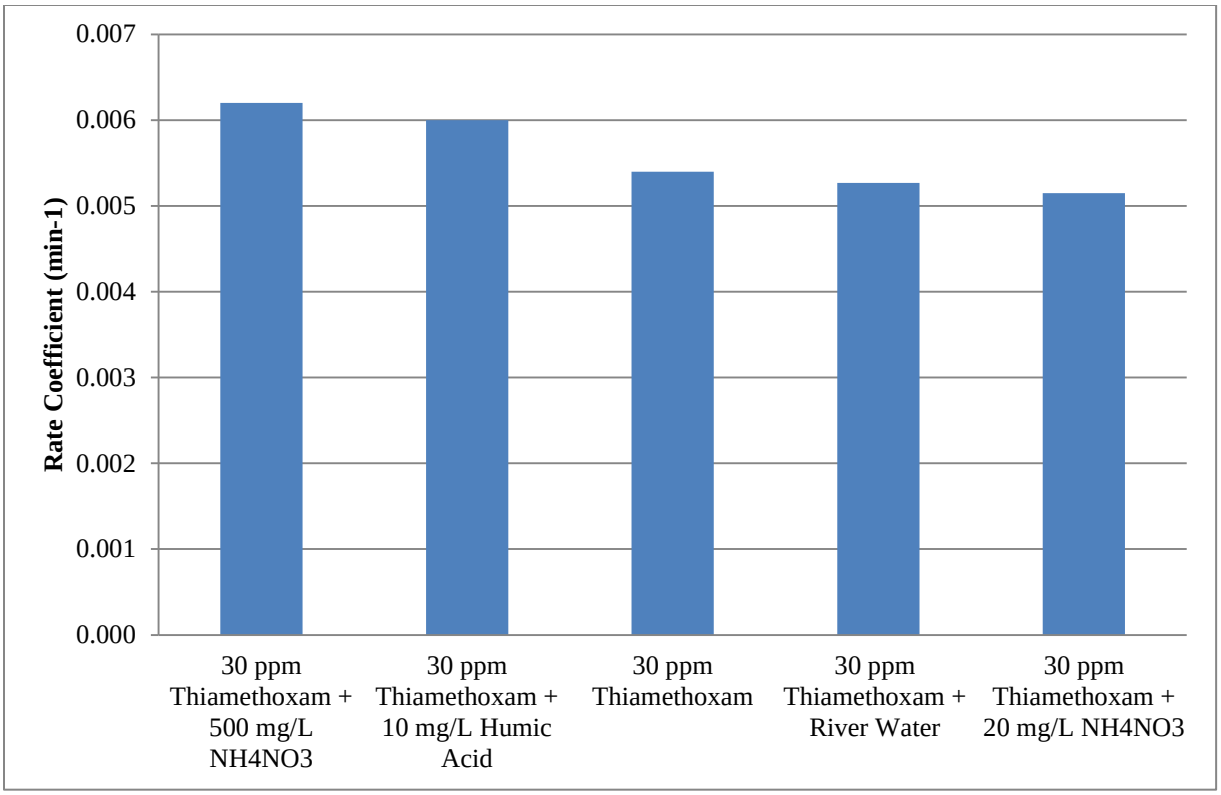

Figure 6: Average Reaction Rate Coefficients

The highest and lowest rate coefficients resulted from the two ammonium nitrate solutions. The 0.0062 min^{-1} rate coefficient achieved by the 500 mg/L solution could be attributed to the large amount of oxidizers added to the system. It is possible that the 0.0052 min^{-1} rate coefficient of the 20mg/L solution could be due to the small amount of additive added, which may have actually adsorbed on the catalyst, inhibiting the reaction rather than accelerating it.

Humic acid is a better additive for this reaction than ammonium nitrate, as it had a greater impact on the rate coefficient at a lower concentration. The river water performed better than the 20 mg/L ammonium nitrate, possibly due to a small amount of humic acid in the water.

However, even the largest increase was only about a 0.001 difference in the rate coefficient. While this small increase in reaction rate coefficient made very little difference in overall reaction time for the small-scale reactor used in this research, it may have a significant impact on vessel size or retention time in larger-scale operations.

4.2 Total Organic Carbon

The results from the Total Organic Carbon (TOC) tests for several additives are shown in Table 2. It can be seen that TOC decreased in most cases, an indication that mineralization occurred. The two largest decreases were for the 48-hour experiment of base thiamethoxam and the 8-hour experiment with the humic acid additive.

Table 2: Total Organic Carbon of Original and Degraded Samples

Sample Description	Initial TOC (mg C/L)	Final TOC (mg C/L)	% change
30 ppm Thiamethoxam	11.61	9.3595	-19.4
30 ppm Thiamethoxam (48-hour run)	11.61	7.809	-32.7
30 ppm Thiamethoxam + 500 mg/L NH_4NO_3	12	8.912	-25.7
30 ppm Thiamethoxam + 20 mg/L NH_4NO_3	13.5	14.955	10.0
30 ppm Thiamethoxam + 10 mg/L Humic Acid	13.84	9.3318	-32.6
30 ppm Thiamethoxam + River Water	14.51	14.8675	2.5

The humic acid solution displayed nearly the same decrease in TOC as the 48-hour base thiamethoxam test, but in only 8 hours. This suggests that humic acid is very effective as an additive for this reaction, particularly when considering the small amount that needed to be added to achieve this result. The effectiveness of humic acid could be due to it generating a larger number of free radicals during photocatalysis, and thus accelerating the degradation process. It has been found in previous research that partially degraded humic acid absorbs much more UV energy than its original form (Uyguner and Bekbolet, 2005), which may have allowed the compounds to be more reactive and thus more likely to mineralize. Furthermore, degradation containing humic acid occurs more quickly at lower pH's (Bekbolet and Ozkosemen, 1996). While the pH of the degradation experiments was not recorded, it can be assumed that the pH decreased with the addition of humic acid, which in turn increased the reaction rate and allowed for more complete mineralization.

The 48-hour experiment showed the largest decrease in TOC, which may infer that longer reaction times could result in larger degrees of mineralization. The longer test length allowed the

thiamethoxam to degrade completely, which was not observed in any 8-hour test. However, the continuing presence of organic content in the solution suggests that the thiamethoxam is degrading into other organic compounds, not mineralizing completely. Longer tests should be conducted overall to see how the solutions will degrade, and further analysis and identification of degradation byproducts should be undertaken to determine the final composition. This information could be used determine proper additional treatment if toxic compounds still exist after photocatalytic degradation.

The TOC of the sample with river water and the 20 mg/L NH_4NO_3 solution showed a slight increase, unlike all other solutions tested. The 20 mg/L NH_4NO_3 solution was the slowest tested reaction. The slowness of the reaction may have allowed thiamethoxam to break down into other organic substances, but hindered the further breakdown of these byproducts, resulting in an increase in TOC. The river water's higher TOC could be due to the possible presence of many unidentified organic substances in the water, which may have reacted differently than the components of other solutions tested. However, this increase was small, therefore it is possible that some of the new products formed from the photocatalysis of the river water also degraded. A longer test should be conducted to see how mineralization progresses given more time. In addition, the composition of the river water should be assessed before experimentation to better understand its degradation and final composition.

4.3 Total Nitrogen

Table 3 summarizes the results from the Total Nitrogen (TN) tests. In most cases, the total nitrogen increased between the original and degraded samples, which is generally a sign mineralization did not occur. However, this increase in nitrogen is most likely due to the fact that only some of the nitrogen in thiamethoxam originally can be detected due to the character of the bonds and rings of its structure. The thiamethoxam solution should have contained 7.20 mg/L N based on its molecular composition, but only 5.56 mg/L N were originally detected by this method. As the thiamethoxam degraded and broke apart into different nitrogen-containing compounds, they were able to be identified by the TN detector, making it seem as if the total nitrogen was increasing. A study conducted by Low, McEvoy, and Matthews (1991) agreed with this hypothesis, proving that 15 different nitrogen-containing pesticides degrade to both nitrate and ammonia in the presence of TiO_2 and UV light. An official study sponsored by Shimadzu

found that ammonium and nitrate are both readily detected by the TN test method (Walker, Stojowski, & Clifford, 2001). However, if the original measurement of total nitrogen was inaccurate, it is impossible to say whether or not any of this nitrogen escaped as N_2 during degradation.

Table 3: Total Nitrogen of Original and Degraded Samples

Sample Description	Initial TN (mg N/L)	Final TN (mg N/L)	% change
30 ppm Thiamethoxam	5.56	7.16	28.82
30 ppm Thiamethoxam (48-hour run)	5.56	7.55	35.96
30 ppm Thiamethoxam + 500 mg/L NH_4NO_3	170.00	166.90	-1.82
30 ppm Thiamethoxam + 20 mg/L NH_4NO_3	13.46	17.29	28.42
30 ppm Thiamethoxam + 10 mg/L Humic Acid	5.85	7.21	23.18
30 ppm Thiamethoxam + River Water	7.89	9.82	24.41

The solution with 500 mg/L NH_4NO_3 was the only solution which showed a decrease in total nitrogen. This solution was also the fastest, according to its kinetic rate constant, which means that it may have degraded the thiamethoxam degradation byproducts in this solution more thoroughly than that of the other solutions. This may have allowed N_2 gas to form which would have left the system and showed a decrease in total nitrogen. It is also possible that the original count for total nitrogen was more accurate for the ammonium nitrate solution, because ammonium and nitrate are both readily detected by the TN test method (Walker, Stojowski, & Clifford, 2001). This makes it more likely that any N_2 gas escaping would have been accurately accounted for.

This test does not identify which compounds are being formed or whether they are plant-helpful or plant-harmful substances. Further tests to identify the compounds that have been synthesized should be conducted to fully characterize the degradation process, and whether it is more harmful or more helpful to the ecosystem.

4.4 Toxicity

To test for toxicity, lettuce seeds were germinated in each original and degraded test solutions for 5 days. The positive control seeds were grown in mineral water, while the negative control seeds were grown in a salt solution of 5 mg/L NaCl. After 5 days, the lettuce seedlings were measured and their lengths recorded and averaged. Their relative toxicities were calculated according to the methods described in Chapter 3, Toxicity Test. Figure 7 shows the relative toxicities of the original and degraded solutions as compared to the positive and negative controls.

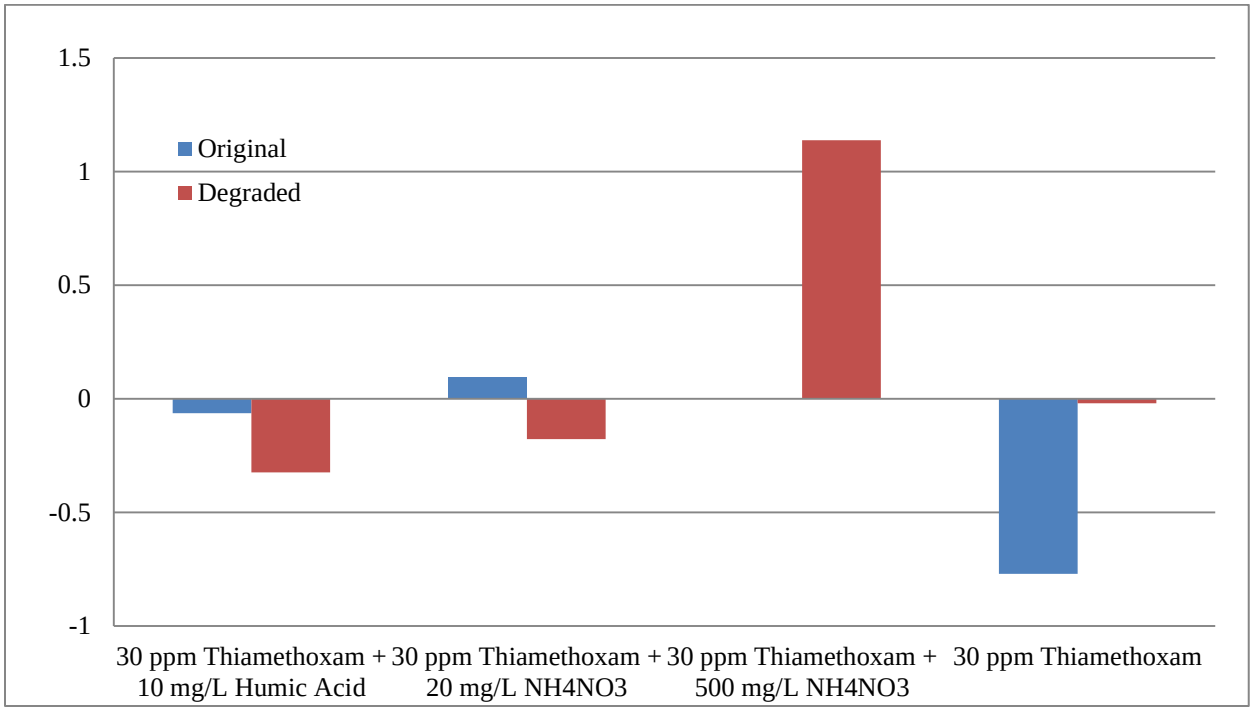

Figure 7: Relative Toxicity of Original and Degraded Samples

In Figure 7, the positive control has a relative toxicity 0, while the negative control has a relative toxicity of 1. All samples with relative toxicities less than 0 grew the lettuce seeds better than the mineral water. All samples with relative toxicities greater than 0 resulted in shorter overall seedlings than those grown with mineral water, suggesting increasing toxicity.

Two of the tested solutions, 10 mg/L humic acid, and 20 mg/L NH_4NO_3, decreased in toxicity after being degraded. The biggest drop in toxicity was recorded for the 10 mg/L humic acid solution, with final toxicity being nearly 5 times less toxic than the original solution. The final toxicity of the 20 mg/L NH_4NO_3 solution was nearly 3 times less toxic than its original solution. The observed decreases in toxicity may be partially contributed to the presence of additives, in

that these additives potentially also oxidized some toxic byproducts of thiamethoxam degradation. This unselective oxidation may have reduced the toxicity of the solution overall. In addition, a study conducted by Lobit et al in 2006 found that ammonium nitrate was not toxic to plants in small concentrations (101).

In contrast, the original base thiamethoxam solution increased in toxicity after being degraded. In this case, the increase in toxicity did not impact the plants very significantly, with relative toxicities around the same as the positive control. However, the increase in toxicity infers that new compounds that are more toxic than the original pesticide were formed during the degradation process, and these new compounds were not fully degraded during the length of the experiment conducted. It will be important for further research to identify these newly formed compounds in order to better understand their implications on plant and animal life in real-world applications.

It is also important to note that the original base 30 ppm thiamethoxam solution was significantly less toxic than not only the positive control, but also all other solutions, original and degraded. From this, it can be inferred that either the additives themselves or the interactions these additives had with thiamethoxam before photocatalysis raised the toxicity of these solutions even before degradation. The addition of ammonium nitrate increased the toxicity of the original solutions the most drastically. The most toxic solution tested was the 500 mg/L NH_4NO_3 solution, the degraded sample of which was still more toxic than the negative control.

Most likely, the addition of ammonium ions at such a large concentration poisoned the solution for the lettuce plants. In fact, this finding is in agreement with the results of a study conducted by Lobit et al in 2006 on the effects of ammonium nitrate on avocado plant development. In the study, they found that "increasing the proportion of ammonium in in solution decreased vegetative growth" (101). Further, they cite Crowley's work in 1997 when they argue that "NH^{4+} has been shown to decrease root growth and root hair formation" (102). Indeed, when measuring the lettuce sprouts from the tests, it was noted that the roots grown in the 500 mg/L NH_4NO_3 solution were brown, brittle, and very weak.

Quantitative toxicity data on the river water solutions and the original 500 mg/L NH_4NO_3 solution could not be determined due to inconclusive results from the positive and negative

controls. It can be inferred that the degradation process reduced the toxicity of the original 500 mg/L NH_4NO_3 solution, as was the case for the 20 mg/L NH_4NO_3 solution. Additionally, the river water solutions were able to be compared on the basis of the real lengths of the lettuce sprouts, instead of using the relative toxicity formula (Equation 1, Section 3.7). However, the results are qualitative at best and should not be compared to the rest of the toxicity data. These experiments were not repeated due to the time constraints of this project, but they should be repeated and verified in the future for more quantitative data that can be compared readily with the other experimental data.

There is an important distinction to be made when considering future applications for this toxicity test and photocatalysis of thiamethoxam via TiO_2. It can be inferred from the results of this test that solutions with a relative toxicity less than zero may have contained compounds which promoted better plant growth than in the mineral water, but does not by any means ensure that these solutions are any cleaner, and perhaps not even less toxic, than the mineral water. While some of the degraded solutions may improve the ability to grow lettuce plants, they may still contain compounds harmful to other species. Further testing should be done to determine the composition of these degraded solutions and to determine exactly what is causing promoted or repressed plant growth.

5.0 Conclusions

The goal of this project was to characterize the photocatalytic degradation of the pesticide thiamethoxam and the effects of the additives ammonium nitrate, river water, and humic acid on this degradation by measuring reaction kinetics, degree of mineralization, and toxicity. This section of the paper provides: 1) a discussion of the key points of this research as they relate to the degradation of base thiamethoxam, 2) a summary of the main results obtained from the addition of each additive, and 3) recommendations for future work.

5.1 Thiamethoxam

Thiamethoxam degraded at a rate of 0.0054 min^{-1}. It showed indications of mineralization, as TOC decreased. In fact, the longer the test was run, the more TOC decreased. On the other hand, as experiment length increased, TN increased. This was attributed to the nitrogen in thiamethoxam becoming more detectable as it degraded. Interestingly, solution toxicity increased

during the degradation of thiamethoxam, which may have important implications for its effects on the environment and merits further research.

5.2 Additives

5.2.1 Ammonium Nitrate

The results for ammonium nitrate were very different between the 500 mg/L solution and the 20 mg/L solution. Highlights from both concentrations are provided below.

20 mg/L

The 20 mg/L solution resulted in the slowest rate. It did not show indications of mineralization; instead, there were increases in both TOC and TN. These increases were attributed to the slow rate, perhaps caused by adsorption to the catalyst. This solution decreased in toxicity after degradation. At small concentrations, research shows that ammonium nitrate is beneficial to plants, which may have promoted growth in the lettuce plants, unlike the 500 mg/L solution.

500 mg/L

The 500 mg/L solution resulted in the fastest rate. This was attributed to the sheer volume of oxidizing additive used. It showed indications of mineralization; there were decreases in both TOC and TN. These decreases were attributed to the fast reaction rate, which allowed the solution to degrade to a larger degree in an 8-hour experiment. This solution decreased in toxicity after degradation, but still remained the most toxic solution. Research has shown that at large concentrations, ammonium is toxic to plants.

5.2.2 River Water

The solution made with river water degraded more slowly than the base thiamethoxam solution. It did not show indications of mineralization; instead, there were increases in both TOC and TN. The toxicity tests for this additive were inconclusive; however, solutions appeared to increase in toxicity after degradation. These phenomena were attributed to unknown compounds that may have been present in the river water.

5.2.3 Humic Acid

The humic acid solution degraded more quickly than the base thiamethoxam solution with a rate coefficient of 0.006 min^{-1}. It also showed indication of mineralization. In fact, it exhibited the largest decrease in TOC for all 8 hour tests. The increase in reaction rate and degree of mineralization were attributed to humic acids' high reactivity in UV/TiO_2 systems. Further, it also showed the largest decrease in toxicity after degradation, at five times less than its original toxicity. Overall, humic acid was the most effective additive for this reaction system and merits further research.

5.3 Future Work

There are 4 recommendations for future work:

- Better reactor design – the reactor chamber was open to the air, allowing for a greater degree of evaporation, which made it difficult to assess concentrations, particularly for longer tests.
- Run tests longer – the 48-hour base thiamethoxam test was the only test to fully degrade thiamethoxam. It would be interesting to see how the other additives degrade over a longer time period as well.
- Study the components of river water for better analysis – if the composition of the river water was known before degradation, the results after degradation would have been easier to analyze.
- Do tests in triplicate – due to strict time constraints while in France, all these tests were conducted in duplicate. More repetition would result in greater statistical significance.

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Appendix A – Calibration Curves

In order to be able to determine the concentration of thiamethoxam from the HPLC detector, a calibration curve needed to be created which could correlate the area under the curve generated by the HPLC to a specific concentration of thiamethoxam. Solutions ranging from 0.5 to 100 ppm thiamethoxam were prepared and analyzed with the HPLC. Figure 8 shows the data collected from two calibration tests with a linear trend line fit to them.

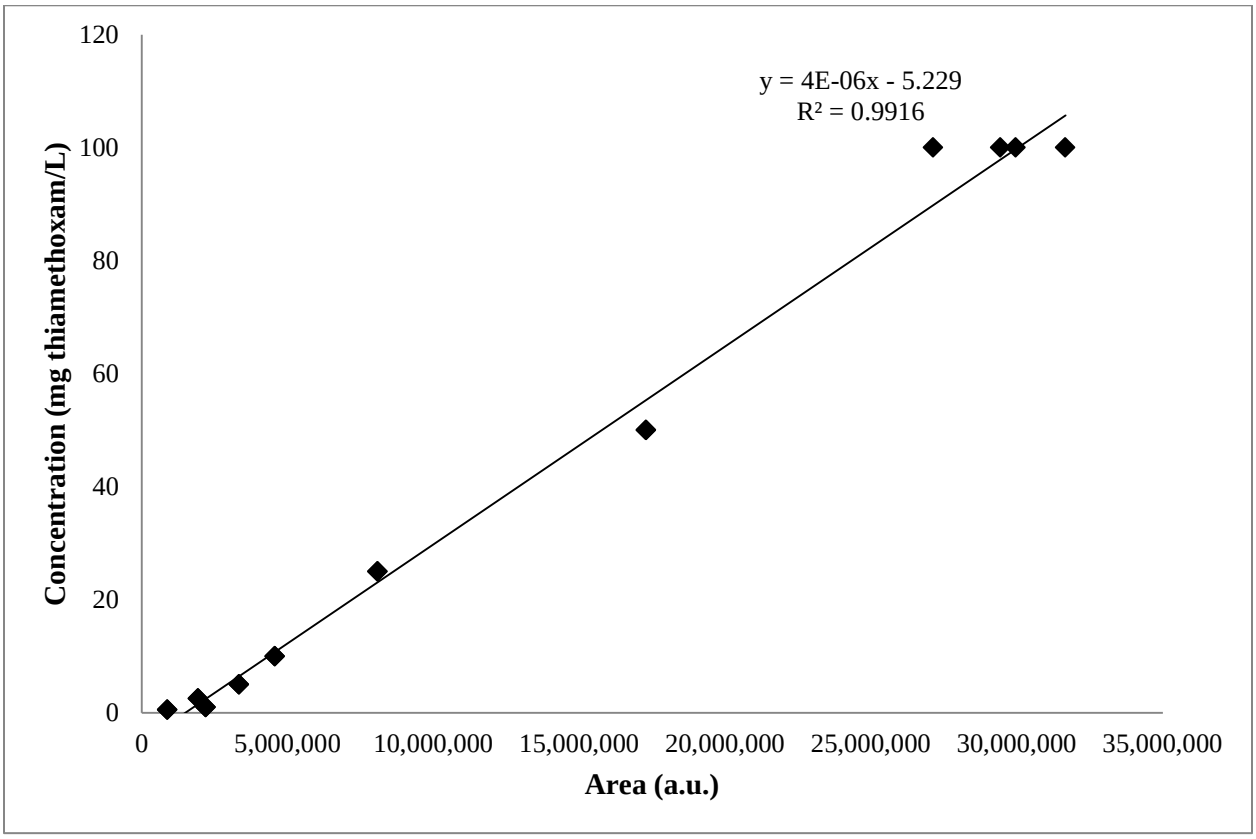

Figure 8: Combined Calibration Curve for Correlating HPLC Absorbance to Concentration

The slight variations in recorded area between the two sets of tests may be the result of pressure fluctuations in the machine, as only the flow rate of the mobile phase could be controlled. Pressure fluctuations have been noted to range from 128 bar to over 140 bar between tests, however for the calibration tests, the pressures were 128 and 132 bar. The equation of the linear trend line was determined to be y=4*10-6x – 5.229. This equation was used to convert all subsequent recorded areas into concentrations of thiamethoxam.

Appendix B – Proof of Concept

Before beginning experiments using the TiO2 catalyst and UV light, it was important to determine the necessity of both elements for effective degradation. Two experiments were completed, one using only UV light and one using only the catalyst. Their results are presented in Figures 9 & 10.

Figure 9 shows the degradation of thiamethoxam in the presence of only UV light during a study which was conducted over 2 days.

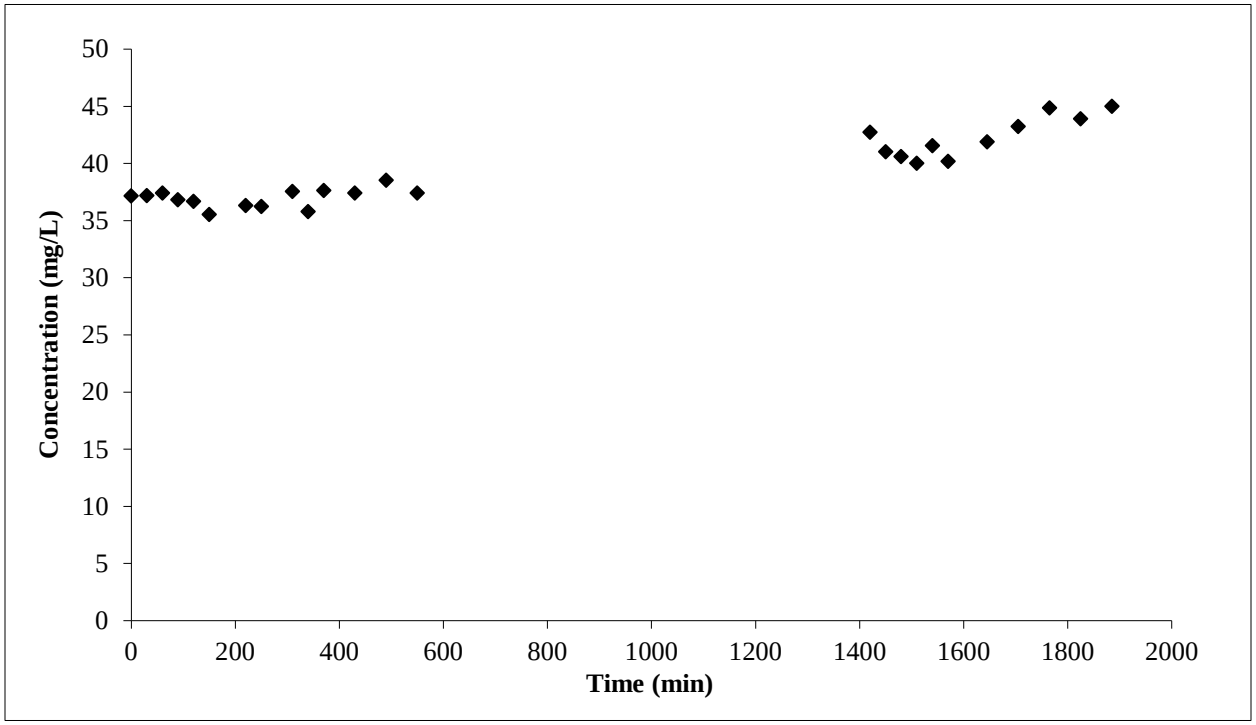

Figure 9: Concentration Data for Thiamethoxam Experiment with UV light and without TiO_2

These data show that the concentration of thiamethoxam increased over the test period instead of staying the same or decreasing. This is most likely due to evaporation of water during the test run. From this, it can be inferred that photolysis alone is not an effective means of degradation for this pesticide. The experiment should be studied in a more closed reactor to obtain more conclusive results on the degradation rate of thiamethoxam in the presence of only UV light.

Figure 10 shows the degradation results of thiamethoxam in the presence of the immobilized TiO_2 catalyst but without any UV light.

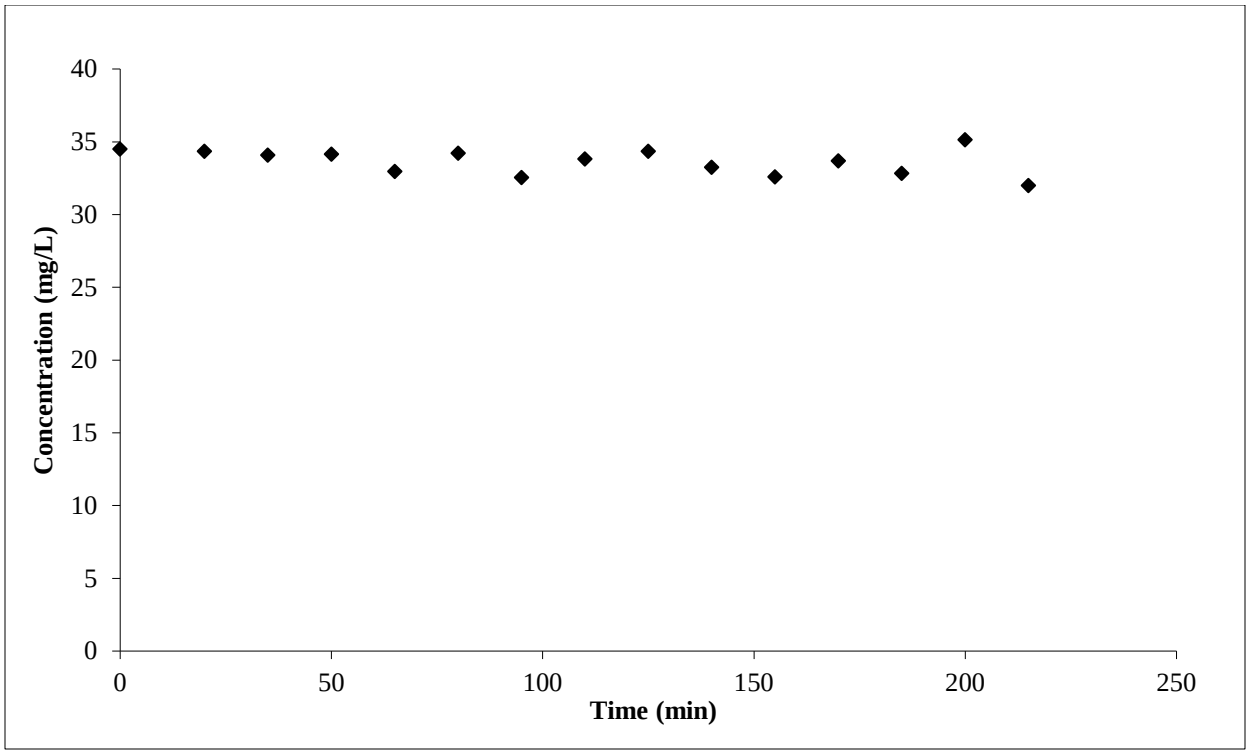

Figure 10: Concentration Data for Thiamethoxam Experiment without UV light and with TiO_2

These data show that with only a catalyst present, the concentration stays approximately the same throughout the experiment.

From these two experiments, it can be concluded that effective degradation of thiamethoxam in this specific reactor cannot be achieved with the presence of only a TiO_2 catalyst or only UV light.

Appendix C – Efficiency of Reactor Cleaning

A test was conducted to ensure that the reactor was being effectively cleaned between runs. Most importantly, it was hypothesized that thiamethoxam which had adsorbed onto the catalyst might desorb into circulating ultrapurified water in the presence of UV light. If thiamethoxam was present or desorbed into the reactor, it would need to be degraded completely between runs to render the reactor clean. Figure 11 shows the thimethoxam concentration data collected over the course of 130 minutes while the reactor ran with only pure water.

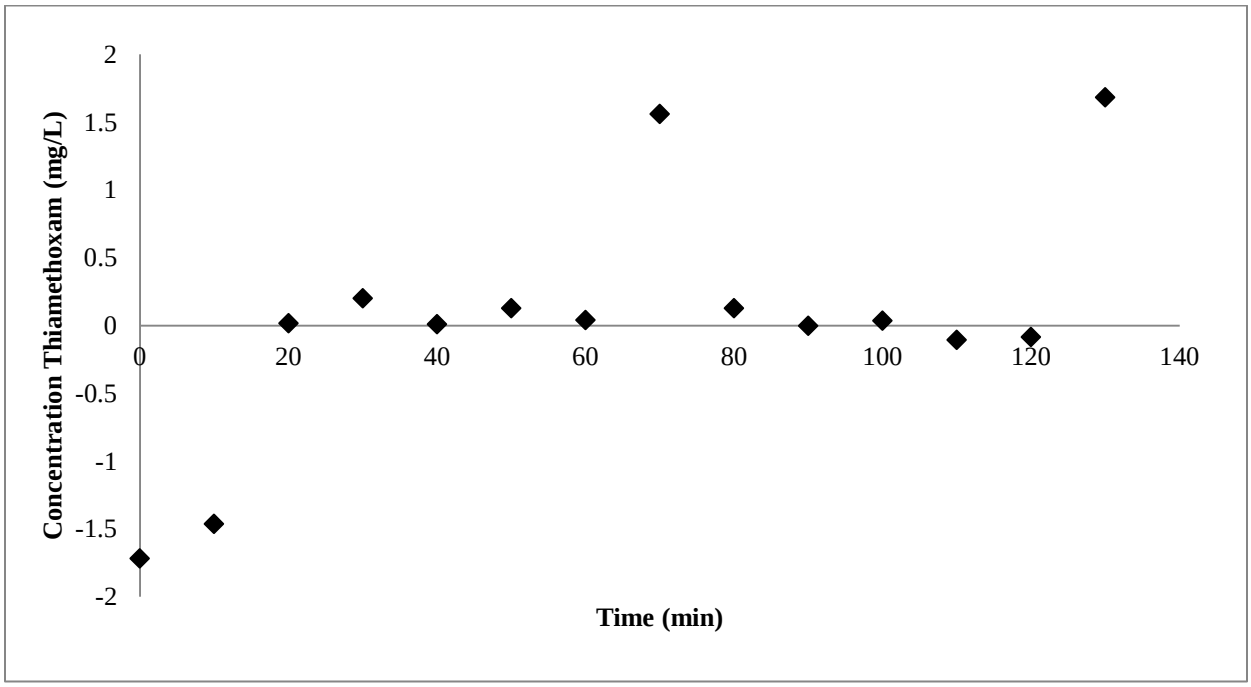

Figure 11: Concentration of Thiamethoxam for 2 Hours after Cleaning

The data showed that the concentration of thiamethoxam in the reactor hovered around 0 for most of the two-hour test. Negative concentrations can be attributed to the imprecision of the calibration curve used on the HPLC data. Concentrations much higher than zero were considered outliers, because of their infrequency and lack of trend. From this data, it was concluded that the reactor was sufficiently clear of thiamethoxam as to be considered clean and ready for a new experiment.

Appendix D – Kinetic Rate Results

This appendix contains the curves generated from concentration data during all degradation experiments.

30 ppm Thiamethoxam, 8 hours

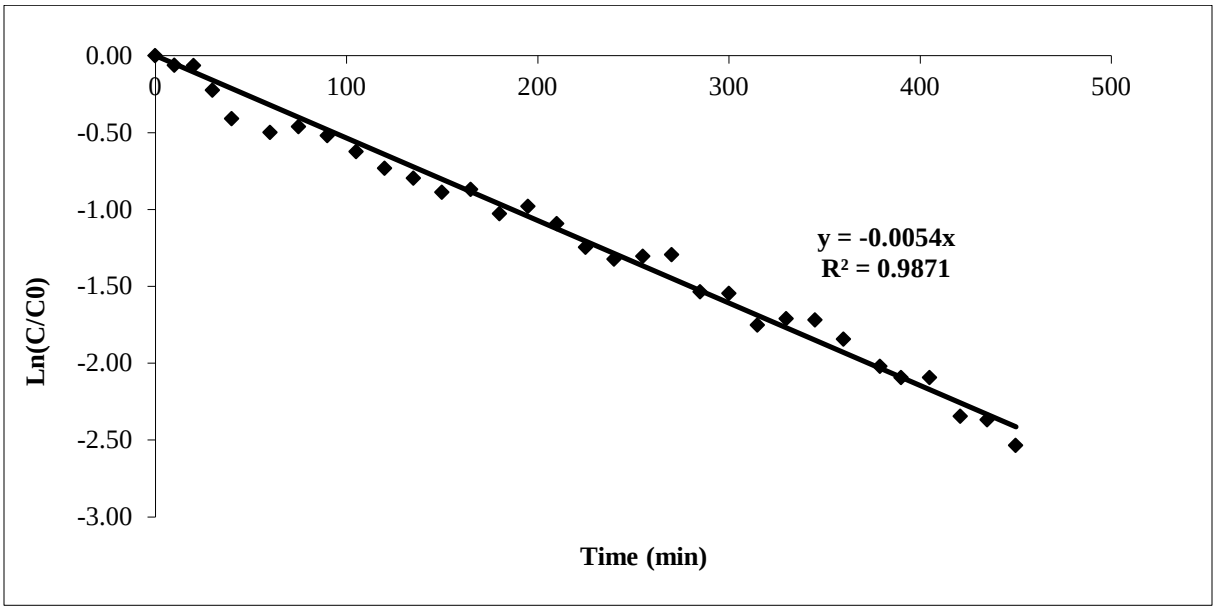

Figure 12: Kinetic Data for 30 ppm Thiamethoxam, Run 1

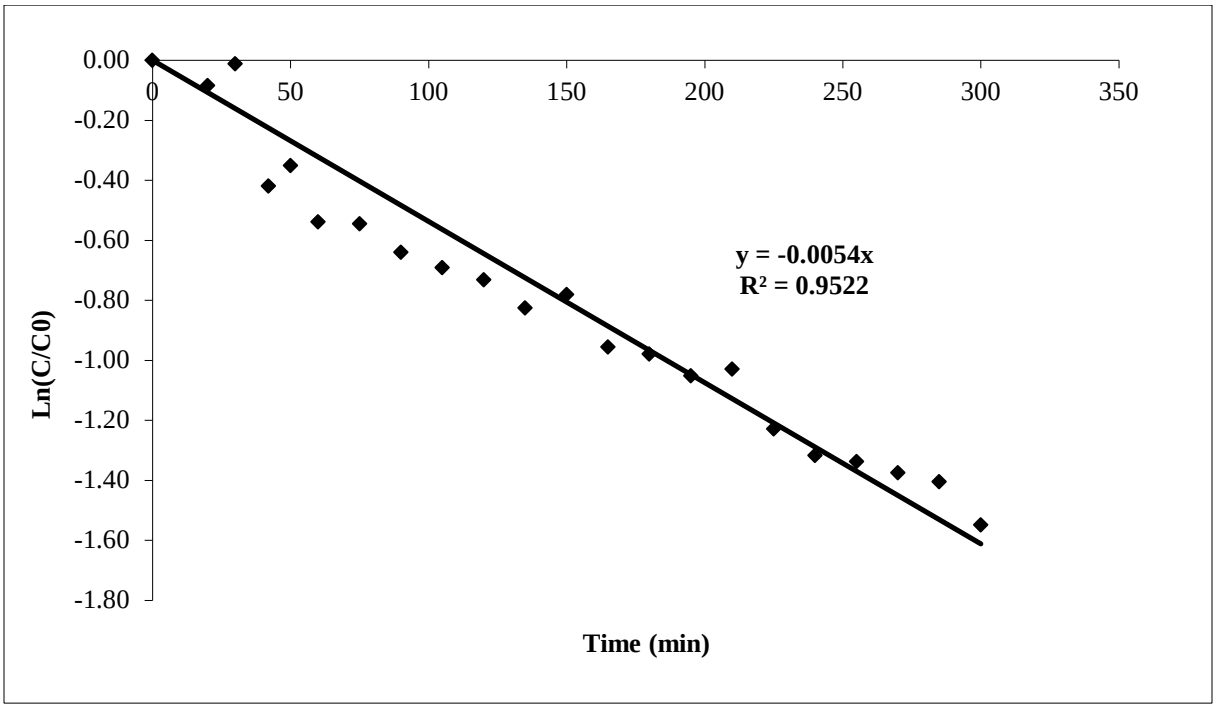

Figure 13: Kinetic Data for 30 ppm Thiamethoxam, Run 2

500 mg/L NH_4NO_3

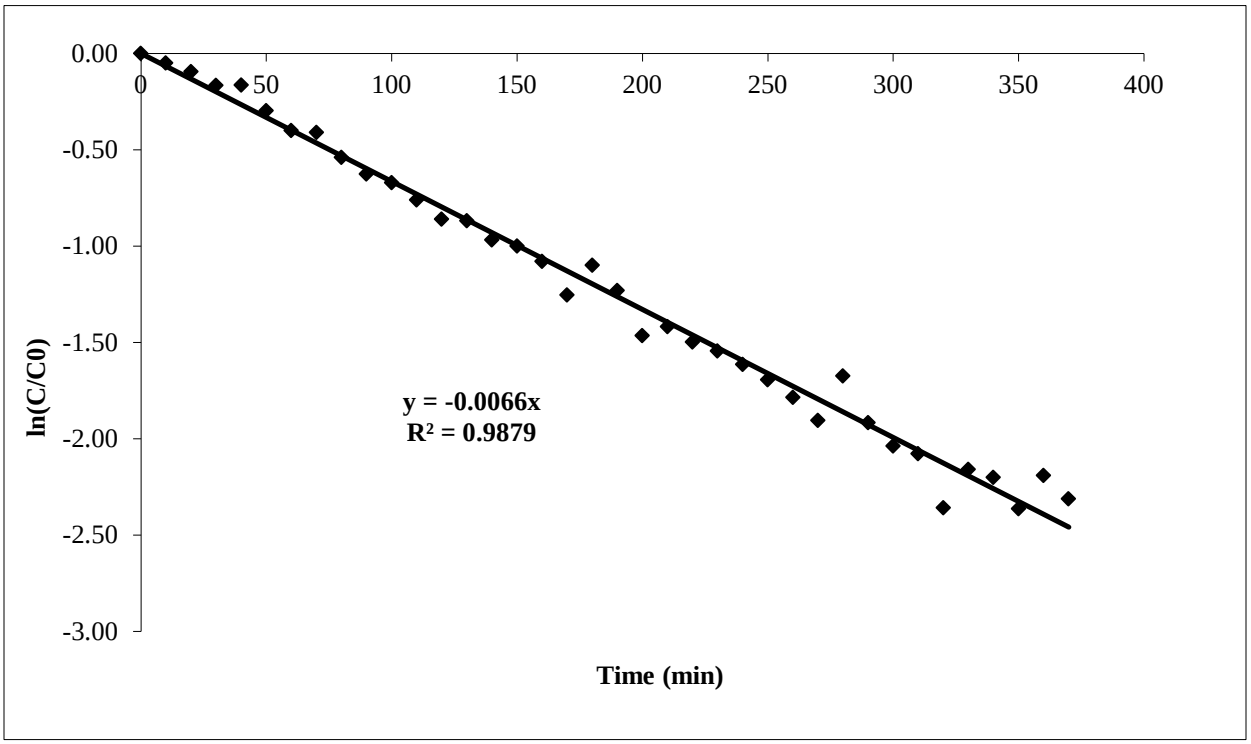

Figure 14: Kinetic Data for 30 ppm Thiamethoxam + 500 mg/L NH_4NO_3, Run 1

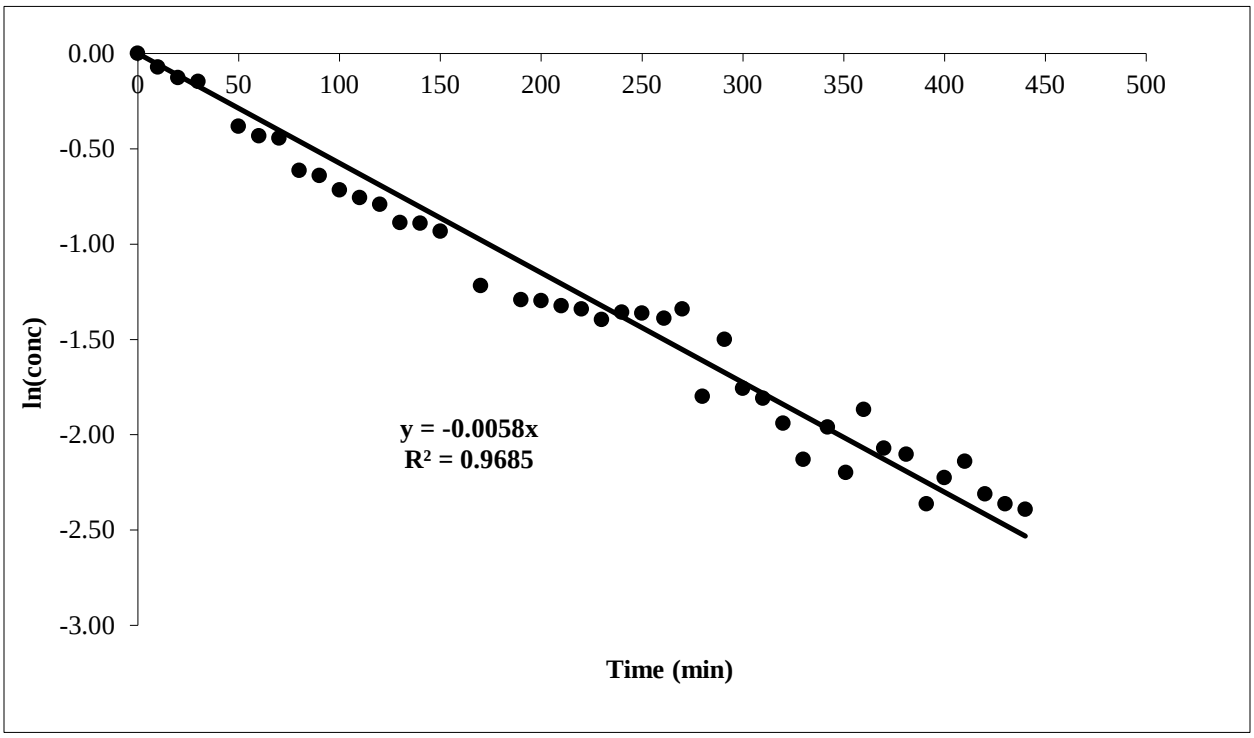

Figure 15: Kinetic Data for 30 ppm Thiamethoxam + 500 mg/L NH_4NO_3, Run 2

20 mg/L NH_4NO_3

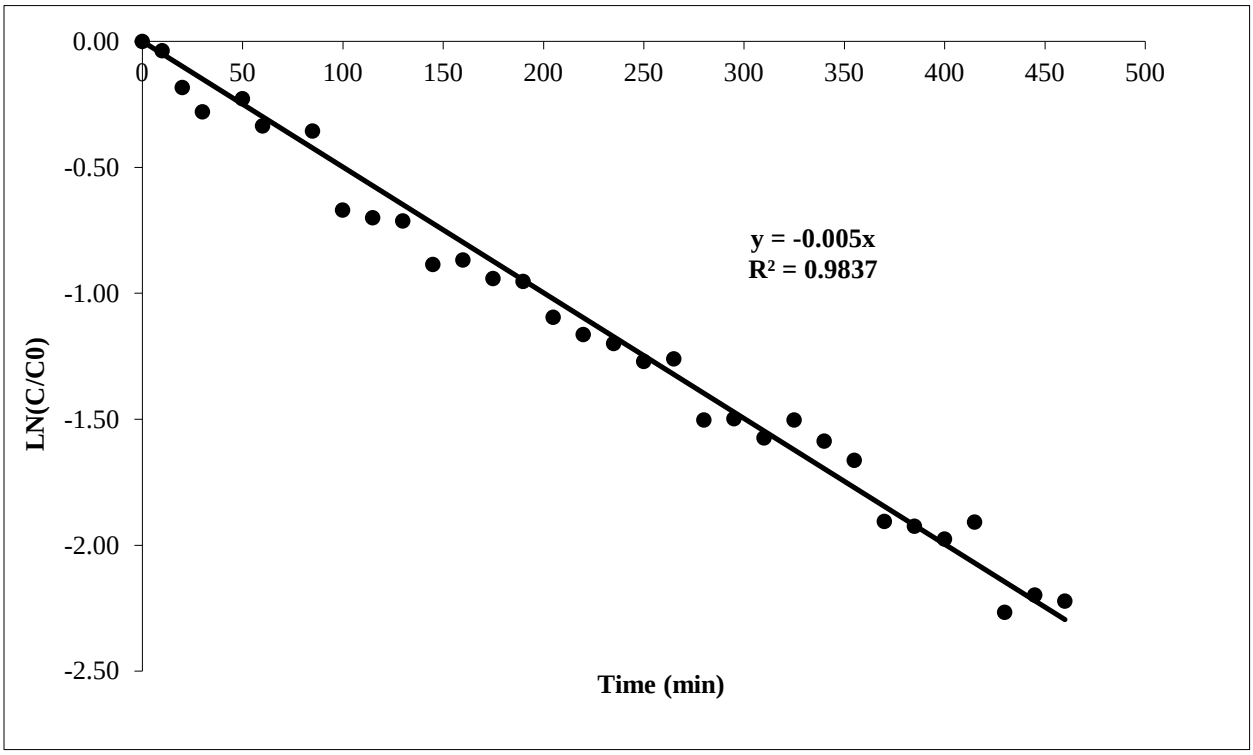

Figure 16: Kinetic Data for 30 ppm Thiamethoxam + 20 mg/L NH_4NO_3, Run 1

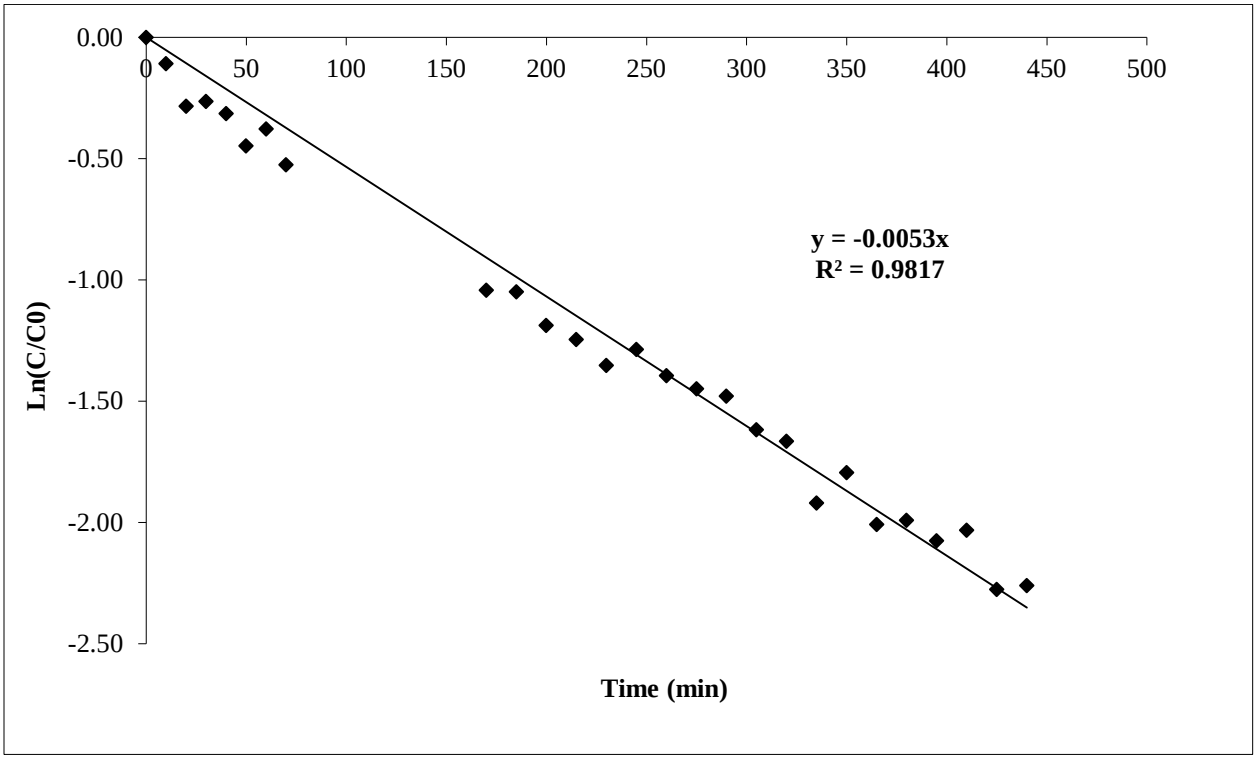

Figure 17: Kinetic Data for 30 ppm Thiamethoxam + 20 mg/L NH_4NO_3, Run 2

10 mg/L Humic Acid

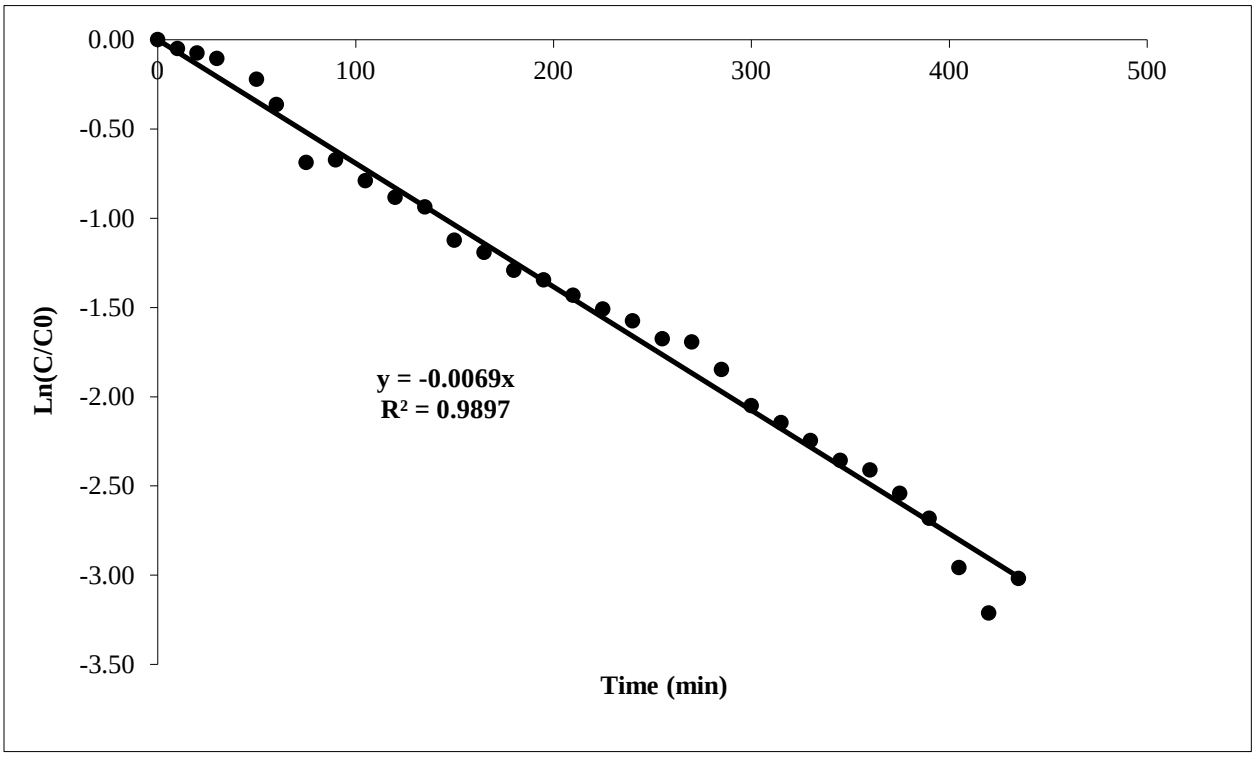

Figure 18: Kinetic Data for 30 ppm Thiamethoxam + 10 mg/L Humic Acid, Run 1

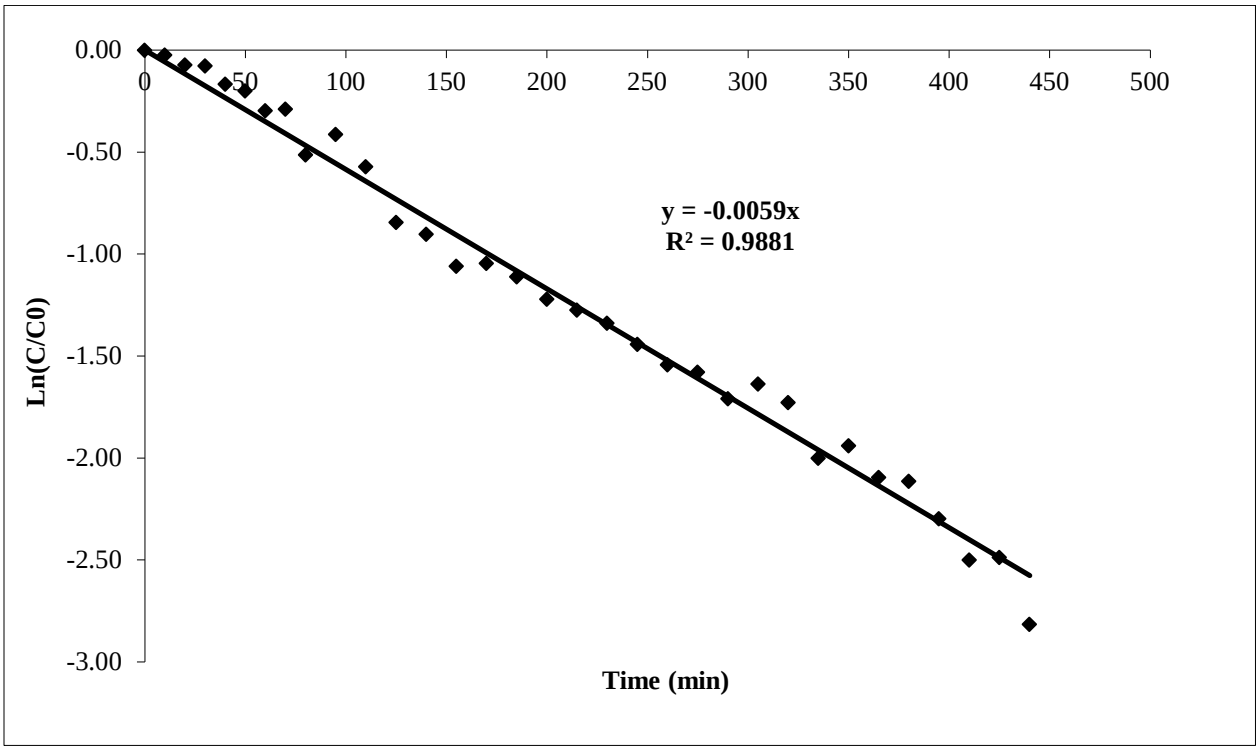

Figure 19: Kinetic Data for 30 ppm Thiamethoxam + 10 mg/L Humic Acid, Run 2

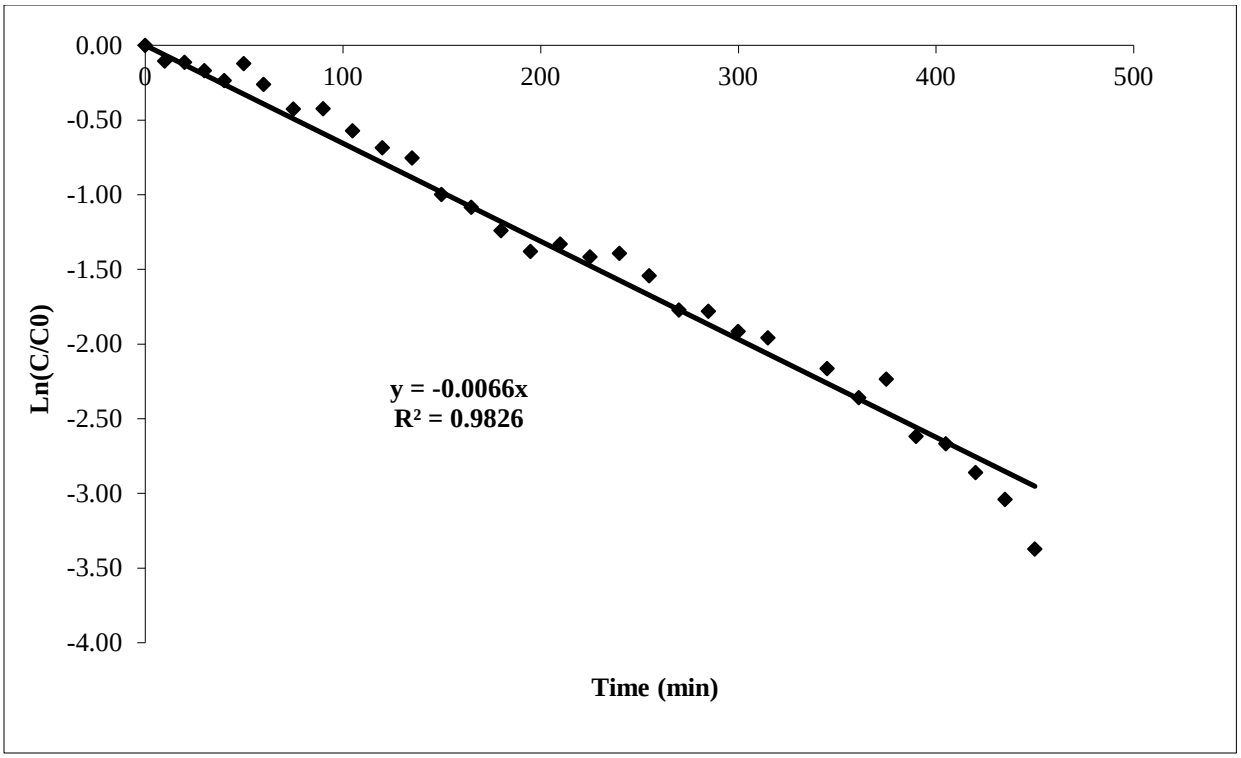

Figure 20: Kinetic Data for 30 ppm Thiamethoxam + 10 mg/L Humic Acid, Run 3

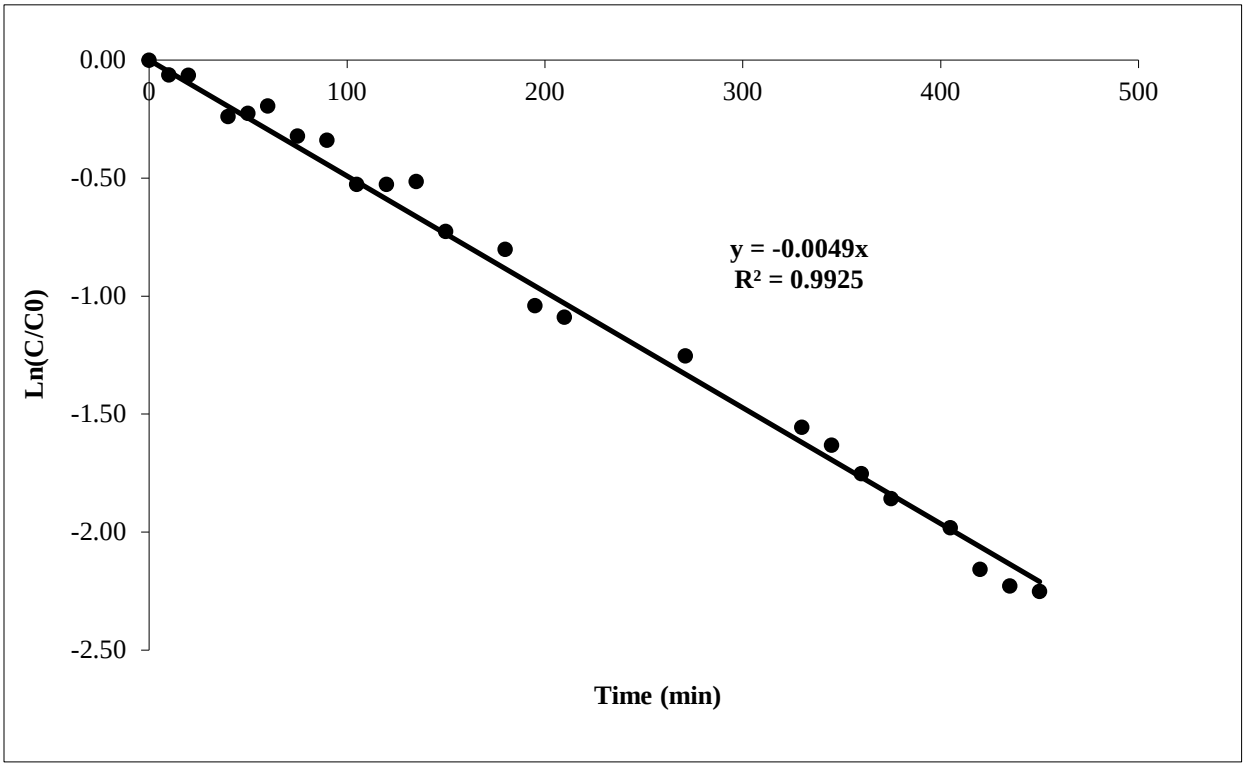

Figure 21: Kinetic Data for 30 ppm Thiamethoxam + 10 mg/L Humic Acid, Run 4

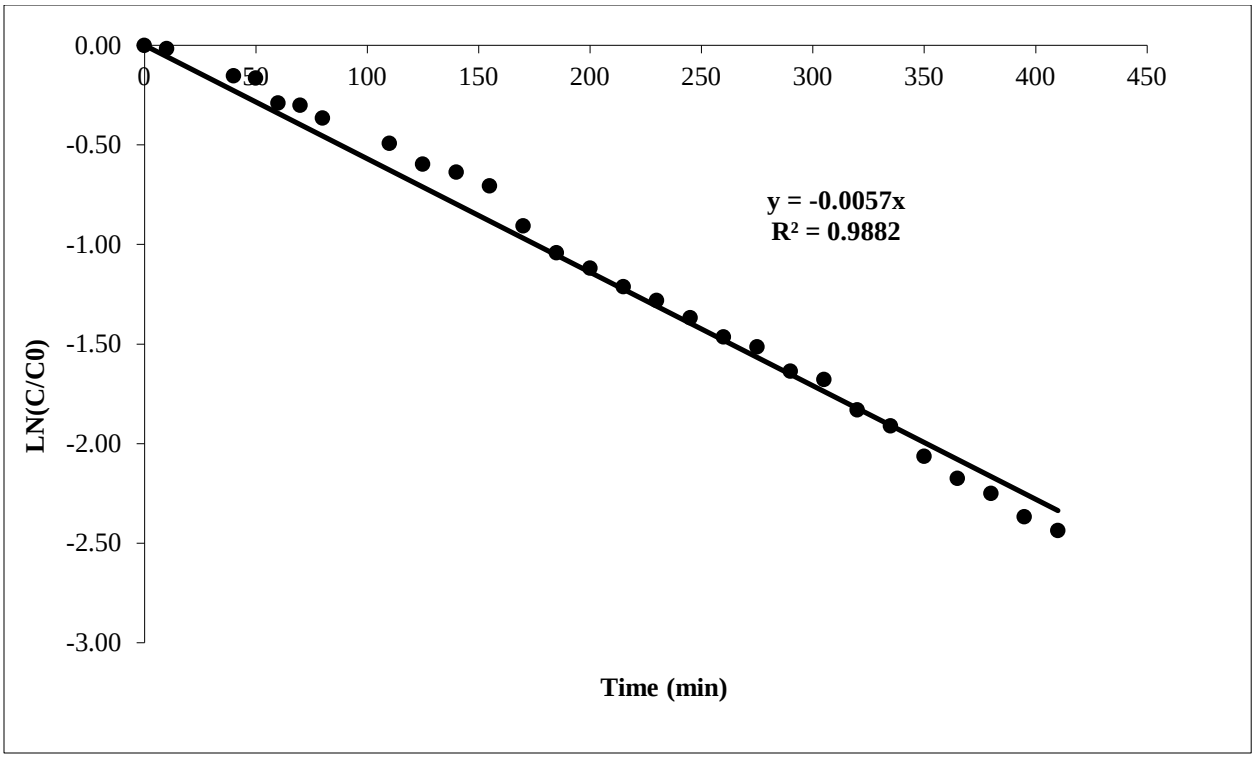

Figure 22: Kinetic Data for 30 ppm Thiamethoxam + 10 mg/L Humic Acid, Filtered

River Water Solution

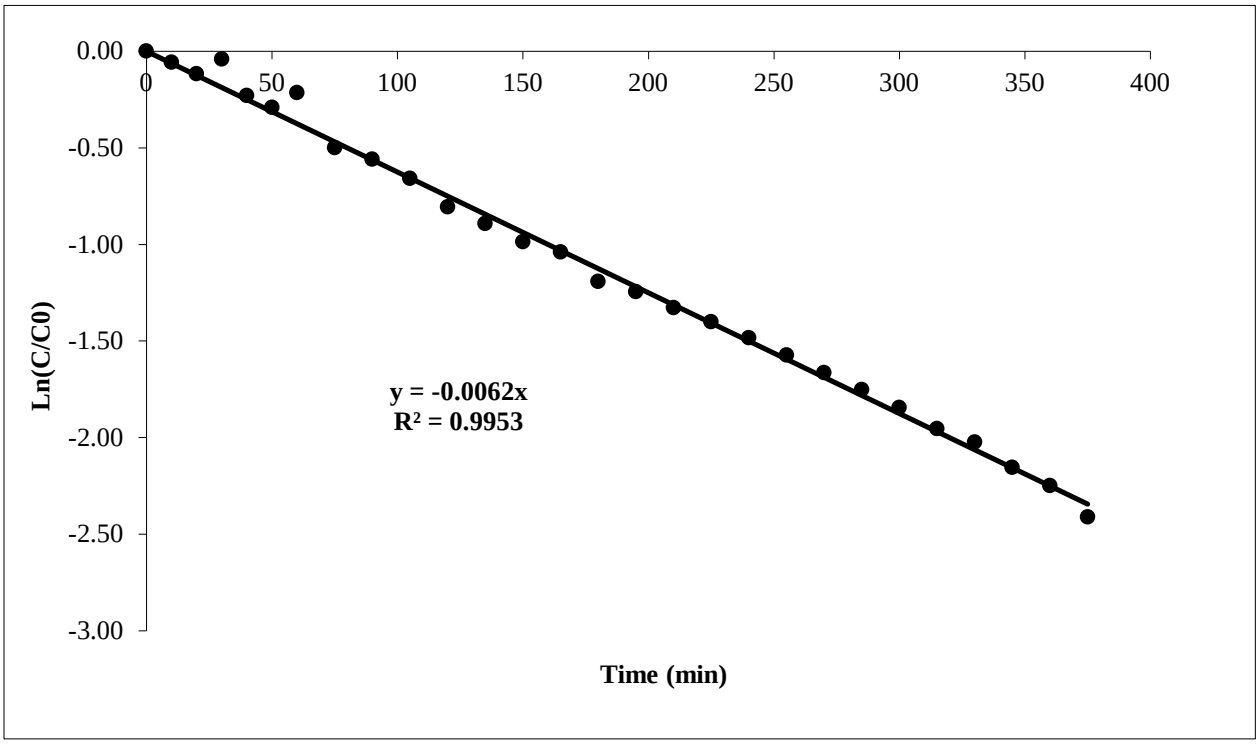

Figure 23: Kinetic Data for 30 ppm Thiamethoxam + River Water, Run 1

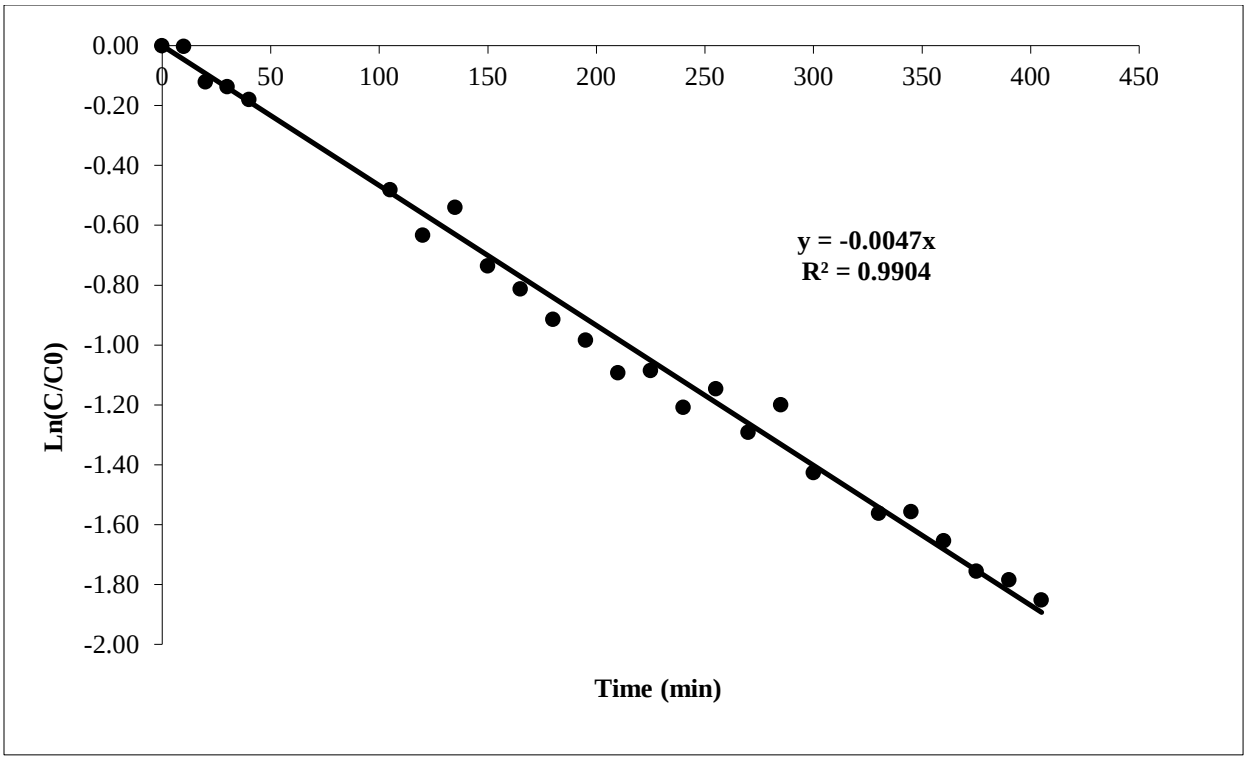

Figure 24: Kinetic Data for 30 ppm Thiamethoxam + River Water, Run 2

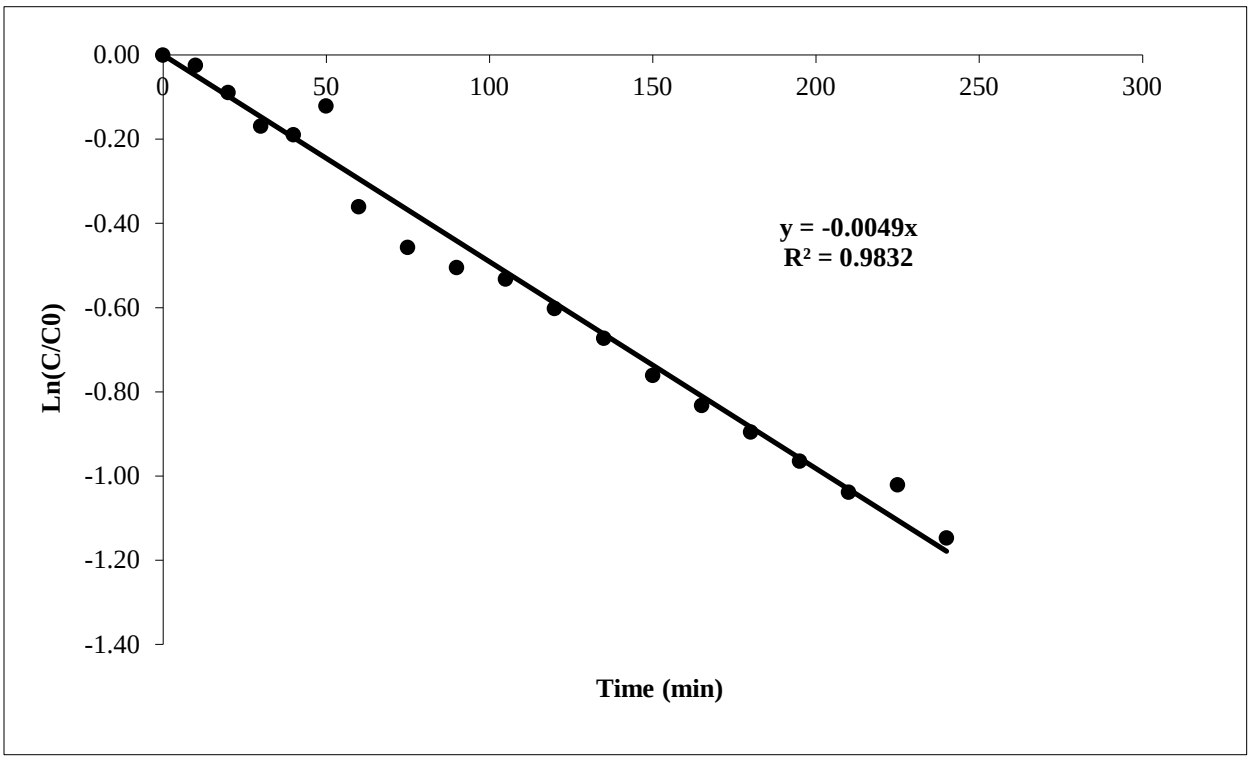

Figure 25: Kinetic Data for 30 ppm Thiamethoxam + River Water, Run 4

Appendix E – Raw Data

All raw data, including kinetics, TOC/TN, and lettuce testing can be accessed by contacting Terri Camesano at terric@wpi.edu.