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Modeling kinetics of hydrolysis of three pesticides in laboratory waters

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MODELING KINETICS OF HYDROLYSIS OF THREE PESTICIDES IN LABORATORY WATERS

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ABSTRACT

Pesticides and pesticide degradates found in drinking water sources are of particular concern to human health. When treated and disinfected at a drinking water plant, pesticides etridiazole, metribuzin, and diazinon undergo many treatment processes including lime softening, where the water pH is raised to 10 for calcium removal or 11 for magnesium removal. This thesis focuses on modeling the kinetics of hydrolysis of three pesticides that have the potential to undergo hydrolysis in drinking water plants. Linearly and non-linearly regressed first order and non-linearly regressed second order models were applied to the experimental data and compared to limited literature values. These three compounds were chosen because they were determined to be highly hydrolysable and are currently used in the field and thus a potential drinking water contamination concern. Additionally, these compounds were compatible in a mixture and analyzed by gas-chromatography with electron capture detection (GC-ECD).

Of the three pesticides included in this study, diazinon was most susceptible to hydrolysis and at the widest range of pH values. Etridiazole experienced only base-catalyzed hydrolysis, while metribuzin and diazinon experienced both acid- and base-catalyzed hydrolysis at the extreme pH levels. Non-linear and linear regression models were created and fit etridiazole and diazinon reasonably well. Only diazinon exhibited a moderate hydrolysis rate ($k' = 0.01\ h^{-1}$) at a pH relevant to lime softening at pH 11, and must be studied further. In general, diazinon's rate constants were compatible with the published literature values. Validation of models in surface and ground water is warranted.

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1. INTRODUCTION

1.1. BACKGROUND

Pesticides are widely-used chemicals that are applied to crops, turf areas, and seeds in order to control unwanted weeds, fungus growth, and insect damage. Many pesticides have been in use for decades, while new ones are being developed and registered for use every day. In fact, in 2006 the United States Environmental Protection Agency (U.S. EPA) registered 4,305 new products or sub-products containing 54 types of active pesticide ingredients (*1*). Pesticides have enabled the agricultural and food industry to maximize food production and deliver reliable and healthy crops to consumers and have allowed homeowners to manage lawns and control pests. Unfortunately, pesticides are designed to be toxic to specific plants and biota, and can be transported off application sites via water movement (rainfall events, groundwater movement), animals and birds that come into contact with these compounds, plant uptake, and volatilization. These compounds can be reduced by degradation through several pathways including microbial, chemical (hydrolysis), photochemical (*2*).

1.1.1. Federal Environmental Regulation. To be used in the U.S., pesticides must first be registered by the U.S. EPA. According to Salzman and Thompson (*3*), the U.S. government has historically employed a range of approaches to regulating pesticides. Regulatory standards have included health based, feasibility, or risk-benefit approaches. An example of a pure health-based, zero-risk standard are the Delaney Clauses in the Federal Food, Drug, and Cosmetic Act, which prohibits unsafe additives in food, drugs, and cosmetics, regardless of the cancer risk. In 1996, the Food Quality Protection Act (FQPA) extended protection from pesticide residues from processed food to include fresh produce, but redefined the zero-risk approach to a standard of less than one in a million lifetime cancer risk (*3*).

Salzman and Thompson (*3*) describe the Safe Drinking Water Act (SDWA) as a feasibility standard approach that sets maximum contaminant level goals (MCGL) based on a health standard. Minimum contaminant levels (MCLs) are the concentrations at which no known adverse effects occur, and are as near the MCGL as technologically and economically feasible. MCLs are the actual limits to which utilities must conform.

Salzman and Thompson (*3*) further explain that the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA), first passed by congress in 1947, is a statute based on risk-benefit analysis. The U.S. EPA first determines a manufacturer's truth in marketing then balances the risks of use to human health and the environment versus the benefits to society in order to determine if the pesticide poses an unreasonable risk. The EPA can deny registration or mandate conditional usage registration, and must reregister these pesticides periodically. In 1988, FIFRA was amended to require reregistration of substances and their marketed products that were first registered with the EPA before November 1984.

1.1.2. Occurrence. Pesticides are used worldwide, so studies investigating the occurrence of pesticides in many environmental sources including surface water, ground water, reservoirs, estuaries, soils, air, snow, and finished drinking water have been conducted throughout the U.S. In fact, several major river basins in the U.S. have had some type of study conducted including the Mississippi Delta (*4-8*), Missouri (*7-11*), Ozark Plateau (*12*), and Lower Tennessee (*13*). Studies have also touched individual states including Iowa (*10, 14-16*), Missouri (*7-10, 17*), Pennsylvania (*18*), Ohio (*19*), New York (*20, 21)*, Washington (*22*), California (*23*), and more general regions, such as the Midwest (*23-27*).

According to a USGS study that spanned nine years (*28*), pesticides or pesticide degradates were detected in more than 90% of samples from streams with agricultural, urban, and mixed land uses. Additionally, major aquifers showed evidence of pesticide presence in more than 30% of samples, and shallow ground water sources reported between 30 to 60% pesticide detection. While most of the concentrations of pesticides detected were below human-health benchmarks, agricultural areas had concentrations above human-health limits in stream water about 10% of the time and in shallow ground water about 1% of the time. Urban areas also were found to have concentrations above human-health levels approximately 7% and 5% of the time for stream water and shallow ground water, respectively. Undeveloped areas had no elevated concentrations, and mixed land use areas had nominal occasions of elevated water concentrations.

Pesticide loading to river waters via soil (*10*) and agricultural (*18*) runoff have been determined to be important contamination pathways. Urban watersheds can also

significantly contribute to pesticide build-up in watersheds, as demonstrated by the USGS study (*28*), a study conducted to account for diazinon and chlorpyrifos frequency in an urban watershed in southern California (*23*), and a study in urban New York (*20, 21*). Surface water contamination with pesticides is widespread.

Not only have pesticides been detected nation-wide in surface water from watersheds with various usage patterns, pesticides and pesticide degradates have even been detected in finished drinking water and groundwater. Detection of pesticides in finished drinking water (*8*) raises human health concerns. Detection in groundwater source wells (*16, 17, 29-32*) is troublesome because it demonstrates the breadth of pesticide contamination. Furthermore, as pesticides degrade in the environment, they become more problematic because of the degradates' increase in solubility in many cases. This is because in general, degradates become more polar with lower K_{ow} values. Thus, degradates can be harder to remove from the aqueous phase than their parent compounds.

1.1.3. Hydrolysis. Hydrolysis reactions are an important degradation mechanism in environmental systems, and can occur in any water, including surface, ground, fog, and pore waters. Hydrolysis generally consists of two mechanisms, nucleophilic substitution and addition-elimination. Nucleophilic substitution reactions, which take place when the leaving group is bonded to a carbon with sp^3 hybridization, are initiated by a nucleophile (*33-34*). Conversely, addition-elimination reactions take place when the leaving group is bonded to an acyl carbon with sp^2 hybridization, and commonly occurs in strongly basic and elevated temperature conditions (*33-34*). Elimination reactions may compete with nucleophilic substitution reactions when good leaving groups are involved, such as a halide or sulfonate (*33-34*). In acidic conditions, the substrate is first protonated such that it bears a formal positive charge, then, after nucleophilic attack, the leaving group is left with an electron pair and a formal charge of zero (*33-34*).

Hydrolysis involves the reaction of an organic molecule (RX) with a nucleophile (water or hydroxide ions) which forms a carbon-oxygen bond, resulting in rupture of the original carbon-X bond in the organic molecule (*33-34*). This reaction results in direct displacement of X by OH^- as shown in Equation 1.1 (*34*).

$$R\text{-}X \longrightarrow R\text{-}OH + X^- + H^+ \quad (1.1)$$

Nucleophilic substitution reactions fit one of the two kinetic patterns of displacement, S_N1 or S_N2. Substitution, nucleophilic, unimolecular (S_N1) reaction rates are independent of concentration and properties of the nucleophile and electron-donating characteristics on the central atom of the organic molecule (*33-34*). S_N1 processes are comprised of two steps, the first of which is intrinsically slow (rate-limiting) heterolysis at the carbon of the organic molecule and the substrate X. The second step, which occurs quickly, is the actual nucleophilic attack (*33-34*). Equations 1.2 and 1.3 give these reactions (*34*).

$$R\text{-}X \longrightarrow R^+ + X^- \quad (1.2)$$

$$R^+ + H_2O \longrightarrow R\text{-}OH + H^+ \quad (1.3)$$

Substitution, nucleophilic, bimolecular (S_N2) reaction rates directly depend on the concentration, optical activity, and the type of nucleophile (*33-34*). S_N2 processes are comprised of a single bi-molecular step in which the nucleophile performs a backside attack on the central carbon atom of the organic molecule, as seen in Equation 1.4 (*34*).

$$R\text{-}X + H_2O \longrightarrow [H_2O \quad R \quad X] \longrightarrow H^+ + R\text{-}OH + X^- \quad (1.4)$$

The relative rates of S_N1 and S_N2 reactions dictate which kinetic pattern an organic molecule and nucleophile will follow. For a given pair of reactants, the pathway yielding faster reaction rates will be most prevalent. The most important parameters include substrate structure, nucleophile concentration and reactivity (in terms of the bimolecular reactions), solvent effects, and nature of the leaving group (*33-34*). In S_N2

reactions, the nucleophile (water) must be able to be within a bond length of the central carbon atom (*33-34*). Therefore, steric hinderance can be a major factor in S_N2 reactions. Factors known to favor S_N1 and S_N2 reactions are organized in Table 1.1 (*33-34*).

Table 1.1 Factors favoring either S_N1 or S_N2 reactions.

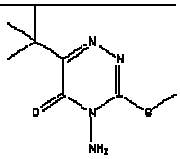
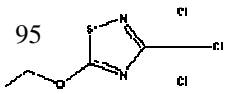
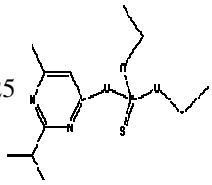
Parameter	S_N1 Favors	S_N2 Favors
R-system carbonium ion stability	good	low
X-system leaving group	good	poor
Solvent	high di-electric (water)	organic acids
Steric hinderance	N/A	low

These models are discrete; however more complex mathematical explanations describing a composite continuum of the reactions expressed above are likely to exist in nature (*33*).

1.2. PESTICIDE CHARACTERISTICS

The pesticides diazinon, etridiazole, and metribuzin were selected for this study based on several factors: (1) they were determined to be highly hydrolysable based on the Chamberlain et al. screening study of pesticides found in water (*35*), and (2) they are currently used in the field and potentially present in drinking water sources, and (3) they were analytically separable and detectable by gas-chromatography with electron capture detection (GC-ECD). The properties of these three pesticides are listed in Table 1.2. Molecular formulas, weights and structures were taken from SciFinder Scholar, water solubility, pK_a, and Log K_{ow} values and boiling points were taken from the ARS Pesticide Properties Database, the pK_a values were taken from the SPARC Database, and the Henry's Constant (K_H) values were taken from the EPI Suite Database.

Table 1.2. Selected pesticide physical and chemical properties. [a] Scifinder Schlolar, [b] ARS Pesticide Properties Database, [c] SPARC Database, [d] EPI Suite Database

Compound, Chemical Class, [CAS #]	Molecular Formula, MW[a] g/mol	Solubility in water[b] mg/L	pK_a[b,c]	K_H[d] Pa m^3/mol	Log K_{ow}[b]	Boiling Point[b] °C	Structure[a]
Metribuzin Triazine [21087-64-9]	$C_8H_{14}N_4OS$ 214.2848	1000	1.0	$3.55x10^{-6}$	1.7	132	
Etridiazole Thiazole [2593-15-9]	$C_5H_5Cl_3N_2OS$ 247.5263	117	2.77	3.02	3.37	95	
Diazinon Organophosphate [333-41-5]	$C_{12}H_{21}N_2O_3PS$ 304.3433	40	3.73	0.072	3.81	125	

1.2.1. Etridiazole. Etridiazole, marketed as Terrazole , is a fungicide registered with the EPA. The EPA Reregistration Eligibility Decision (RED) (*36*) documents that etridiazole is routinely applied to prevent root- and stem-rot. Etridiazole prevents diseases caused by *Fusarium, Rhizoctonia, Pythium,* and *Phytophthora*. The Weed Science Society of America (37) explains that plants affected by *Phytophthora* will develop brown leaves, wilt, and develop a crown rot as the roots rot. Etridiazole is most commonly used on golf-course turf, non-bearing plants such as citrus and coffee, cotton, and nursery ornamental plants. The EPA RED and Wood (*38*) states that Etridiazole is also commonly used to treat the seeds of agricultural plants including barley, beans, corn, cotton, peanuts, peas, sorghum, sugar beets, avocado, strawberries, soybeans, safflower, and wheat. Seven states have special use permits to use etridiazole on floating beds of tobacco transplants. Tolerances, defined as maximum residue limits, have been set at 0.1 parts per million (ppm) by the EPA (*36*) for corn grain, fodder and forage, cottonseed and wheat grain, straw, as well as cotton gin byproducts, peanut nutmeat, hay, sorghum grain,

barley grain and hay, safflower seed, legume vegetables, and legume vegetables' foliage set at 0.1 parts per million (ppm). According to the EPA, the cancer dietary risk from exposure via ingestion of food does not represent a concern. Other thiazole fungicides include ethaboxam, isotianil, metsulfovax, octhilinone, thiabendazole, and thifluzamide. Major manufactures of Etridiazole include Mallinckrodt Chemical Company (St. Louis, MO) and the Olin Corporation (Little Rock, AR). Etridiazole is sold as a wettable powder, emulsifiable concentrate, and in granular, flowable, and dust formulations.

1.2.1.1 Toxicity. Etridiazole is classified by the EPA (*36*) as a probable human carcinogen in Group B2, indicating sufficient evidence of likely carcinogenic effects in exposed animals, but inadequate or no evidence in exposed humans. Etridiazole is characterized by the Fungicide Resistance Action Committee (FRAC) (*39*) in Group 14 based on its mode of toxicity. Etridiazole's key mode of toxicity is lipid peroxidation which impedes lipid and membrane synthesis. Studies in mice by Dalvi et al. (*40*) have shown that etridiazole inhibits the hepatic drug metabolizing enzyme (DME) system when a 100 mg/kg dose is administered orally. Dalvi et al. proposes that etridiazole metabolism causes liver toxicity in mice and that the likely cause is lipid peroxidation of liver membranes. Radzuhn et al. (*41*) found rat liver mitochondria to be very sensitive to etridiazole. In the presence of etridiazole, membrane lipids were observed to hydrolyze, releasing fatty acids and lysophosphatides. In terms of acute toxicity to humans, the EPA RED (*36*) explicates that etridiazole shows low to moderate toxicity, though a skin sensitizer and eye irritant. Pre- and post-natal exposure in rats revealed no increased risk of adverse exposure effects. Acute toxicity doses at which maternal toxicity occurred also caused fetal developmental deformations, suggesting that fetuses are as susceptible to acute toxic doses as the adult parent. The RED concludes that the liver is believed to be the organ the most sensitive to chronic exposure, exhibiting increased weight and tumor development.

By conducting a study to determine the metabolites of etridiazole, van Welie et al. (*42*) found that 5-ethoxy-1,2,4-thiadiazole-3-carboxylic acid (ET-CA) and N-acetyl-S-(5-ethoxy-1,2,4-thiadiazol-3-yl-methyl)-L-cysteine (ET-MA) were formed when fed to rats and human volunteers. These metabolites were detected from urine by gas-chromatography (GC). It was determined that rats metabolized etridiazole to both ET-

CA and ET-MA, but humans only synthesized the ET-CA. Only a very small fraction of the parent compound etridiazole was measured in the rat urine.

The use of etridiazole on golf courses is the application of most concern because etridiazole is applied to golf course turf at 50 times the rate of application to crops. This heavy application has implications for golfers as well as for drinking water sources with watersheds containing golf courses. Additionally, EPA (*35*) has noted that degradate 3-dichloromethyl-5-ethoxy-1,2,4-thiadiazole can be acutely toxic for aquatic biota. Chronic doses of etridiazole create reproductive problems in aquatic biota and birds including some animals and plants on the federal list of endangered and threatened species.

1.2.1.2 Occurrence. Though etridiazole is used in agriculture as a fungicide, data describing its occurrence and/or persistence in natural water and soil systems is not readily available. The pesticide national synthesis project, part of the national water-quality assessment (NAWQA) program headed by the USGS (*28*), estimates that approximately 91,000 lbs of etridiazole was applied to cotton in 1992. Figure 1.1, which is taken from the NAWQA study (*43*), displays the average annual use of etridiazole in 1997 in lbs per square mile of agricultural land in a given U.S. county.

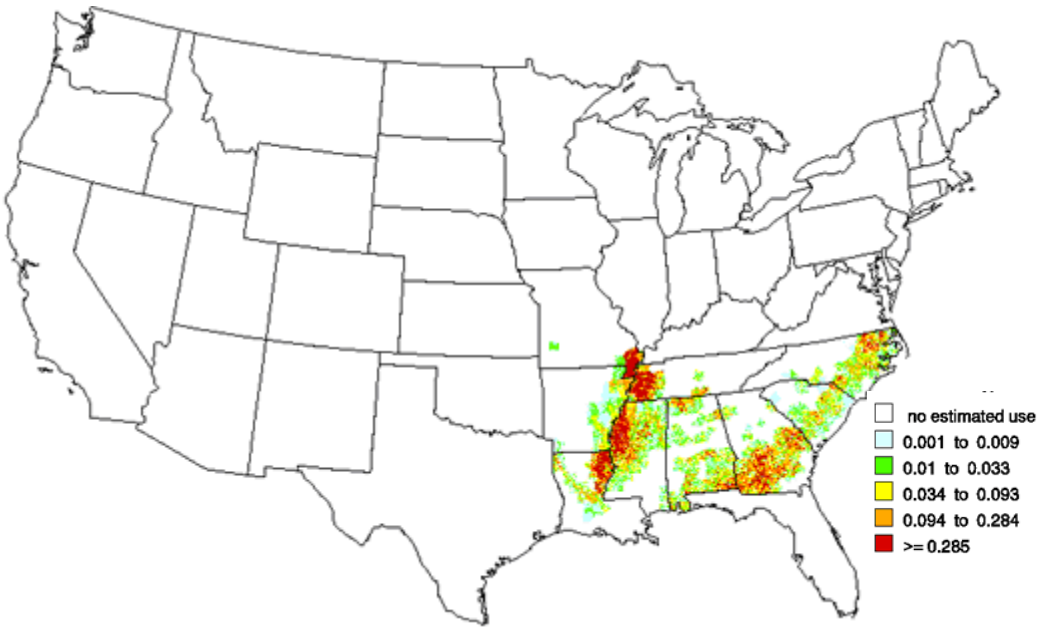


Figure 1.1 Average annual use (lb/mi^2) of etridiazole on U.S. agricultural land in 1997. (Used with permission from USGS Pesticide National Synthesis Project (*43*).)

1.2.1.3 Expected environmental fate. Etridiazole has moderate mobility and high volatility. In Peck et al.'s (*14*) study of gas-phase concentrations of current-use pesticides in Iowa, etridiazole was one of two most frequently detected fungicides at three sampling sites in Iowa with an average concentration of 0.045±0.033 ng/m^3. They found that etridiazole released to the air is reduced by photochemical reactions produced by hydroxyl radicals present in the ambient atmosphere (*14*).

Chamberlain et al. (35) determined that etridiazole undergoes moderate (20 – 50% removal) degradation by hydrolysis at pH 2 and 7, and high (> 50% removal) degradation at pH 12 based on a 7-day experiment. With regard to concerns about drinking water contamination, the U.S. EPA (36) stated in reregistering the pesticide that the expected environmental concern (EEC) concentration of surface water was estimated to be 5 ppb. Though the EPA notes that this concentration exceeds the cancer drinking water level of comparison (DWLOC) of 1 ppb, EPA does not consider it a concern because the EEC concentration was probably derived from overestimated assumptions and the DWLOC concentration was probably underestimated for safety reasons.

1.2.2. Metribuzin. Metribuzin is an herbicide used on vegetable and field crops, as well as on non-crops such as turf grasses primarily intended for recreational purposes. The EPA RED (*43)* documents that metribuzin application is designed to control the growth of broadleaf and grassy weeds. Eighty-six metribuzin containing products are registered with the EPA. ToxNet, the toxicology data network (*45*) lists the manufacturers of metribuzin: DuPont (El Paso, IL), Clean Harbors (El Dorado, AR), Van Diest Supply Company (Webster City, IA), Bayer Cropscience (Kansas City, MO), Veolia Es Technical Solutions (Port Arthur, TX), BPS Inc. (Helena, AR), and Omnium (Blytheville, AR).

1.2.2.1 Toxicity. The EPA (*44*) has designated metribuzin as a class D pesticide in terms of its human carcinogenicity because there was not sufficient evidence that it increased tumor formations over a lifetime oral dose. Class D contains chemicals that are not classifiable as to human carcinogenicity. Metribuzin concentrations in drinking water are governed by drinking water standards and health advisories. No drinking water levels are specified for metribuzin, but several health advisories (*46*) exist for metribuzin, and metribuzin is included on the contaminants of concern list (CCL). These include pesticide concentrations not expected to bring about non-cancer injurious health affects for a 10-kg child consuming 1L of finished drinking water per day for one day, 10 days, and over a lifetime. These values are 5 mg/L for both one-day and ten-day exposure and 0.07 mg/L for life-time exposure. The reference dose, an estimate of daily oral exposure over a lifetime without expected appreciable adverse effects, is 0.01 mg/kg/day for metribuzin. EPA reports the drinking water equivalent level (DWEL), the concentration that is believed not to cause cancer over a lifetime, to be 0.35 mg/l with respect to metribuzin.

Metribuzin's key mode of toxic action is inhibition of photosynthesis at photosystem II. The Herbicide Resistance Action Committee (HRAC) (*47*) classifies metribuzin in group C1 and the Weed Science Society of America (WSSA) (37) classifies metribuzin in group 5 based on its pesticide family and mode of toxicity.

Studies of bacteria and mammalian systems did not provide evidence that metribuzin is mutagenic. As reported by the EPA (*48*), a Mobay Chemical Corporation study in 1974 determined the no-observed effect level (NOEL) to be 100 ppm, and the

lowest-observed-effect level (LOEL) to be 300 ppm based on lower weight gain and observed changes in several important organs including liver, kidneys, uterus, and mammary glands. Metribuzin fed to mice at concentrations of 200, 800, and 3200 ppm for approximately 100 weeks resulted in 25, 111, 438 mg/kg/day for males, and 35, 139, 567 mg/kg/day for females. The results found that administered doses did not alter viability. Weight gain at 800 ppm was observed in females twice in year one of the studies. Benign and malignant hepatocellular tumors were observed primarily in males.

Metribuzin was tested for mutagenicity at the bacterial level by Xu et al. (*49*). DNA damage was not found to result from exposure to metribuzin in the presence or absence of metabolic activation, and spontaneous DNA synthesis was also not observed in rat cultures. Metribuzin metabolism was studied by Bleeke et al. (*50*). It was found that rats retained 36-51% of orally introduced metribuzin, was dogs retained 52-60%. Percent excretion of oral metribuzin doses resulted in an elimination half-life of 19.1-30.4 hours in rats, and 72-120 hours in dogs. Conjugates deamino metrizucin mercapturate, diketo metribuzin, and deaminated diketo metribuzin were assumed to be major components of urinary discharge.

Due to low acute toxicity activity, metribuzin is not considered by the EPA to be a developmental toxicant because of its inconsequential cancer risk and insignificant dietary exposure via crops. Both acute and chronic dietary metribuzin exposure from food residue and contamination of drinking water sources are considered nominal. The EPA (*44*) considers inhalation by handlers during use of metribuzin-containing products to be the pathway of most concern.

1.2.2.2 Occurrence. Metribuzin was detected in surface and ground water in the USGS NAWQA study (*28, 43*). In fact, metribuzin was identified as one of 12 agricultural herbicides and degradates detected most frequently. This is not surprising considering its annual usage. In 1992, the USGS estimated the national usage of metribuzin to be 2,704,051 lb. The number of acres treated per year was estimated as 8,402,249 in 1992. Typical application rates were estimated to be 0.25-4.0 lbs/acre for crops, and 6.0-80 lbs/acre for railroad rights of way. Figure 1.2, which is taken from the USGS NAWQA Data Warehouse (*43*), illustrates the agricultural usage of metribuzin in the US in 1997.

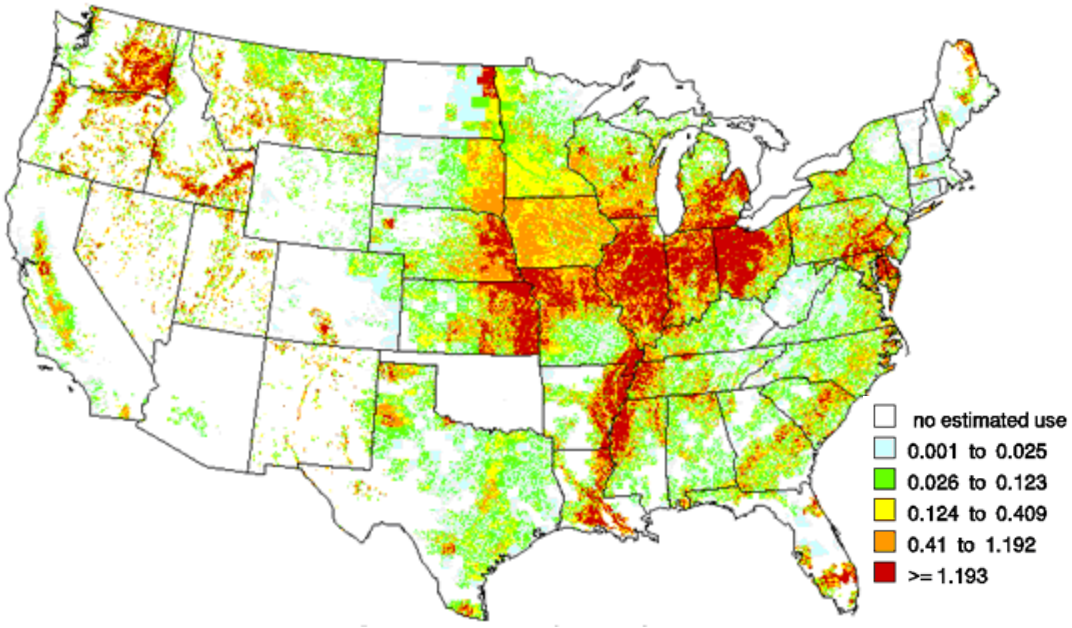


Figure 1.2 Average annual use (lb/mi^2) of metribuzin on U.S. agricultural land in 1997. (Used with permission from USGS Pesticide National Synthesis Project (*43*).)

Studies by Kolpin and colleagues. (*16, 27*) of the occurrence of selected herbicides and degradates in Iowa's ground water compiled from five independent studies reported widespread metribuzin contamination in ground water sources. Kolpin and colleagues reported 0.9 % metribuzin detection at 106 wells and 0.27 mg/L maximum concentration. Iowa statewide rural well water survey (SWRL) reported 1.9% detection at 686 wells, Iowa ground water monitoring program (IGWM) reported 2% detection at 355 wells, Iowa one-time testing program (OTT) reported 0.6% detected at 856 wells, and a Midwest herbicide study (MHS) reported 2.5% detection at 40 wells tested. Metribuzin levels of 1.91% at 2,459 wells tested and a maximum concentration of 0.3 mg/L. Learch et al (*10*) conducted a study of pesticides in near-surface aquifers in northern Missouri and southern Iowa and detected metribuzin in 41.1% of samples in 1997, in 88% of samples1998, and in, 85.8% of samples in 1999, suspected to be primarily from soy bean crops in Missouri where 34,000 kg of active ingredient was applied annually during the time of the study.

Metribuzin has also been found in groundwater near farm chemical supply dealers in Iowa (*30*). Metribuzin concentrations in soils of the supply loading and rinsing areas were 52,000 mg/L. Maximum ground water concentrations were 8 mg/L.

Surface water is another source water in which metribuzin has been detected. In a 2006 pesticide monitoring summary study in the state of Washington (*22*), several watersheds were monitored for metribuzin and other pesticide concentrations. At Big Ditch slough, 2.7% of samples tested contained metribuzin with a median concentration of 0.1605 mg/L, and maximum concentration of 0.23 mg/L. At Brown's slough, 3% samples contained metribuzin with median and maximum concentrations of 0.0089 mg/L. At Marian drain, 3% samples contained metribuzin with median and maximum concentrations of 0.0049 mg/L. Thurman et al. (*27*) studied the effect of herbicides on regional surface water quality in a 10-state area in the Midwestern U.S. cornbelt region. Samples of surface waters were taken pre-planting, post-planting, and at harvesting. Metribuzin was detected pre- and post-planting at 2% (out of 55) and 40% (out of 132) respectively, median concentrations of less than 0.05 mg/L for both planting seasons, and maximum concentrations of 0.16 and 1.4 mg/L, respectively. At harvest, metribuzin was not detected in any of the 145 samples tested. Figure 1.3, which was generated by U.S. Geological Survey (USGS) National Water Quality Assessment (NAWQA) data warehouse tools (*43*) depicts metribuzin detected in surface waters.

It should be noted that the human hazard concentration is 100 µg/L (*43*), and all of the concentrations in Figure 1.3 are well below the threshold at which concentrations pose a risk to human health. However, metribuzin has been detected, albeit at low environmental concentrations, across the U.S., and it is widely accepted that such a prevalent pesticide must be monitored.

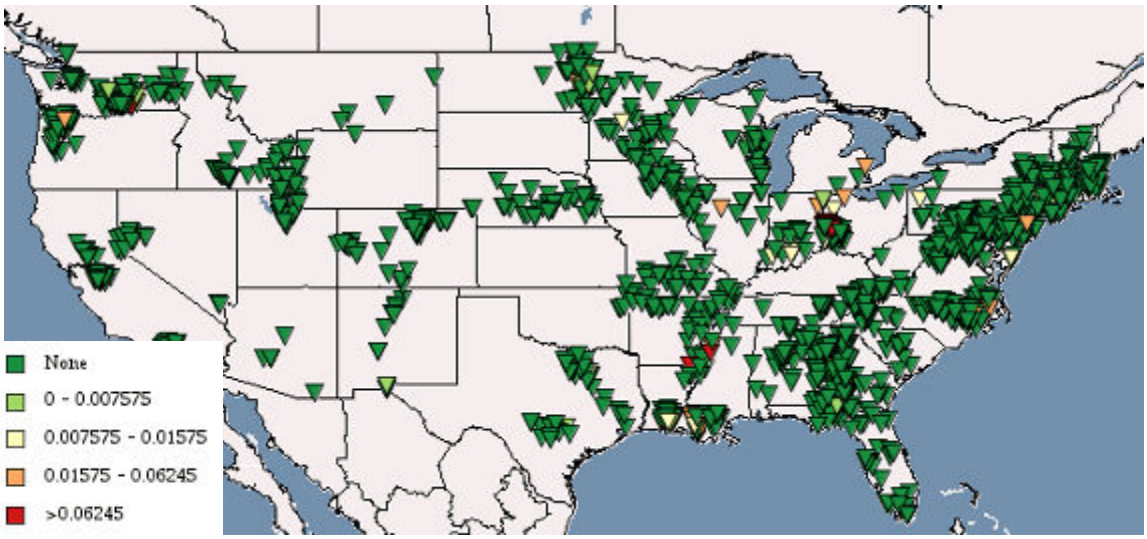


Figure 1.3 Filtered surface water samples analyzed for metribuzin (µg/L). (Used with permission from USGS NAWQA Data Warehouse (*43*).)

1.2.2.3 Expected environmental fate. Environmental fate of metribuzin is largely unknown, but the EPA (*44*) states that metribuzin is primarily degraded by bacterial and photolytic degradation on treated soil and shallow surface waters where light penetration can occur. The EPA states that metribuzin is stable to hydrolysis and is expected to persist in the environment once the compound reaches the subsurface and is no longer susceptible to photolysis. Chamberlain et al. (*35*) found high metribuzin hydrolysis at pH 2 and 12, and low (< 20% removal) at pH 7 based on a 7-day experiment. Metribuzin groundwater contamination is of concern to the EPA, especially due to its current widespread use, and low LogKow value indicating high likelihood of mobility in aqueous environments. In order to mitigate risk to animals and non-target plants, the EPA's RED for metribuzin (*44*) prohibits metribuzin application by aerial spraying. To reduce introduction to water sources, the RED specifies that best management practices (BMP) as listed on product labels should be followed and suggests reducing application in areas where groundwater contamination is riskiest. A literature review (*51*) investigating the degradation of pesticides in subsurface soils found that microbiological activity was the dominant mechanism for degradation, except for aldicarb, which is controlled by chemical hydrolysis. Kempson-Jones et al. (*52*) examined metribuzin degradation conditions by varying temperature, soil type (lab versus

field), organic carbon content of soil, moisture content of soil, and concentration of applied product. A half-life value range of 2-43 weeks resulted from this study. Applying an empirical equation to model this microbial degradation resulted in a variable order of reaction from 1.36-6.26. Subsurface degradation of metribuzin followed a half-order progression. Ludvik et al. (53) investigated electrochemical reduction of metribuzin and determined that metribuzin is reduced in two electron steps. After the first reduction, 1,6-dihydrometribuzin is subsequently reduced via acid catalyzed hydrolysis.

1.2.3. Diazinon. A widely-used organophosphate insecticide, acaricide, and nematicide**,** diazinon, which was first registered with the U.S. EPA (*54*) in 1956, was designed to control pests, including insects found in the soil that could infest fruit, vegetable, and legume crops. Diazinon is used on an extensive list of produce as well as field and forage crops including nuts (e.g., almonds), berries (e.g., blackberries, blueberries), fruit (e.g., apples, apricots, nectarines, pears, figs, melons, peaches), leafy vegetables (e.g., cabbage, collards, endive, lettuce, kale), other vegetables (sweet corn, onions, beets, tomatoes), and other crops (e.g., hops). Diazinon is also used with special local need registrations on bananas, celery, cucumbers, parsley, parsnips, peas, peppers, Irish and sweet potatoes, summer and winter squash, and turnips. Until all indoor and outdoor residential uses were cancelled in 2002 (*54*) and phased out in 2004 (*54*), diazinon was also used for controlling household insects, grubs, worms, flies, fleas, ticks, and mites that infest pet animals. Before this phase-out, the U. S. Department of Agriculture (USDA) (*55*) documented diazinon as one of the most popular and widely used household and garden insecticides, representing up to 70% on a mass basis of the total active ingredients applied at the residential level. Diazinon was one of two major restricted pesticides used in USDA Program States swine operations with a total application of 1,702 lbs (*55*). Typical crop application rates include 0.5 lb active ingredient/acre (ai/acre) for foliage crops, 1-3 lb ai/acre for fruit and nut tree crops, and 4 lb ai/acre for soil and granular applications. The Agency for Toxic Substances and Disease Registry (ATSDR) (*56*) list Diazinon is designated for restricted use for commercial agriculture products, with the exception of cattle ear tags, due to diazinon's toxicity to bird and aquatic biota populations. Diazinon can be found in the form of dust;

granules; impregnated or encapsulated material; emulsifiable, soluble, and flowable concentrates; wettable powders; liquid; ready-to-use solutions; and as a treatment on seed. Spectracide, D.Z.N., Knox-Out, Alfatox, Basudin, AG 500, Dazzel, Gardentox, and Diazol are some of the commonly marketed diazinon containing products.

1.2.3.1 Toxicity. The U.S. EPA (*54*) has classified diazinon as a cancer category Group E substance, signifying that there is no evidence of carcinogenicity for humans. The EPA provides no drinking water standards for diazinon, but health advisories are specified (*46*). These advisories include an RfD of 0.0002 mg/kg/day, and one-day, ten-day, and lifetime health advisories of 0.02 mg/L, 0.02 mg/L, and 0.001 mg/L, respectively. The DWEL is set at a fairly low concentration of 0.007 mg/L. An assessment of acute dietary exposure, the no observed adverse effect level (NOAEL) was found to be 0.25 mg/kg/day and the lowest observed adverse effect level (LOAEL) was determined to be 2.5 mg/kg/day from an acute neurotoxicity study in rats. An assessment of chronic dietary exposure, the diazinon RED (*54*) lists a NOAEL of 0.02 mg/kg/day based on various studies including multi timeframe dog and rat studies.

Organophosphates' main mode of toxic action is inhibition of acetylcholine esterase, resulting in over stimulation of the nervous system (*57*). Bruce et al. (*58*) determined cholinesterase inhibition by introducing diazinon to rat plasma, red blood cells, and brain cells in vitro. Investigation with both rats and dogs in vivo and in vitro, they determined that diazinon caused inhibition of cholinesterase. Subacute feeding resulted in reduction in enzyme activity of red blood cells. At a concentration of 1000 ppm, red blood cells and brain cells were inhibited, while no similar observations were made with respect to plasma. Chronic feeding to dogs resulted in suppressed cholinesterase activity to less than 30% of normal activity levels for plasma, and less than 40% of normal activity levels in red blood cells. Major signs of toxicity were only observed when the cholinesterase activity was suppressed to less than 10% of normal activity levels. Gomaa et al. (*59*) found that degradation product diazoxon has a greater cholinesterase inhibition ability than its parent compound, diazinon.

1.2.3.2 Occurrence. Diazinon, a widely-used insecticide, has been detected in environmental systems in both ground and surface waters, and was one of six most frequently detected insecticides by the USGS NAWQA study (*28*). The USDA (*55*)

estimated the national usage of diazinon in 1992 as 1,578,980 lb. Acres treated in 1992 were estimated to be 1,050,974. Typical application rates were estimated to be 0.19-10.0 lbs/acre for crops. Figure 1.4, which is reproduced from the USGS NAWQA Data Warehouse (*43*), illustrates the agricultural usage of diazinon in the U.S. in 1997.

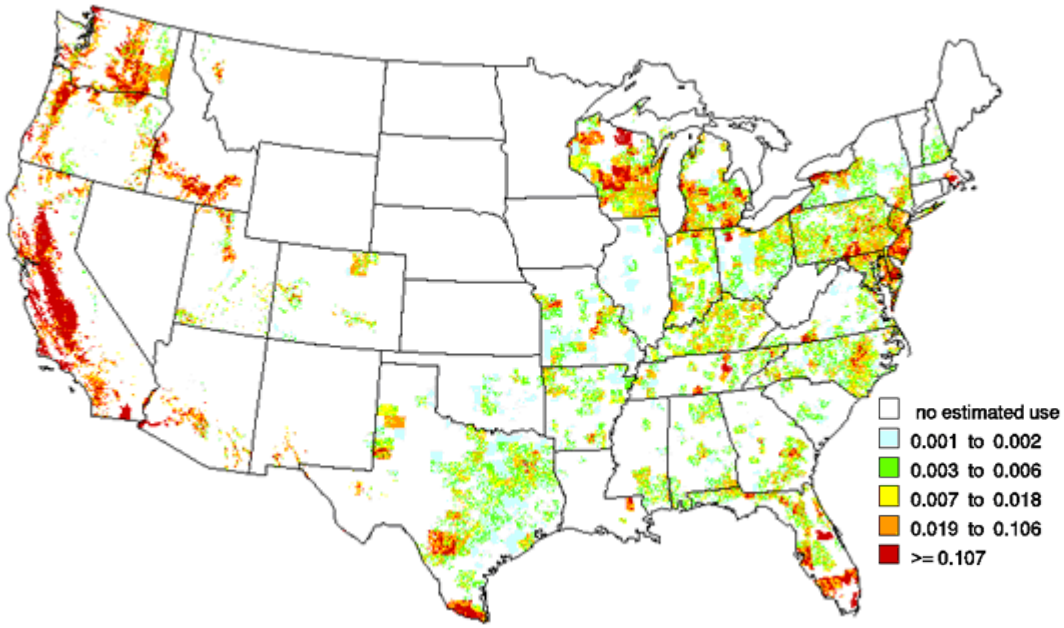


Figure 1.4 Average annual use (lb/mi^2) of diazinon on U.S. agricultural land in 1997. (Used with permission from USGS Pesticide National Synthesis Project (*43*).)

Kolpin et al. (*29*) analyzed U.S. ground water sources for pesticides from 1992 to1996 and found that, of 2,459 samples, 1.3% contained diazinon with a maximum concentration of 0.16 mg/L.

In terms of surface water occurrence, a study by Pereira et al. (*7*) found diazinon in the Illinois River at Hardin, IL, and in the Mississippi River at Thebes, IL. In a study to determine effects of seasonal and stormflows on concentrations of pesticides in surface water run-off in southeast New York state, Phillips et al. (*21*) detected diazinon in 71% of samples with 1.9% having greater than 0.10 mg/L concentration and a maximum concentration of 0.24 mg/L for Kisko stream, and 45% samples detected with zero samples having concentrations greater than 0.1 mg/L and a maximum concentration of

0.044 for Middle Branch. Higher concentrations of diazinon were found in run-off from more urbanized areas. The study by Phillips et al. pointed out that aquatic life protection water quality criterion of the Great Lakes is 0.8 mg/L, and the run-off analyzed in their studies exceeded the criterion.

In a 2006 pesticide monitoring summary study in the state of Washington, Anderson et al (*22*) monitored several watersheds for diazinon and other pesticides. In the Cedar-Summamish Watershed 6% of samples tested contained diazinon with a median concentration of 0.047 mg/L and a maximum concentration of 0.076 mg/L. At Big Ditch slough in the lower Skugit-Samish watersheds, 7% of samples contained diazinon with a median concentration of 0.1605 mg/L and maximum concentration of 0.23 mg/L. At Indian slough, 3% of samples contained metribuzin with median and maximum concentrations of 0.024 mg/L. Diazinon levels in surface waters as measured by the USGS NAWQA data warehouse tools (*43*), are shown in Figure 1.5.

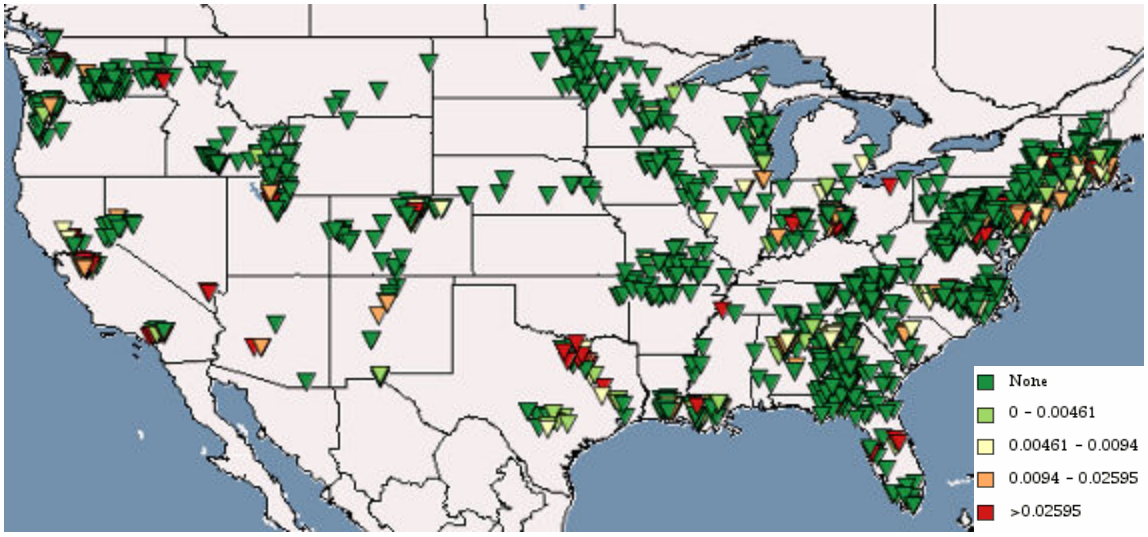


Figure 1.5 Filtered surface water samples analyzed for diazinon (µg/L).
(Used with permission from USGS NAWQA Data Warehouse (*43*).)

1.2.3.3 Expected environmental fate. The EPA RED document (*54*) lists diazinon as moderately environmentally persistent and transportable. Ecological risks to populations of birds, bees, fish, and aquatic invertebrates have been identified and

mitigation measures put into place, including cancellation of all outdoor and indoor residential uses, seed treatments, and some commercial agricultural uses, and reduction of application frequency per growing season where diazinon is lawfully applied. The cancellation of all residential, lawn and garden uses in 2002 and 2004 was an effort in part to reduce the ecological risk of diazinon use (*54*). Use of diazinon on golf courses and other turf areas was cancelled by EPA (*54*) due to its high toxicity in avian and beneficial insect species (including the honey bee) by the acute oral pathway. Human exposure to diazinon from residues in food was not identified as a problem. The half-life of diazinon in natural environmental systems is estimated to range from 3 hours to 2 weeks. ATSDR (*56*) notes that diazinon can be biodegraded. Several hydrolysis studies have reported susceptibility of diazinon to hydrolysis. Chamberlain et al. (*35*) found diazinon hydrolysis to be high at pH levels 2 and 12, and low (< 20% removal) at pH 7 based on a 7-day experiment. In terms of soil system, hydrolysis, Konrad et al. (*60*) determined diazinon hydrolysis to be adsorption catalyzed rather than acid catalyzed since more rapid hydrolysis prevailed in soil systems versus soil-free systems. In the soil-free system, diazinon hydrolysis occurred rapidly at pH 2, moderately rapidly at pH 4, and was relatively stable at pH 6. Microbial degradation was not deemed to be a significant contributing factor in diazinon degradation, even if such bacteria were present in the system. Additionally, Gomaa et al. (*59*) determined diazinon to be more stable at pH 6 than pH 7 and pH 8 in aqueous solutions with 3.5% acetone.

Diazinon has a several identified degradation pathways and products and under various conditions (*61*). Oxidations by free chlorine results in the oxon degradate, diazoxon (*62*). Hydrolytic breakage of the P-O bond results in diethyl thiophosphoric acid and 2-isopropyl-4-methyl-6-hydroxypurimidine (IMP) (*60*). Compared to diazoxon, diazoxon is hydrolyzed more readily with a hydrolysis rate 10 times the hydrolysis rate of diazinon at pH 7 conditions. This increased hydrolysis rate is expected to be due to the electrophilic nature of the phosphorous in the bond P=O in diazoxon versus the bond P=S in diazinon, where the P=O bond is more subject to nucleophilic attack. According to Gomaa et al. (*60*), hydrolysis of diazinon and diazoxon was found to be acid or base catalyzed with first order kinetics and the rate constants reported in Table 1.3, which is taken from Gomaa et al.'s study (*59*).

Table 1.3 Rates of diazinon and diazoxon hydrolysis at 20°C. (From Gomaa et al. (*59*))

pH	Diazinon		Diazoxon	
	K_{ob}	$t_{1/2}$	K_{ob}	$t_{1/2}$
3.1	9.8169×10^{-4} min^{-1}	706.1 min	3.0411×10^{-2} min^{-1}	22.8 min
5.0	9.3575×10^{-4} hr^{-1}	740.7 hr	2.2569×10^{-2} hr^{-1}	30.7 hr
7.4	1.5627×10^{-4} hr^{-1}	4435.8 hr	9.9953×10^{-4} hr^{-1}	693.5 hr
9.0	2.1244×10^{-4} hr^{-1}	3263 hr	1.5709×10^{-3} hr^{-1}	441.2 hr
10.4	4.782×10^{-3} hr^{-1}	144.9 hr	6.8629×10^{-2} hr^{-1}	10.1 hr

Activation energies of hydrolysis reactions were also determined by Gomaa et al. (*59*). They ranged from approximately 13 to 14 Kcal/mol at pH values of 3.1 and 10.4 for diazinon, and 12 to 13 Kcal/mol for diazoxon. Ku et al. (*62*) also observed first order kinetics of diazinon. A linear summation two-species distribution model was prepared to describe the hydrolysis rate constants of protonated and unprotonated species in buffer solutions at acid pH levels.

Ku et al. (*62*) determined photolysis to be an independent contributing mechanism for diazinon degradation via sequential breakage of the P-O and P-S bonds. They developed an overall hydrolytic rate constant comprised of both photolysis and hydrolysis components. Mortland et al. (*63*) found that Cu(II) can catalyze diazinon hycrolysis, in addition to hydrolysis of other organophosphorous pesticides.

Noblet et al. (*65*), found that, using first order kinetics, the half-life of diazinon was approximately 19.5 days for natural water and 17 days for Milli-Q laboratory water. They observed that dissolved organic matter (DOM) slowed diazinon hydrolysis rates by association or binding of the pesticide to the DOM, and notes that hydrolysis in the natural environment is complex with influencing factors such as catalysis, microbial degradation, and DOM complexation. They also concluded that vigorous mixing has only a minimal effect on hydrolysis rates that is equivalent to an increase in temperature of 1-2°C.

Ohashi et al. (*66*) found that loss of diazinon via volatilization from rice plant leaves is significant. Fifty percent of diazinon was lost in a 9 day study. Loss via volatilization was also observed in a compost disposal system. Other studies (*67*) have determined that diazinon is absorbed and transported in plants from diazinon application

on leaf surfaces and soil, though diazinon is not readily absorbed and translocated in the plant. Diazinon was found to metabolize in plants, specifically garden bean plants, by hydrolyzing the pyrimidyl ester bond followed by metabolism of IMP to CO_2. Only small amounts were reduced and released from the plant in a mineralized form as CO_2. Repeated application of diazinon to rice paddies promotes rapid hydrolysis in paddy water and rhizosphere soil. Aerobic microbial-assisted hydrolysis degradation of diazinon was observed to occur after repeated use of diazinon had encouraged growth of the bacterial with such capabilities. Sethunathan et al. (*68*) conducted laboratory and field studies that found diazinon mineralized in 75 to 100 hours. A study (*69*) to determine whether composting of organophosphorous and organochlorine pesticides would be a feasible disposal and destruction route found that diazinon hydrolyzed nearly completely to IMHP hydrolysis product at 65°C. The organism responsible for the conversion, *flavobacterium* sp., used diazinon as a singular carbon source.

1.3. DRINKING WATER TREATMENT

1.3.1. Water Characteristics. There are many compounds found in natural waters**.** They include the following inorganic soil components: clay and silt particles, bicarbonate and other ions, colloidal material, minerals, vitamins, and organics from various sources such as algae, decaying matter, nutrients, bacteria, viruses, synthetic organic compounds, and various organic acids (*70*). In natural waters, the concentrations of H^+ and OH^- (the pH), and the bicarbonate (HCO_3^-) control the alkalinity (*70*). Stumm et al. (*71*) notes that the carbonate-bicarbonate system allows for buffering capacity, complexation of metals, and formation of solids. The constituents of this system include H_2CO_3, HCO_3^-, CO_3^{2-}, CO_2, OH^-, and H^+.

Faure (*72*) explains that the water cycle delivers water in the form of precipitation, during which atmospheric gases and that contain trace mineral and particulate fractions can taint the water before it reaches the earth. As water evaporates from surface waters, salts are concentrated. Groundwater is generally composed of much greater concentrations of constituents of natural waters due to greater contact time for physical and chemical leaching of minerals to occur. However, other factors also act on

the hydrologic system, including sorptive processes, biological uptake, and return of constituents via death and decay of organisms. Weathering and soil-ion exchange leach minerals from rocks. Several ions are found commonly in ground waters: calcium, magnesium, iron, manganese, potassium, and sodium, with calcium, magnesium, iron, and manganese most prevalent (*690*). Calcium and magnesium ion concentrations in parts per million of water from the lower Mississippi River and its tributaries are gathered by Livingstone and the USGS (*73*), and is compiled in Table 1.4.

Table 1.4 Constituents of water from the lower Mississippi River and its tributaries.

River	Location	Ca^{+2} ppm	Mg^{+2} ppm
St. Francis River	Marked Tree, AK	42	11
White River	Batesville, AK	36	12
Black River	Black river, AK	31	17
White River	Newport, AK	30	13
Little Red River	Heber Springs, AK	5.9	1.2
Cimarron River	Ute Park, NM	49	10
Arkansas River	Dardanelle, AK	44	9.6
Mississippi River	New Orleans, LA	34	8.9
Mississippi River	Baton Rouge, LA	34	7.6
Ouachita River	Malvern AK	6.3	1.5
Ouachita River	Arkadelphia, AK	7.1	1.9
Smackover Creek	Smackover, AK	48	13

1.3.1.1 Calcium. Calcium is the most commonly found mineral in natural waters and is the predominant component next to bicarbonate, of surface waters (*70*). The common mineral forms that contribute to calcium in natural waters include calcite

(aragonite, $CaCO_3$), ikaite ($CaCO_3$ $6H_2O$), gypsum ($CaSO_4$ $2H_2O$), anhydrite ($CaSO_4$), fluorite (CaF_2) (*72*). Calcium is commonly found as Ca^{2+} ion or sorbed to soil in natural systems (*71*).

MWH (*70*) states that when present at sufficient levels in drinking water, calcium can precipitate as CaCO3 scale on cast iron or steel pipes and cause reduction in heat transfer and restrict flow. Scale formation on shower heads, fixtures, and on soap also cause flow restriction, maintenance, and nuisance problems. Conversely, scale precipitation prevents metal pipe corrosion, but generally must be removed to ensure efficient and maintained infrastructure.

1.3.1.2 Magnesium. Magnesium is less prevalent than calcium in rocks and water, though it is more soluble. Faure (*72*) notes that magnesium has properties that allow for its precipitation as an impurity in limestone. Magnesium is mostly found as an Mg^{2+} ion in natural waters, though its solubility is difficult to express as a whole due to magnesium ability to exist in impure solid configurations. Magnesium is found in mineral form as magnesite ($MgCO_3$), Nesquehonite ($MgCO_3$ $3H_2O$), lansfordite ($MgCO_3$ $5H_2O$), and dolomite ($MgCa(CO_3)_2$).

Magnesium is a critical component of water in terms of human health. MWH (*70*) reports that studies have shown that correlations can exist between magnesium concentrations in drinking water and risk of cardiovascular disease. Laxative effects can be caused by at high magnesium concentrations. Like calcium, magnesium can cause problems in industrial and residential washing, as well as in commercial operations such as brewing, film development, and processes using boiler water where high temperatures and pressures can cause precipitates in the form of magnesium silicates and magnesium phosphates.

1.3.1.3 Water hardness. Hardness is a measure of the presence of multivalent cations in water. Stumm (*71*) explains hardness is measured as the sum of the concentrations of calcium and magnesium in meq/L in water, and generally expressed as mg/L of $CaCO_3$. Hardness is classified as carbonate hardness and noncarbonate hardness. Carbonate hardness is total hardness in the form of bicarbonate salts ($Ca(HCO_3)_2$ and $Mg(HCO_3)_2$), and carbonate compounds ($CaCO_3$ and $MgCO_3$). Noncarbonate hardness is hardness as noncarbonated salts ($CaSO_4$, $CaCl_2$, $MgSO_4$, and

MgCl). Typical water hardness classifications as listed by MWH (*69*) are shown in Table 1.5. A map illustrating the patterns of natural water hardness across the U.S., which is taken from a USGS NAWQA report (*74*) on the quality of rivers in the U.S., is shown in Figure 1.6.

Table 1.5 Typical water hardness classifications.

Water Classification	Hardness mg/L as $CaCO_3$
Soft	0 to <50
Moderately Hard	50 to <100
Hard	100 to <150
Very Hard	>150

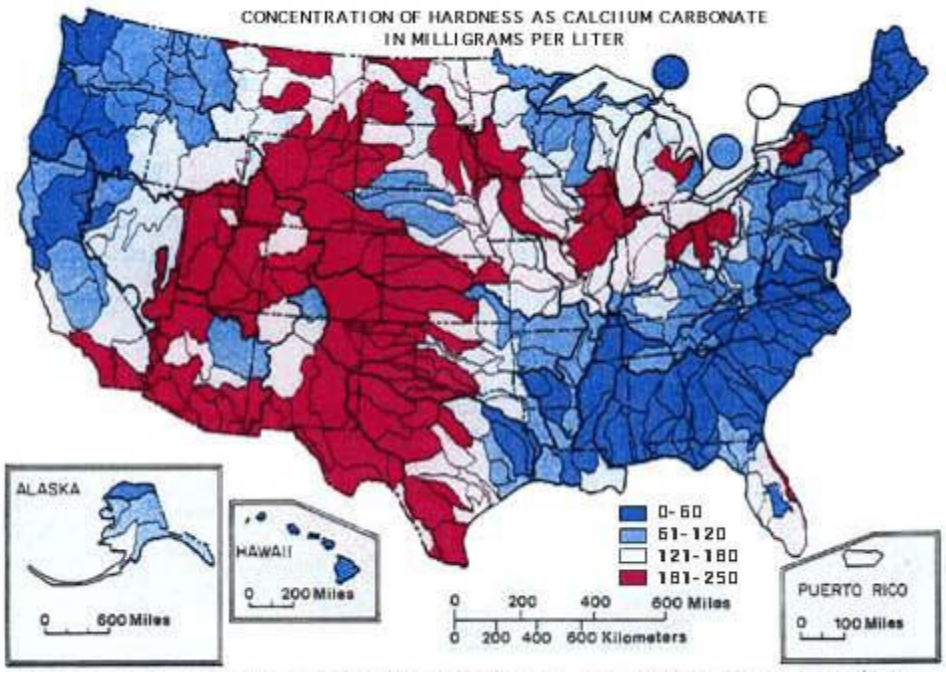


Figure 1.6 U.S. map of mean hardness in mg/L as $CaCO_3$.
(Used with permission from USGS (1977) Briggs et al. report (*74*).)

1.3.2. Water Treatment Methods. Conventional water treatment plant systems consist of a series of technologies including screens, pH control, oxidant/disinfectant addition, rapid mix with coagulant addition, flocculation and sedimentation, granular filtration, oxidant and disinfectant addition, and clearwell storage. Membrane technologies, which reject pathogens by size exclusion, can also be employed in water treatment facilities, although they are not currently as widely used as conventional treatment methods because of the high energy costs and residuals management required. Figure 1.7 depicts a typical water treatment facility based on information found in publications by MWH (*70*).

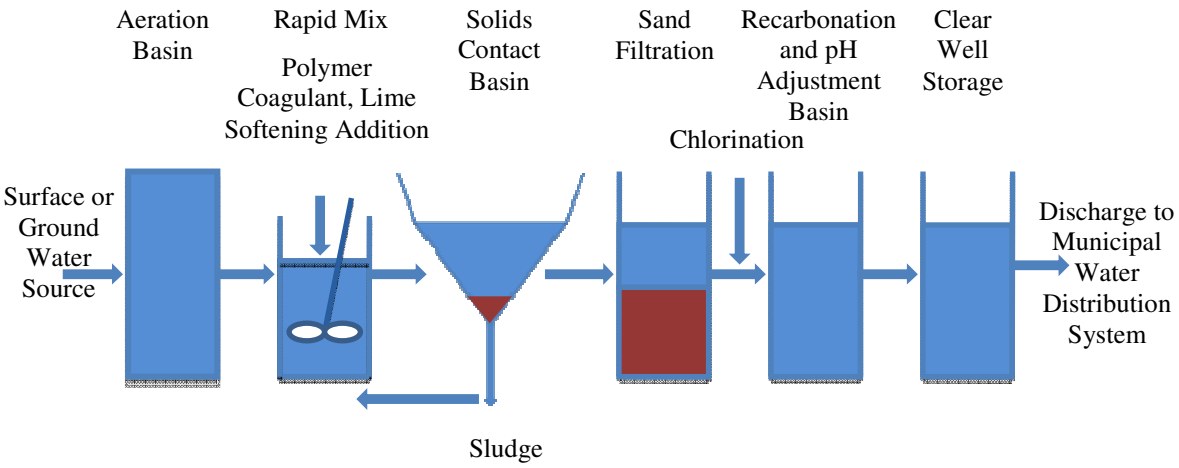


Figure 1.7 Schematic of a typical water treatment plant where lime softening is employed.

MWH (*70*) and Benefield et al. (*75*) discuss that aeration can initially be employed to removed CO_2, especially in groundwater sources where high concentrations of CO_2 can exist. Aeration can also oxidize and cause precipitation of iron and manganese species if present. Additions made to the rapid mix basin to manage calcium and magnesium in water treatment require the pH of the water to be increased to pH levels of approximately 10 for calcium removal and 11 for magnesium removal. In order to raise the pH to control hardness, calcium hydroxide ($Ca(OH)_2$) is added as slaked or hydrated lime. Calcium hydroxide is a milky liquid of lime. When a nominal amount of

magnesium persists, lime and sodium carbonate, otherwise known as soda ash, (Na_2CO_3) is added. Caustic soda (NaOH) can be used in place of any of these treatments, but is generally more costly. Elevated pH conditions by increasing the OH^- concentration shifts the system equilibrium such that the alkalinity is changed from HCO_3^- to CO_3^{2} (*74*). This causes precipitation of calcium carbonate ($CaCO_3$) and magnesium hydroxide ($Mg(OH)_2$), if present, out of solution. Equations 1.5 and 1.6 describe the solubility equilibrium for $CaCO_3$ and $Mg(OH)_2$, taken from Benefield et al. (*75*).

$$CaCO_{3\,(s)} \leftrightarrow Ca^{2+}{}_{(aq)} + CO_3^{2-}{}_{(aq)} \tag{1.5}$$

$$Mg(OH)_2 \leftrightarrow Mg^{2+}{}_{(aq)} + 2OH^-{}_{(aq)} \tag{1.6}$$

AWWA standards for lime softening dictate minimum requirements for manufactures and purchasers with respect to physical and chemical characteristics, and packaging, shipping, and testing for use in drinking water treatment (*75*).

Coagulant addition such as alum or ferric chloride to destabilize colloids and allow flocs to form and settle follows lime softening as described by MWH (*70*). The solids contact basin allows coagulation and flocculation to happen. Sand filtration removes water contaminants via physical filtration. Chlorination is a typical oxidant added to oxidize harmful bacteria, viruses, and any compounds still present in the water. Recarbonation (remineralization) and stabilization of the softened water is achieved by adding CO_2 and hardening agent (typically lime, $CaCO_3$) to increase the calcium and bicarbonate ions in solution to prevent caustic corrosion in distribution systems and to provide neutral water to customers.

2. GOALS AND OBJECTIVES

2.1. OVERARCHING GOALS

The purpose of this study was to develop kinetic models of experimentally determined hydrolysis rate constants of three pesticides: etridiazole, metribuzin, and diazinon. This work was identified to be important and necessary based on the Chamberlain et al. (*35*) comprehensive screening study of pesticide degradation by various water treatment options analyzed by GC, in which surprising hydrolysis degradability was found for many of the pesticides studied over a 7-day period. Three pesticides were chosen from the compounds classified in Group 1 as a result of the Chamberlain et al. study, indicating high reactivity (>50% removal) was observed for at least one of the three pH conditions studied (pH=2, 7, 12). Specifically, the three pesticides selected for this work were decided upon based on several factors: (1) they were determined to be highly hydrolysable based on the Chamberlain et al. screening study of pesticides found in water (*35*), and (2) they were currently used in the field and potentially present in drinking water sources, (3) they were analytically separable and detectable by gas-chromatography with electron capture detection (GC-ECD) and (4) they represented three main types of pesticides (insecticides, herbicides, and fungicides).

Hydrolysis is an important fate for pesticides and organic compounds in drinking water sources that must not be overlooked. Chamberlain et al. (*35*) found 20 pesticides to be susceptible to hydrolysis degradation. Hydrolysis values may exist in the literature for environmental and even acidic conditions, however, data is lacking for hydrolysis at basic conditions, which would be incurred during the lime softening process in a drinking water plant. This is the case for diazinon. Estimation Program Interface Suite (EPI Suite) developed by EPA's Office of Pollution Prevention Toxics is a program designed to predict physicochemical properties and environmental fate of environmental contaminants. The HYDROWIN model predicts acid and base hydrolysis rate constants and half-live under typical environmental conditions, and also keeps track of experimental values found in the literature. When this program was run for the three pesticides in this study, the program not only did not give any predicted degradation values, but also did not provide any corresponding values in the literature. No previous

hydrolysis constants work was found regarding etridiazole and metribuzin. This further explains the need for this study. It is important to know the hydrolysis rates at pH levels 10 and 11 that would be experienced at the time of lime softening to know what compounds may be present in finished drinking water. Degradation may be helpful or harmful depending on properties of the parent compounds and properties of the degradates. For example, literature identifies organophosphate diazinon degradate, diazoxon, to have greater cholinesterase inhibiting power than diazinon (*59*), making the presence of diazoxon in drinking water more hazardous than diazinon.

A comprehensive range of pH levels was studied for completeness and in order to compare hydrolysis rate constant values to literature. Models were employed to predict the hydrolysis at any given pH.

2.2. SPECIFIC RESEARCH OBJECTIVES

Specific research objectives included

1. Determining several pesticides for which to develop kinetic models.
2. Developing experimental and analytical methods to obtain statistically supported experimental data.
3. Conducting hydrolysis experiments for all selected compounds at 11 pH levels (2, 4, 6, 7, 8, 9, 10, 11, 12, and 13) in batch experiments in deionized laboratory water.
4. Using experimental results in laboratory waters to model for pesticide acid (k_A; $L \cdot mol^{-1} \cdot h^{-1}$), neutral ($k_N$; h^{-1}) and basic (k_B; $L \cdot mol^{-1} \cdot h^{-1}$) rate constants based on non-linear regression and pseudo-first order hydrolysis models as appropriate.
5. Comparing results to estimated values given in the literature.

3. METHODS AND MATERIALS

3.1. MATERIALS

3.1.1. Chemicals. All pesticides were purchased from Sigma-Alderich (St. Louis, MO). All solvents (e.g., hexane) and other necessary chemicals (e.g., sodium phosphate, sodium sulfide, and calibration buffer) were purchased from Fisher Scientific (Fairlawn, NJ) and were at least pesticide grade. Experiments were conducted in 5 mM phosphate buffer solutions at a comprehensive range of pH levels (pH = 2, 4, 6, 7, 8, 9, 10, 11, 12, 13) freshly prepared in 4 L amber glass bottles with monobasic and dibasic sodium phosphate, phosphoric acid, and sodium hydroxide, and allowed to equilibrate with the atmosphere for approximately 48 hours before use. Milli-Q laboratory water with a resistivity of greater than 18.2 MW cm was prepared from distilled water using a Millipore purification system (Model Simplicity 185, Millipore Co., Bedford, MA), which was used for all laboratory water requirements and hydrolysis reactor media.

3.1.2. Instrumentation. Samples were analyzed using an Agilent 6890N Series gas chromatograph (GC) outfitted with a micro-electron capture detector (μ-ECD) and 7683 Series injector (Palo Alto, CA). The instrument was operated with an inlet pressure of 20 psi, and gas flow of 24.5 mL/min. An Agilent HP-5MS capillary column (30 m · 320 μm · 0.25 μm) performed the separations. Two Corning pH meters (Models 320 and 430) and general, all-purpose reference probes (Model 476086) were calibrated with standard pH 4 and pH 10 buffers before every sampling event with a calibration curve of at least 98%. A standard pH 7 buffer was employed as a check standard after calibration to ensure proper measurement within ±0.1. When not in use, probes were stored in saturated KCl pH probe storage solution.

3.1.3. Experimental Apparatus. A custom-made wooden box with circular sides and a hinged lid was constructed. Dow Styrofoam boards were cut to make 32 wells (16 wells for each of two layers) in which 500 mL reactor bottles would reside. An electric rotator (Diamond Pacific Tool Corporation) was used to turn the tumbler at a rate of 7 rpm. The tumbler was operated in the temperature control room, which was maintained at a temperature of 22°C. Spiking, pH measurements, and liquid-liquid extraction (LLE) to hexane all took place in the temperature control room.

3.2. METHODS

3.2.1. Experimental Design. Etridiazole, metribuzin, and diazinon stock solutions were prepared from powder or oil purchased from Sigma-Aldrich (St. Louis, MO) in methanol at 5,000, 1,985.3, and 1,912.5 mg/L, respectively. All stock and substock solutions were prepared in clean amber glass vials or bottles with Teflon coated lids and were stored at -20°C in the absence of light. Substock solutions were created in hexane at 100 and 10 mg/L and further diluted to 100 μg/L for validation and optimization by injection on the GC-ECD. A reaction media mix of etridiazole, metribuzin, and diazinon pesticides was created at 800 mg/L in hexane from stock solutions, and substock created at 10 mg/L in hexane. The reaction media was also validated by injection on the GC-ECD at 5, 10, and 100 μg/L.

Experiments were initiated by spiking 20 μL of 100 mg/L reaction media into 400 mL of buffer in a 500 mL reactor bottle, mixing the solution by hand shaking, and removing an initial 35-mL sample on which LLE into 2 mL hexane was performed. This process also served to quench the experiment. All prepared samples were either immediately queued in the autosampler plate for injection on the GC-ECD, or stored at in the dark at 4°C and injected within 48 hours. Mixing was maintained in the dark via the rotating tumbler for the two week duration of the experiment, and reactors were removed only to measure pH and take samples. Samples were sacrificed 10 times from each reactor over the course of the study. Specifically, samples were taken at approximately 0 h (initial samples), 2 h, 6 h, 12 h, 24 h, 3 d, 5 d, 7 d, 11 d, and 14 d. The experiments were performed in duplicate with laboratory blank reactors at pH levels of 2, 7, and 13. The experimental standard operating procedure (SOP) followed is shown in Appendix A.

3.2.2. LLE Method. LLE was performed by following EPA Method 505 with minor modifications. The method used in this study involved taking a 5-mL sample into a 40-mL extraction vial and spiking with 50 μL of 5 mg/L chlorpyrifos in isooctane as the extraction surrogate. Extraction was assisted by adding 6 g of $NaSO_4$ to increase the ionic strength of the sample solutions. Hexane was immediately added and the time was noted as the quenching time of the experiment. Extraction efficiencies for all pesticides in mixture and surrogate were tested and reported as part of the experimental quality control. Vials were shaken by hand for one minute, then organic and aqueous

phases were allowed to separate for at least 10 minutes until all samples were taken and extracted. Of the hexane layer, 1 mL was carefully removed and put into an autosampler vial, and spiked with 10 µL of 2 mg/L 2,4,5,6-tetrachloroxylene (TCX) in isooctane as the internal standard. The extraction process was performed on each set of duplicates at a time (2 vials at a time) to prevent errors caused by evaporation of the organics added to the vials. Caps were placed on vials whenever possible in order to further reduce evaporation. The LLE SOP followed is shown in Appendix A.

3.2.3. GC-ECD Method. With minor modifications, EPA Method 505 was followed to process and analyze experimental samples. A 1 µL sample was injected at in initial oven temperature held at 50 C. for 1 min. Temperature gradients of 20 C/min ramp to 120 C, 5 C/min ramp to 185 C held for 1 min, 15 C/min ramp to 220 C held for 6 min, and a post-run temperature of 50 C. The detector temperature was 300 C. GC-ECD method specifics, oven ramps, retention times, and chromatogram are shown in Appendix B.

3.2.4. Quality Control Methods. Standard curves for each pesticide studied were based on at least a 6 points with regression coefficients of at least 0.993. Standard curves were performed in 5 mM phosphate buffer solutions at pH levels of 2, 7, and 13 to ensure that matrix effects did not significantly affect analysis. Percent relative standard deviations (%RSD) were found to be 2.8, 8.0, and 0.6 for diazinon, etridiazole, and metribuzin, respectively, between the 3 pH levels tested, which indicated that one standard curve could be used for all buffers. The curve obtained for the pH 7 buffer was employed in the study. Extraction efficiencies for each compound were found to be within the commonly accepted recovery range of 70-120%, at 84%, 109%, 70%, and 73% for etridiazole, diazinon, metribuzin, and chlorpyrifos (surrogate), respectively. Method detection levels were based on a concentration of 0.1 µg/L for each compound extracted and analyzed seven times resulted in MDLs of 0.04, 0.04, and 0.09 µg/L for etridiazole, metribuzin, and diazinon, respectively. In order to quantitatively measure consistency and precision, chlorpyrifos, a surrogate compound, was analyzed over the course of the experiment. The average %RSD of the area of the surrogate compound divided by the average area of the internal standard (IS) compound for all experimental samples in the study was 13.3, which signifies good replication and experimental and

analytical efficiencies throughout the experimental process. Additionally, the average %RSD between the duplicate samples of 6.6 indicates precision between samples. The extraction efficiencies, MDLs, standard curves, and experimental standards are shown in Appendix A.

3.2.5. Development of Models. The data obtained in this study was modeled in several different ways. First a non-linear regression approach was taken to describe a second order model of the hydrolysis observed experimentally. The 2nd order rate constants (L $h^{-1}mol^{-1}$) for acid, neutral, and base hydrolysis obtained from this method were then converted to pseudo-first order rate constants (h^{-1}) at specific acidic pH values (pH 2 – 4) and basic pH values (pH 10 – 13). Linear regression was then performed on the experimental data, and when behavior indicated sufficient linearity by observation and a regression coefficient (R^2) of greater than 0.75, a non-linear regression approach was applied to the first order approach.

3.2.5.1 Non-linear regression. A non-linear regression approach was used to model the hydrolysis observed in the samples. Acid hydrolysis of pesticides in aqueous solution may be expected to occur by second-order kinetics. Similarly, alkaline hydrolysis in aqueous solution typically occurs and can be modeled by second-order kinetics, as shown in Equations 3.1 and 3.2, respectively (*77, 78*).

$$\frac{dP}{dt} = -k_A[H^+][P] \tag{3.1}$$

$$\frac{dP}{dt} = -k_B[OH^-][P] \tag{3.2}$$

Conversely, neutral hydrolysis in aqueous solution generally occurs via a first-order reaction as shown in Equation 3.3 (*77, 78*).

$$\frac{dP}{dt} = -k_N[P] \tag{3.3}$$

A pesticide's overall hydrolysis rate is a combination of simultaneous acid, neutral, and basic hydrolysis terms as illustrated in Equation 3.4 (*77, 78*).

$$\frac{dP}{dt} = \underbrace{-k_A[P][H^+]}_{\text{Acid hydrolysis}} \; - \; \underbrace{k_N[P]}_{\text{Neutral hydrolysis}} \; - \; \underbrace{k_B[P][OH^-]}_{\text{Base hydrolysis}} \tag{3.4}$$

Non-linear regression techniques were used to assess these assumptions and to determine the hydrolysis rate constants (acidic, neutral, and basic) as necessary for each study compound. Average recorded experimental pH values were used for the regression model. Table 3.1 shows the values used.

Table 3.1 Averaged pH values used in non-linear regression model.

pH goal	pH NLR model
2	2.10
4	4.26
6	6.19
7	7.16
8	7.89
9	8.83
10	8.87
11	10.77
12	12.02
13	12.95

If no noteworthy hydrolysis was observed, the rate constant at that specific pH range was assumed to be insignificant and was neglected. Non-linear regression techniques were employed by minimizing the sum of the squares of the differences between experimentally determined and model k-values using k_A, k_N, and k_B as fitting parameters over all pH levels. When the second order rate constants k_A and k_B were known, the values of the pseudo-first order constants were then also known, as shown in

Equation 3.5 (*77*). These were compared to k-values from the pseudo-first order model and the published literature.

$$k'_A = k_A[H^+] = k_A\left(10^{-pH}\right)$$
$$k'_B = k_B[OH^-] = k_B\left(\frac{10^{-14}}{10^{-pH}}\right) \tag{3.5}$$

3.2.5.2 Pseudo-first order. In theory, at any specific pH both $[H^+]$ and $[OH^-]$ are constant and relate as shown in Equation 3.6.

$$[H^+] = 10^{-pH}$$
$$[OH^-] = \frac{K_W}{[H^+]} = \frac{10^{-14}}{10^{-pH}} \tag{3.6}$$

Therefore, both acidic and basic hydrolysis simplifies to pseudo-first order rate kinetics and reduces to a single pseudo-first order rate expression, such as shown in Equation 3.7 (*78, 79*).

$$\begin{aligned}\frac{dP}{dt} &= -k_A[P][H^+] - k_N[P] - k_B[P][OH^-] \\ &= -\left(k_A[H^+] + k_N + k_B[OH^-]\right)[P] \\ &= -\left(k_A\left(10^{-pH}\right) + k_N + k_B\frac{10^{-14}}{10^{-pH}}\right)[P] \\ &= -k'_{Hydrolysis}[P]\end{aligned} \tag{3.7}$$

For experimental samples at pH levels 2 – 4, both neutral and basic hydrolysis were found to be negligible and, thus, $k'_{Hydrolysis} \sim k'_A$. Similarly, for samples from experiments at pH levels 10 – 13, both acid and neutral hydrolysis were found to be negligible and, thus, $k'_{Hydrolysis} \sim k'_B$. The three rate constants (k_A, k_N, and k_B) were determined using non-linear regression techniques by minimizing the sum of the squares of the differences between experimentally determined $k'_{Hydrolysis}$ values with model values using k_A, k_N and k_B as the fitting parameters over all pH levels. Linear regression was used to assess the pseudo-first order assumption at specific pH levels, and to determine the hydrolysis rate constant for each study compound when first-order behavior with an R^2 value greater than 0.75 was observed from a plot of the negative natural logarithm of C/C_o versus reaction time (*77, 78*). These values were compared with the non-linearly regressed second order rate constant values at specific pH levels.

4. RESULTS AND DISCUSSION

4.1. EXPERIMENTAL FINDINGS

4.1.1. pH Variance of Buffer Solutions. Figure 4.1 displays the pH variance in the buffer solutions measured in the reaction vessels over the course of the experiment. Two pH meters and probes were used to quantify the pH of the reaction media. The probes were calibrated before each sampling event with standard pH 4.01 and 10.01 buffer solutions with calibration curves of at least 98%. The probes were checked to be within ± 0.02 pH units of 7.00 in standard pH 7 buffer solution following calibration. The readings from both pH probes and meters are reported in Figure 4.1.

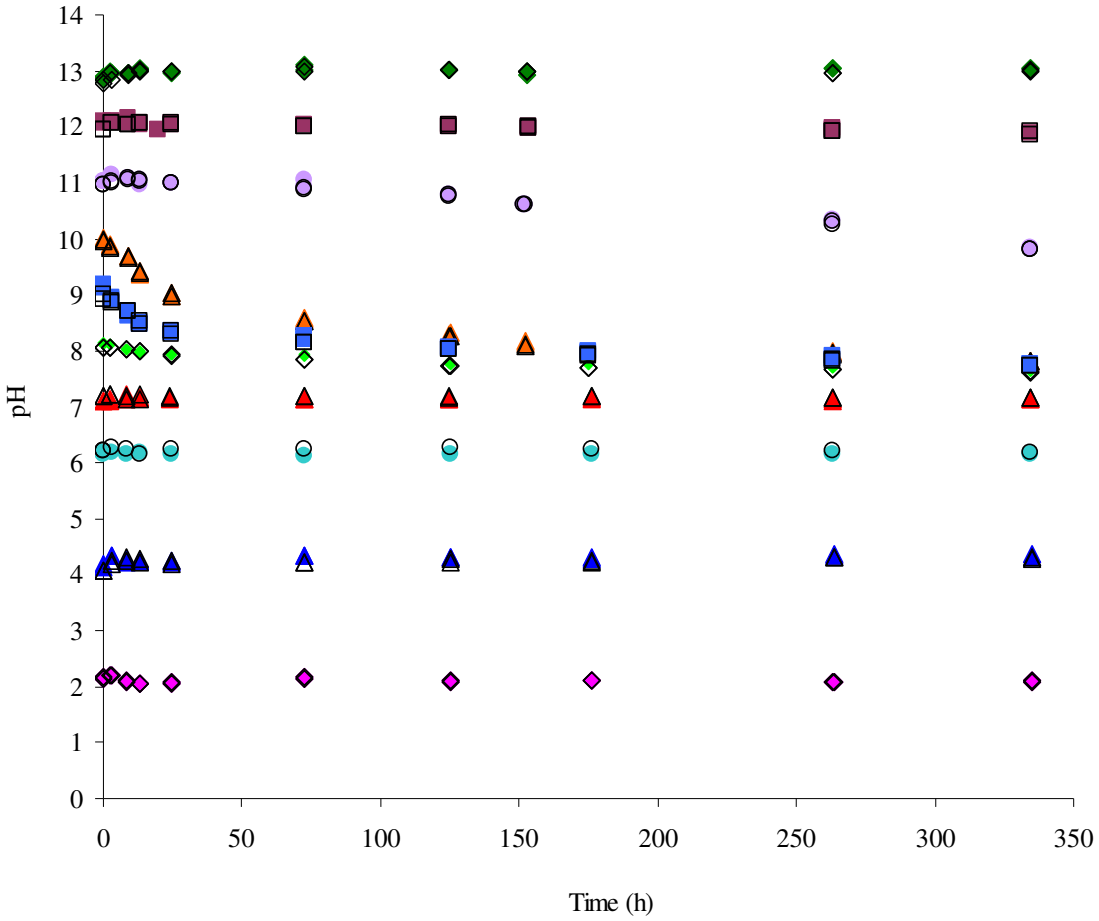


Figure 4.1 Buffer pH variations in each reactor.
(Solid colored shapes represent pH probe A; unfilled shapes represent pH probe B)

Buffer solutions of pH levels 2 – 7 were relatively stable. Buffers of pH levels 8 – 11 were not as stable and became more acidic over time. This acidification is expected to be caused by atmospheric CO_2 introduction to the reaction media. Every time samples were taken, the lids of the reaction bottles were removed and 35 mLs of water were removed, increasing the headspace and allowing ambient air to enter the bottle. In fact, the headspace was already 190 mL by the end of the first day of sampling (after 24 h sample), when only half of the samples had been taken. The initial headspace was a volume of 15 mL on top of 385 mL of reaction media.

4.1.2. Concentration Versus Time. The concentrations of the pesticides etridiazole, metribuzin, and diazinon decreased in specific pH buffers over time. All experiments were conducted in duplicate except for the reactor at pH 6. The duplicate reactor for the pH 6 buffer was lost due to leakage of the reaction media from a nick in the lip of the reactor that compromised the seal of the lid.

4.1.2.1 Etridiazole. Figures 4.2 and 4.3 plot the average concentrations of pesticide versus reaction time for etridiazole. Confidence intervals represent plus or minus one standard deviation based on duplicate reactors. Standard deviations are based on average concentrations. Observed noise between sampling time points is due to deviations in method performance on different days over the two week experiment.

Hydrolysis of etridiazole was observed at basic pH levels 11 – 13. At pH 13, etridiazole exhibited extremely rapid hydrolysis, such that the detection limit was reached by the third sampling event (6 hours).

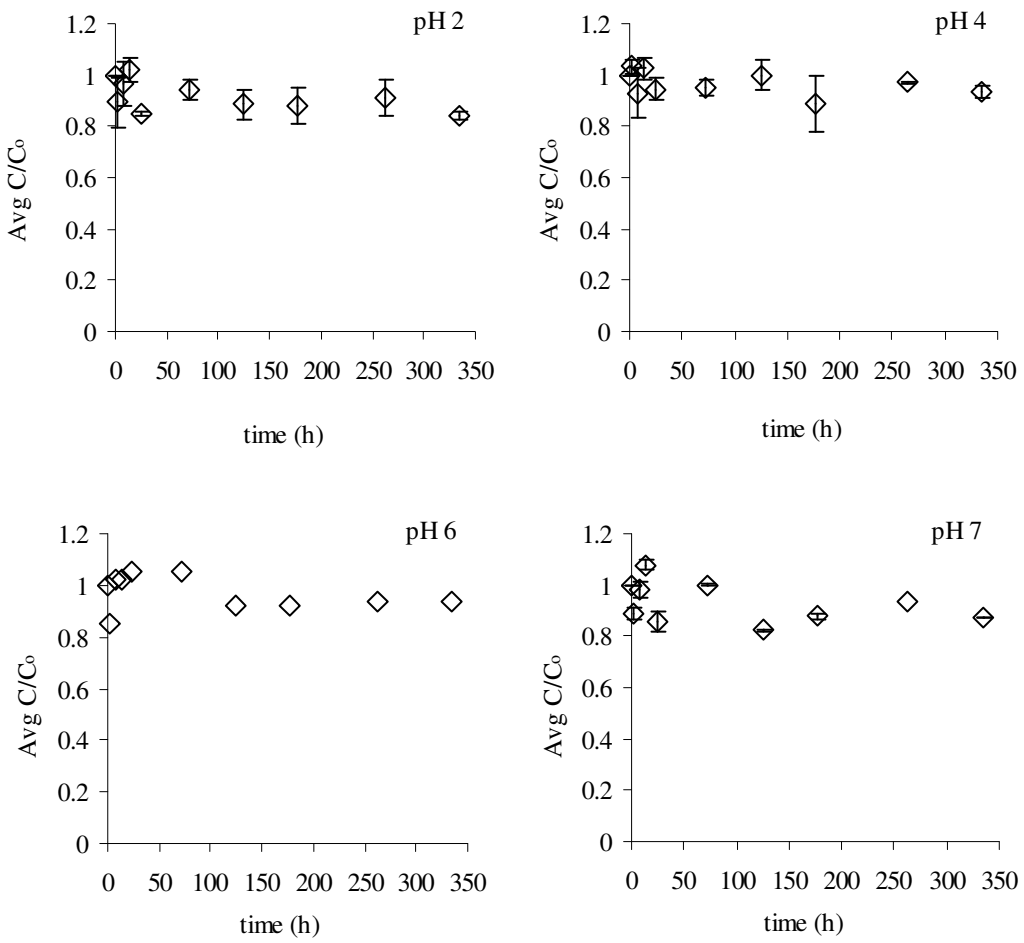


Figure 4.2 Average C/C_o observed for etridiazole in solution at pH 2 – 7.
(Confidence intervals represent ± one standard deviation based on duplicate reactors.)

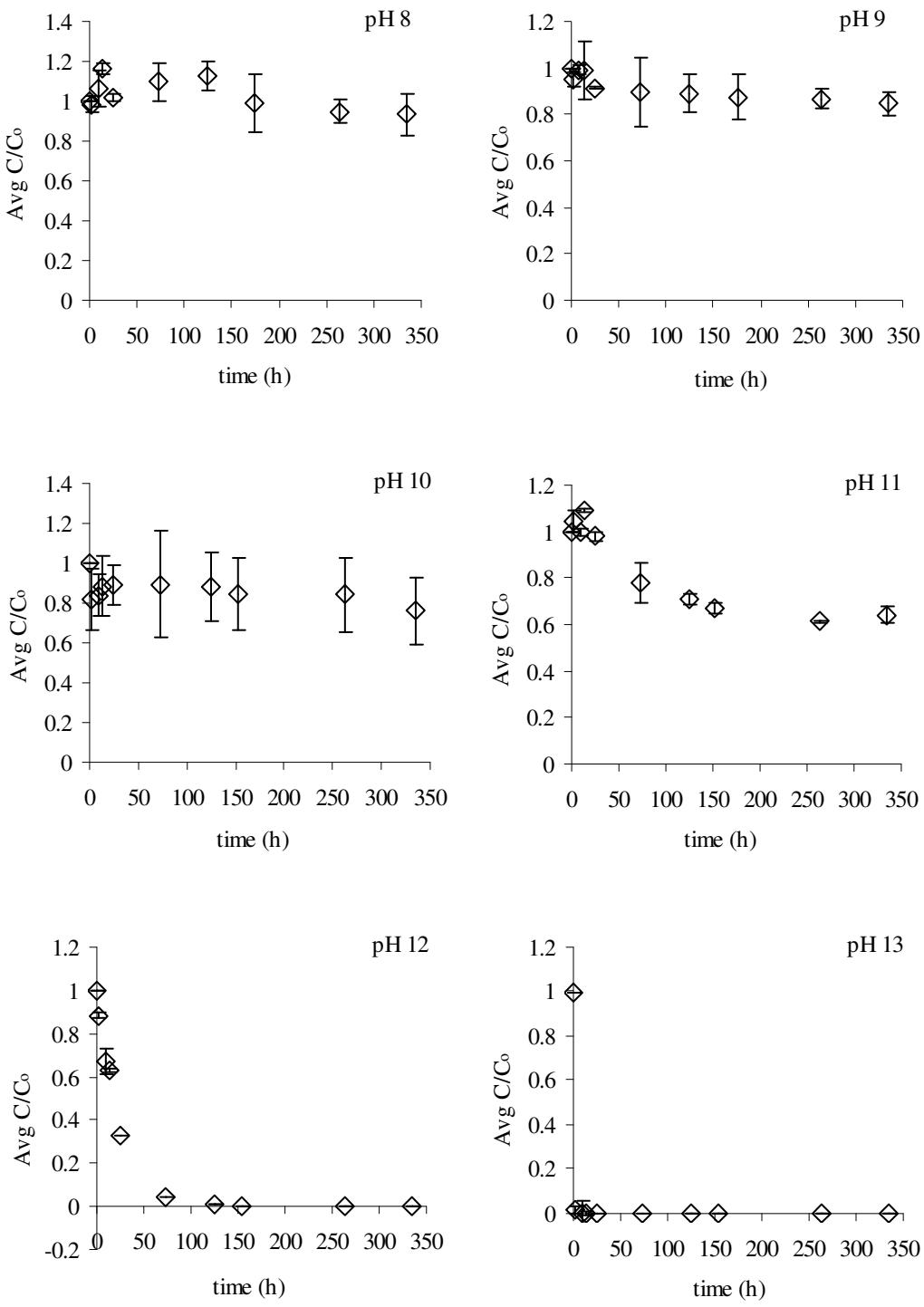


Figure 4.3 Average C/C_o observed for etridiazole in solution at pH 8 – 13.
(Confidence intervals represent ± one standard deviation based on duplicate reactors.)

4.1.2.1 Metribuzin. Figures 4.4 and 4.5 plot the average concentrations of pesticides versus reaction time for metribuzin. Confidence intervals represent plus or minus one standard deviation based on duplicate reactors. Standard deviations are based on average concentrations. Observed noise between sampling time points is due to deviations in method performance on different days over the two week experiment.

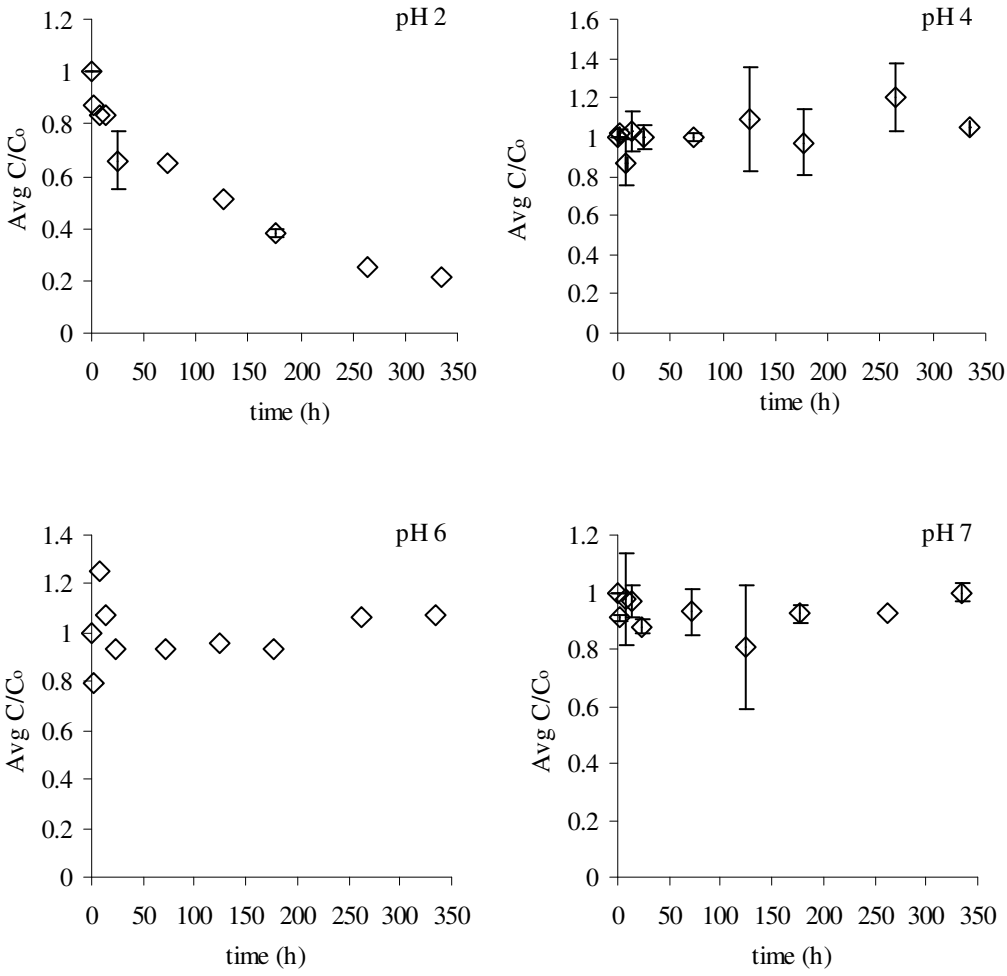


Figure 4.4 Average C/C_o observed for metribuzin in solution at pH 2 – 7. (Confidence intervals represent ± one standard deviation based on duplicate reactors.)

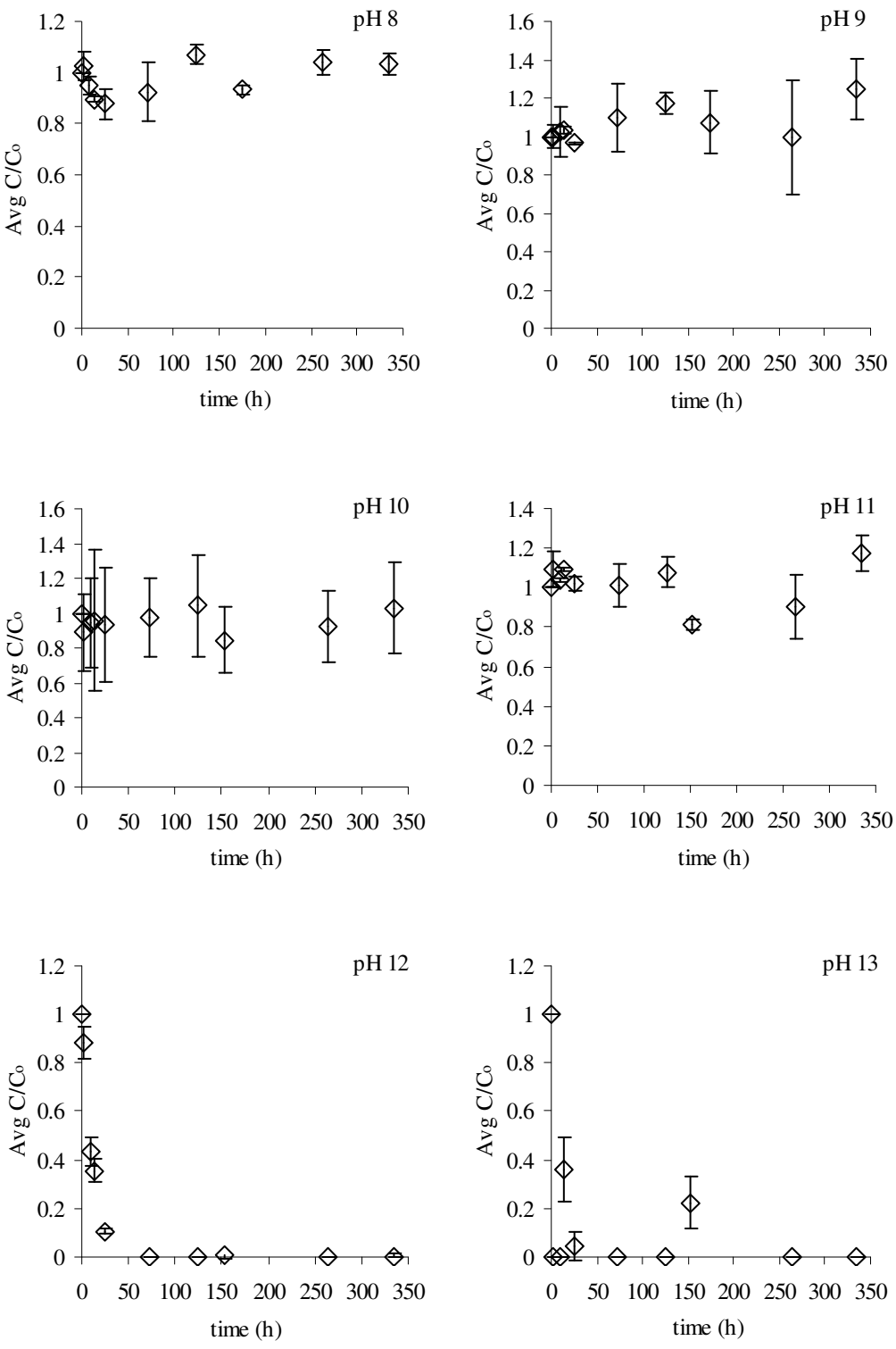


Figure 4.5 Average C/C_o observed for metribuzin in solution at pH 8 – 13. (Confidence intervals represent ± one standard deviation based on duplicate reactors.)

Metribuzin underwent rapid hydrolysis at acidic pH levels (pH<4) and at basic pH levels (pH>11). In fact, the rate of hydrolysis at pH 13 could not be determined for metribuzin due to its rapid degradation. Metribuzin was scarcely detected in either of the initial duplicate samples at pH 13, suggesting that rapid hydrolysis occurred in the 3 to 5 minutes required to spike in and extract the initial samples. Initial concentrations of <1 µg/L were detected for metribuzin.

4.1.2.2 Diazinon. Figures 4.6 and 4.7 plot the average concentrations of pesticides versus reaction time for diazinon. Confidence intervals represent plus or minus one standard deviation based on duplicate reactors. Standard deviations are based on average concentrations. Noise between points is from inevitable method error.

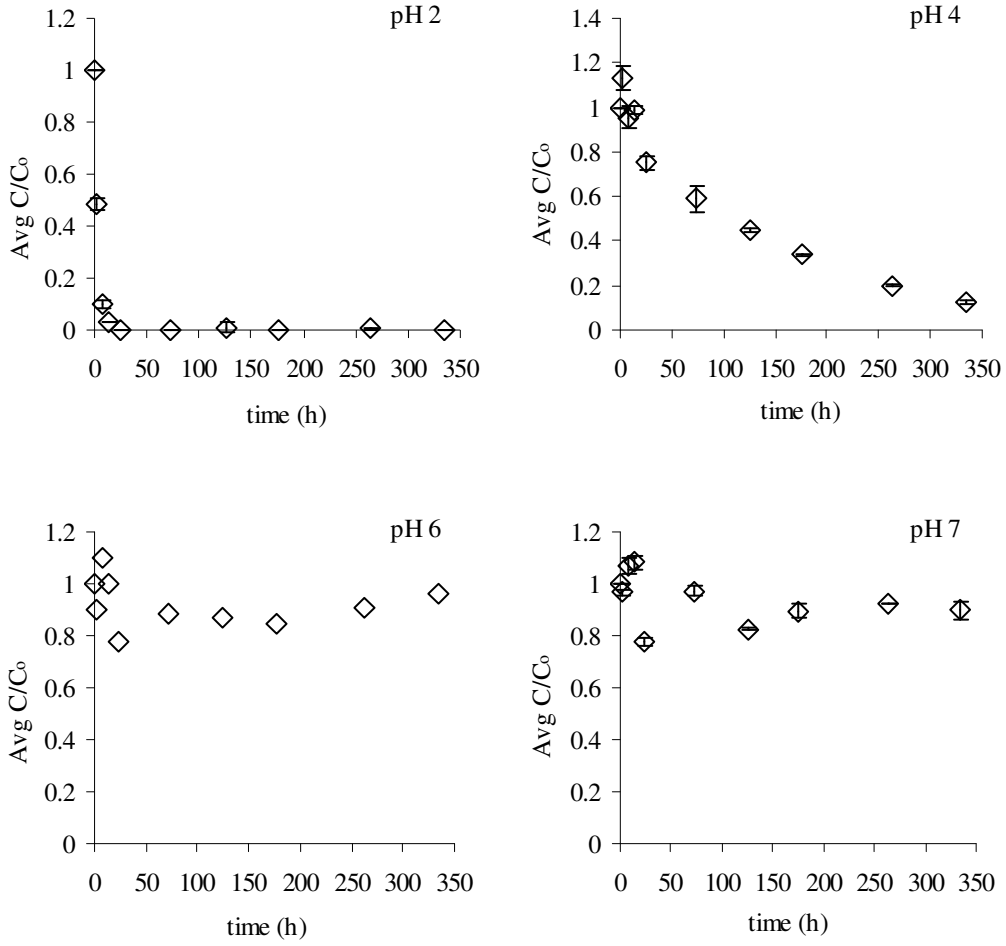


Figure 4.6 Average C/C_o observed for diazinon in solution at pH 2 – 7.
(Confidence intervals represent ± one standard deviation based on duplicate reactors.)

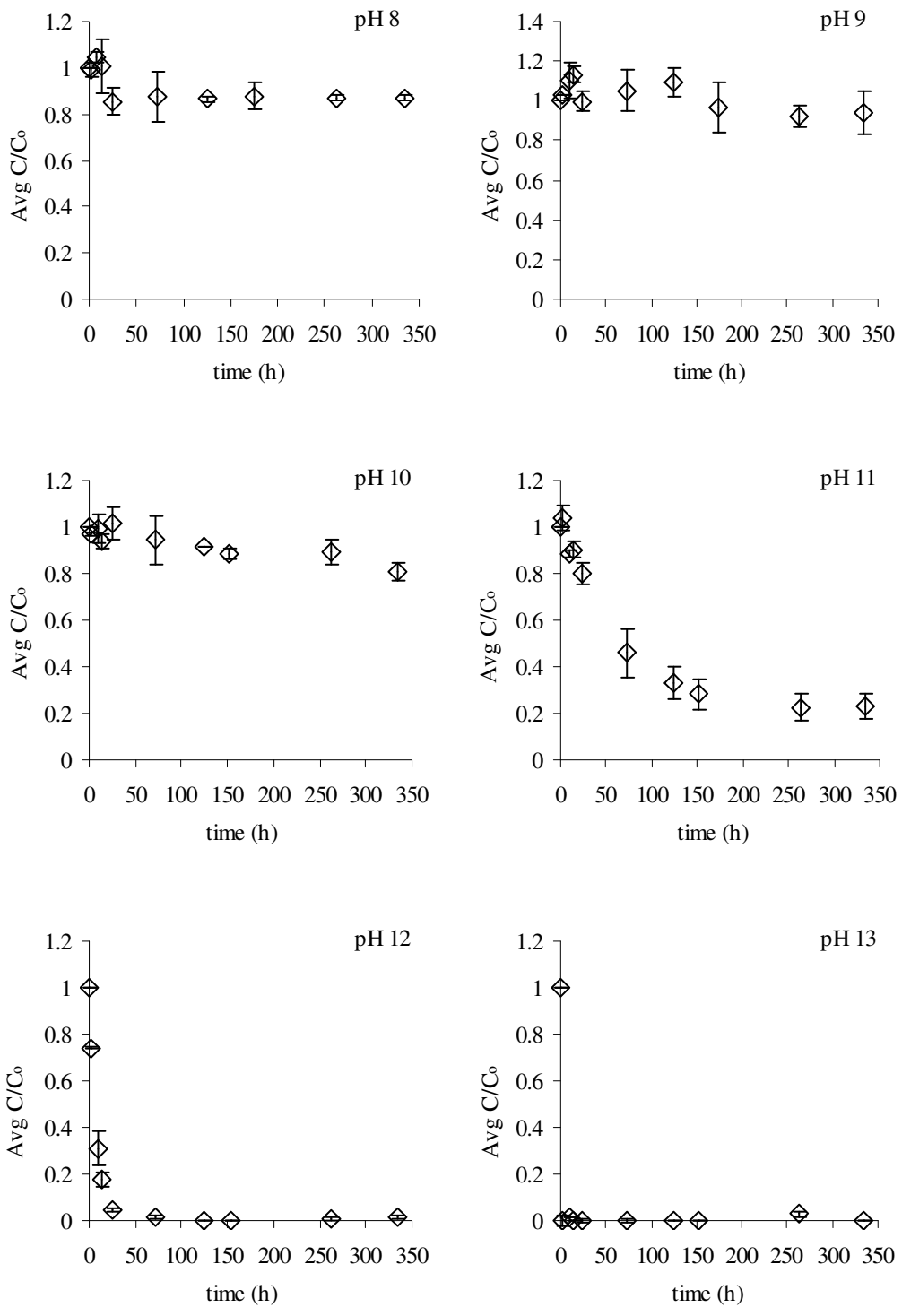


Figure 4.7 Average C/C_o observed for diazinon in solution at pH 8 – 13.
(Confidence intervals represent ± one standard deviation based on duplicate reactors.)

Diazinon underwent rapid hydrolysis at acidic pH values (pH<6) and at basic pH values (pH>10). Such fast hydrolysis occurred at pH 13 that the detection limit was reached by the third sampling event (6 hours).

4.1.2.3 Comparisons. Etridiazole underwent base-catalyzed hydrolysis and metribuzin and diazinon underwent both acid- and base-catalyzed hydrolysis. Of the three pesticides included in this study, diazinon was the most susceptible to hydrolysis and was susceptible at the widest range of pH levels. Hydrolysis is not the only possible reaction, sorption and volatilization are other possible degradation mechanisms. However, these processes are not observed to be significant in the results obtained. If volatilization and sorption were dominant mechanisms, they would be observed for all the pH levels, not at select extreme pH levels.

These results are relatively consistent with the comprehensive screening study by Chamberlain et al. of pesticide degradation by various water treatment operations analyzed by GC. They studied hydrolysis at alkaline, neutral, and acid pH levels, specifically at pH levels 2, 7, and 12. For etridiazole, Chamberlain et al. (*35*) found moderate (20 – 50% removal) hydrolysis at pH levels 2 and 7, and high (> 50% removal) hydrolysis at pH 12. For metribuzin and diazinon, they found high degradability at pH levels of 2 and 12, and low (< 20% removal) at pH 7. For diazinon, Ku, et al. (*62*) found acid-catalyzed hydrolysis of diazinon at solution pH levels of 2 and 3, and He, et al. (*64*) found acid- and base-catalyzed hydrolysis at solution pH levels of 2, 4, and 5, and pH 10, respectively.

4.2. MODELS

4.2.1. Non-Linear Regression. Non-linear regression was applied to the results described by a second order model when degradation was observed to occur. Only base-catalyzed hydrolysis was observed for etridiazole, but for metribuzin and diazinon, both acid- and base-catalyzed hydrolysis were observed. Thus, two regressions were performed for the latter two pesticide systems. Averages of the measured pH values were used for pH levels for the second order non-linear regression model. The non-linear regression model is dependent on the pH, sampling time point, and regression rate

constant fit by minimizing the sum of the squares between the experimental and modeled values.

4.2.1.1 Etridiazole. The rate constants for acid and neutral hydrolysis were observed to be zero. Thus, the non-linear regression only took into account the basic (pH>7) hydrolysis data. Figure 4.8 plots the regressed data as concentration by initial concentration versus reaction time.

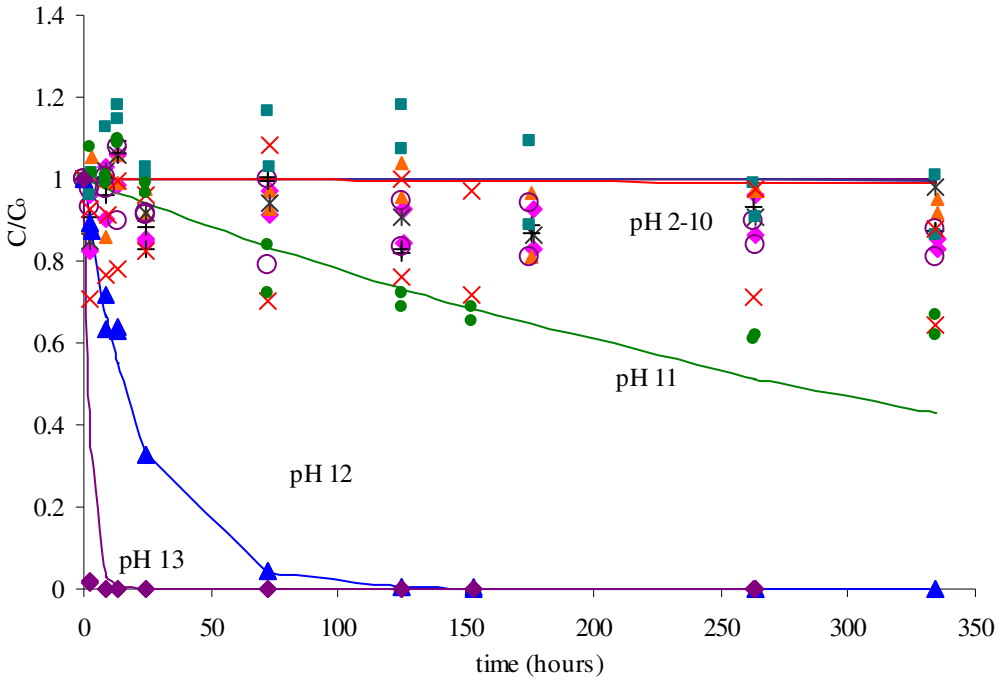


Figure 4.8 Non-linear regression model for base hydrolysis of etridiazole. Experimental and modeled data at pH levels 2 – 10 are aggregated demonstrating limited hydrolysis. Hydrolysis is observed a pH levels 11 – 13. (Colored shapes represent experimental data, colored lines represent corresponding models.)

This model appears to fit the data well and mathematically model the hydrolysis of etridiazole over all pH levels. Experimental and modeled data at pH levels 2 – 10 are lumped near the C/C_o value of one for all time points because no significant hydrolysis was observed. Minimal hydrolysis was observed at pH 10, and became more pronounced at pH levels 11 – 13. The overall second order basic rate constant was found to be 4.32

L mol^{-1} h^{-1} fit by minimizing the difference of the squares of the experimental and model hydrolysis rate constants.

4.2.1.2 Metribuzin. The rate constants for neutral hydrolysis were observed to be zero for metribuzin. Thus, acidic and basic non-linear regression models were constructed as shown in Figure 4.9.

For acid hydrolysis of metribuzin, the model appears to fit the data very well for hydrolysis at pH 2. Experimental and modeled data at pH levels 6 and 7 are lumped near the C/C_o value of one for all time points because no significant hydrolysis was observed in the neutral pH region. Minimal hydrolysis was observed at pH 4. More pronounced hydrolysis was observed at pH level 2. Noise in the experimental data at pH 2 is expected to be due to method error. The initial data shows large deviation between duplicate extractions. For the basic hydrolysis, the model fits moderately well, but predicts that hydrolysis will occur more slowly than experimental data suggests at the extreme basic pH levels (pH 12 and 13). Due to such rapid hydrolysis at the extreme pH levels, it was difficult to accurately measure the hydrolysis reaction kinetics. Experimental and modeled data at pH levels 7 – 10 are lumped near the C/C_o value of one for all time points because no significant hydrolysis was observed. Minimal hydrolysis was observed at pH 10. Hydrolysis became more pronounced at pH levels 11 – 13. The overall acid and base rate constants were found to be 0.72 L mol^{-1} h^{-1} and 3.50 L mol^{-1} h^{-1}, respectively, fit by minimizing the difference of the squares between the observed and model hydrolysis rate constants.

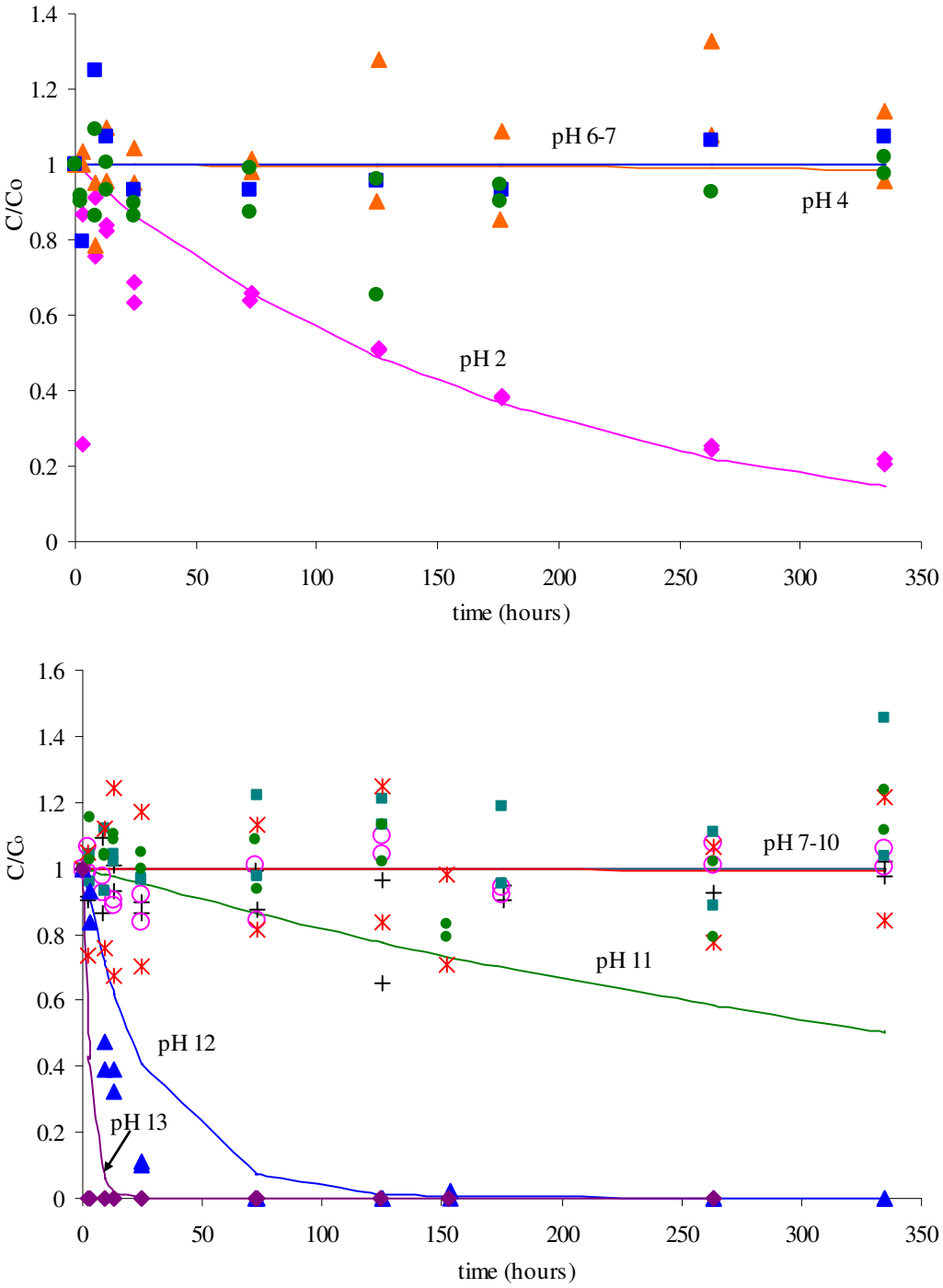


Figure 4.9 Non-linear regression model for acid (top) and base (bottom) hydrolysis of metribuzin. For both models, experimental and modeled data are aggregated in the neutral pH region. Hydrolysis is only observed at extreme acid and base pH levels (pH 2 and pH 11 – 13). (Colored shapes represent experimental data, colored lines represent corresponding models.)

4.2.1.3 Diazinon. The rate constants for neutral hydrolysis was observed to be zero for diazinon. Thus, acidic and basic non-linear regression models were determined, as shown in Figure 4.10.

Non-linear regression models fit the diazinon data fairly well for both acid and base hydrolysis data sets. For acid hydrolysis, experimental and modeled data at pH levels 6 and 7 are lumped near the C/C_o value of one for all time points because limited hydrolysis was observed in the neutral pH region though minimal hydrolysis was observed at pH 6. More pronounced hydrolysis was observed at pH levels 2 and 4. For base hydrolysis, experimental and modeled data at pH levels 7 – 10 are lumped near the C/C_o value of one for all time points because limited hydrolysis was observed, though minimal hydrolysis was observed at pH 10. Hydrolysis became more pronounced at pH levels 11 – 13. The overall acid and base hydrolysis rate constants were found to be 100.20 L mol^{-1} h^{-1} and 13.32 L mol^{-1} h^{-1}, respectively, fit by minimizing the difference of the squares between the observed and model hydrolysis rate constants.

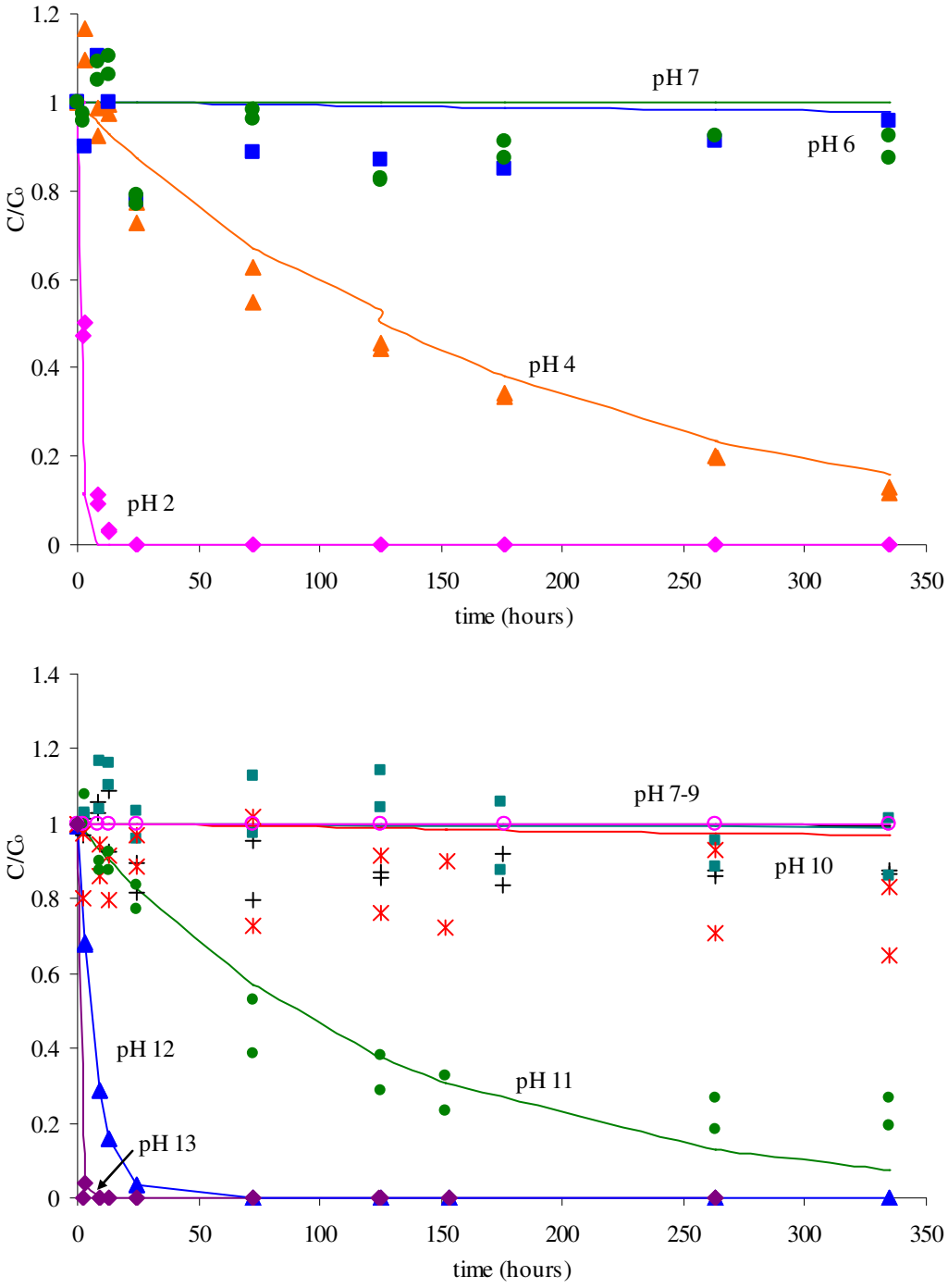


Figure 4.10 Non-linear regression model for acid (top) and base (bottom) hydrolysis of diazinon. For both models, experimental and modeled data are aggregated in the neutral pH region. Hydrolysis is only observed at extreme acid and base pH levels (pH 2 – 4 and pH 11 – 13). (Colored shapes represent experimental data, colored lines represent corresponding models.)

4.2.1.4 Non-linear regression summary. Table 4.1 summarizes the overall acidic, neutral, and basic rate constants as fitted parameters from the non-linear model of the second order representation.

Table 4.1 Overall rate constants from non-linear model.

	Second order model rate constants		
	k_{Acid} (L mol^{-1} h^{-1})	$k_{Neutral}$ (L mol^{-1} h^{-1})	k_{Base} (L mol^{-1} h^{-1})
Etridiazole	---	---	4.32
Metribuzin	0.72	---	3.50
Diazinon	100.20	---	13.32
	Pseudo-first order rate constants from second order model		
	k_{Acid} (pH 2) (h^{-1})	$k_{Neutral}$ (h^{-1})	k_{Base} (pH 13) (h^{-1})
Etridiazole	---	---	0.43
Metribuzin	7.18E-3	---	0.35
Diazinon	1.00	---	1.33

Comparing diazinon's pseudo-first order hydrolysis value at pH 2 to estimated published literature values, the k_{Acid} applied at pH 2 was found to be within an order of magnitude of published values. For diazinon, Ku et al. (*62*) found an acid-catalyzed hydrolysis rate constant value at pH 2 solution of 0.36 h^{-1} by linear regression and 0.33 h^{-1} by non-linear regression of pseudo-first order representation. He et al. (*64*) found an acid-catalyzed hydrolysis rate constant value at solution pH 2 of 0.28 h^{-1} by non-linear regression of pseudo-first order represented data.

4.2.2. Pseudo-first Order Kinetics. When linear behavior was observed (R^2>75) from applying first order kinetics by plotting the negative natural logarithm of C/C_o versus reaction time, a non-linear regression pseudo-first order model was applied. Pseudo-first order rate constants at all other pH values were determined to be zero.

4.2.2.1 Etridiazole. Figure 4.11 shows the pseudo-first order behavior of etridiazole resulting from degradation of the parent compound plotted as the average concentration versus reaction time and, subsequently, Figure 4.12 shows the pseudo-first order model applied as rate constants versus pH levels. As shown in Figure 4.11, the data only appear to follow a linear relationship until a certain reaction time point. This deviation from linearity was assumed to be because the pesticide concentrations

approached the detection limit near the end of the experiment. Near the detection limit, experimental and analytical errors can be exaggerated. The regression cut-off point was determined by either the instrument detection limit or when confidence in the data was lost, such as when duplicates deviated greatly, and especially when one duplicate was not detected at all. For pH 11, the concentrations leveled out by 150 h near an approximate concentration of 0.6 µg/L. Confidence was lost such that data gathered past 150 h was not included in the regression. For pH 12, data up to 120 h was included. Data from subsequent extractions was not included because etridiazole concentrations were not detected in one of the duplicate reactors. For pH 13, rapid hydrolysis was observed such that only two data points could be included. All subsequent data was observed to be below detection limit.

As shown in Figure 4.12, the pseudo-first order model appears to fit etridiazole experimental data fairly well, though deviating slightly at pH 12, where the model predicts faster hydrolysis than the experimental data record. No hydrolysis was observed (and thus modeled) at acid and neutral conditions. The overall non-linearly regressed base rate constant for etridiazole was determined to be 12.87 L mol^{-1} h^{-1}, fit by minimizing the difference of the squares of the experimental and model rate constants.

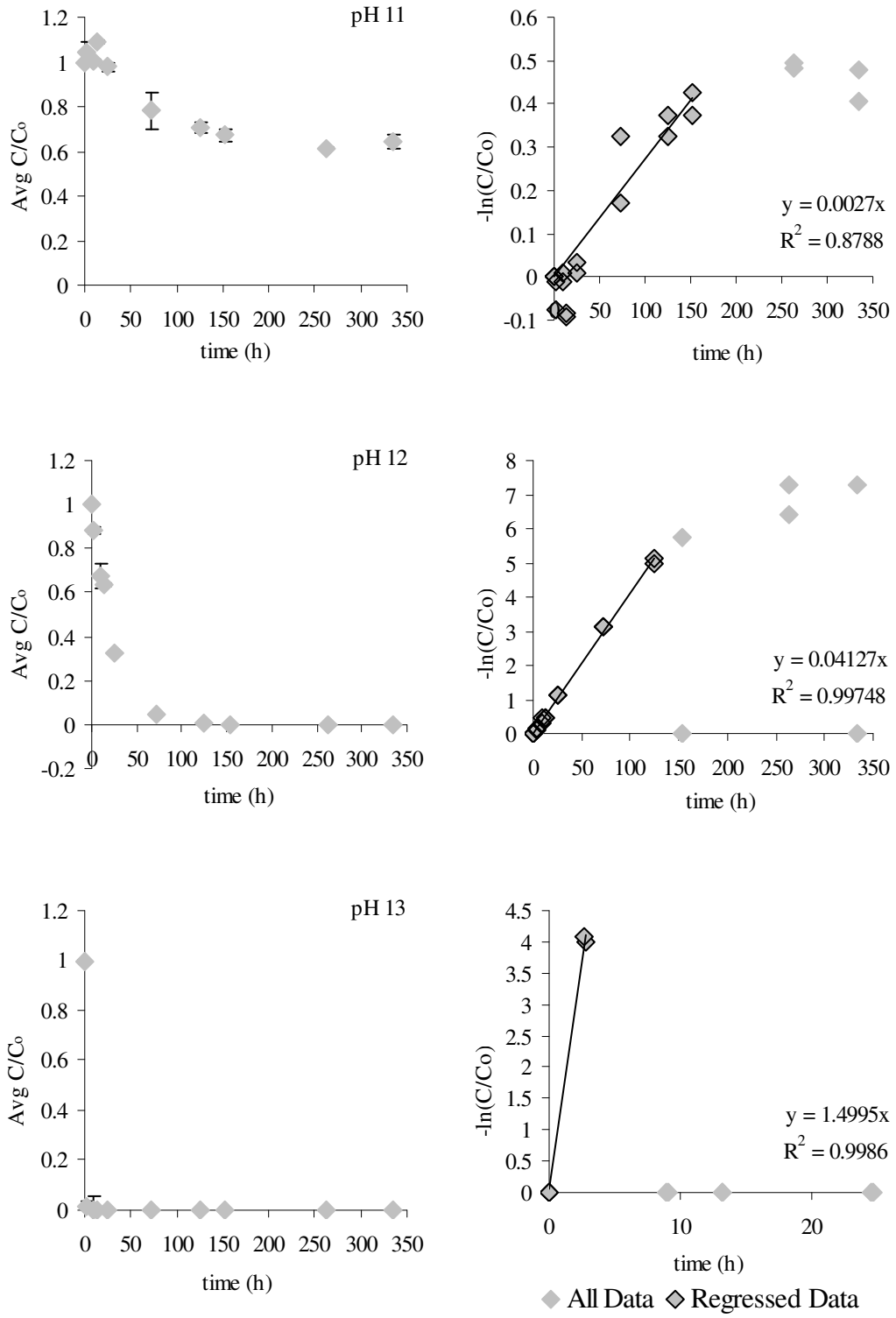


Figure 4.11 Linearly regressed first order behavior of etridiazole at pH 11 (top), 12 (middle), and 13 (bottom). (Solid shapes represent all data; unfilled shapes represent data included in regression.)

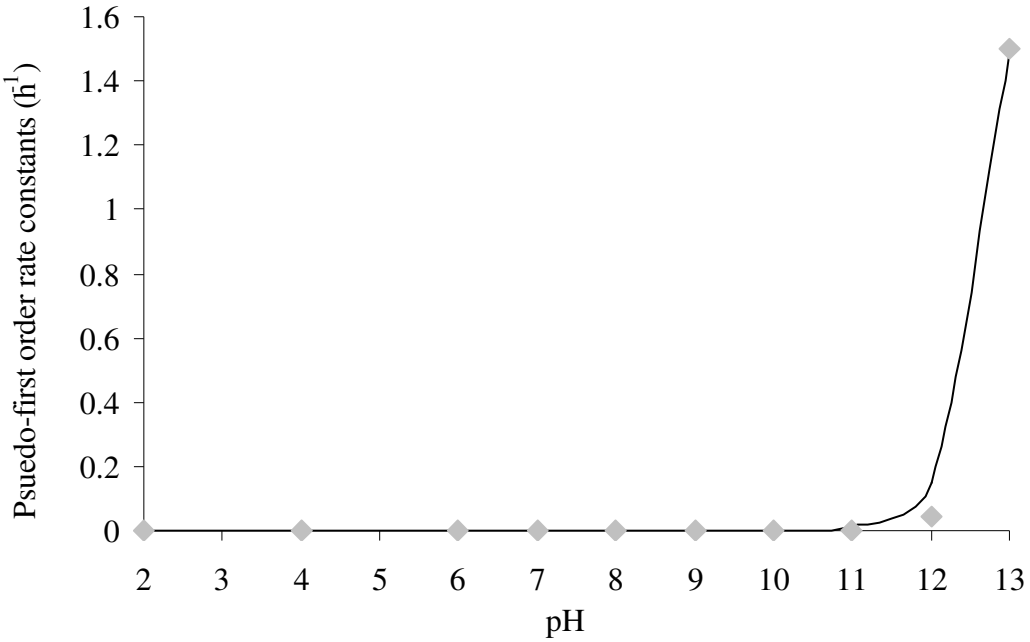


Figure 4.12 Non-linearly regressed pseudo-first order hydrolysis model for etridiazole. (Solid shapes represent experimental data; line represents model.)

4.2.2.2 Metribuzin. Figure 4.13 shows the pseudo-first order behavior of metribuzin resulting from degradation of the parent compound, and subsequently, Figure 4.14 shows the pseudo-first order model applied by plotting rate constants versus pH and minimizing the difference of the squares of the experimental and modeled k-values. As seen in Figure 4.13 at pH levels 12 and 13, the data only appear to follow a linear relationship until a certain reaction time point. This deviation from linearity was because the pesticide concentrations reached the detection limit near the end of the experiment. Near the detection limit, experimental and analytical errors can be exaggerated. The regression cut-off point was determined by either the instrument detection limit or when confidence in the data was lost, such as when duplicates deviated greatly, and especially when one duplicate was not detected at all. For pH 12, the cut-off was set at 10% of initial C/C_o because concentrations below 0.1 µg/L were not detected. For pH 13, rapid hydrolysis was observed such that the rate could not be accurately measured. Using the data points that were gathered, linear regression was performed in order to have a starting place for the non-linear model.

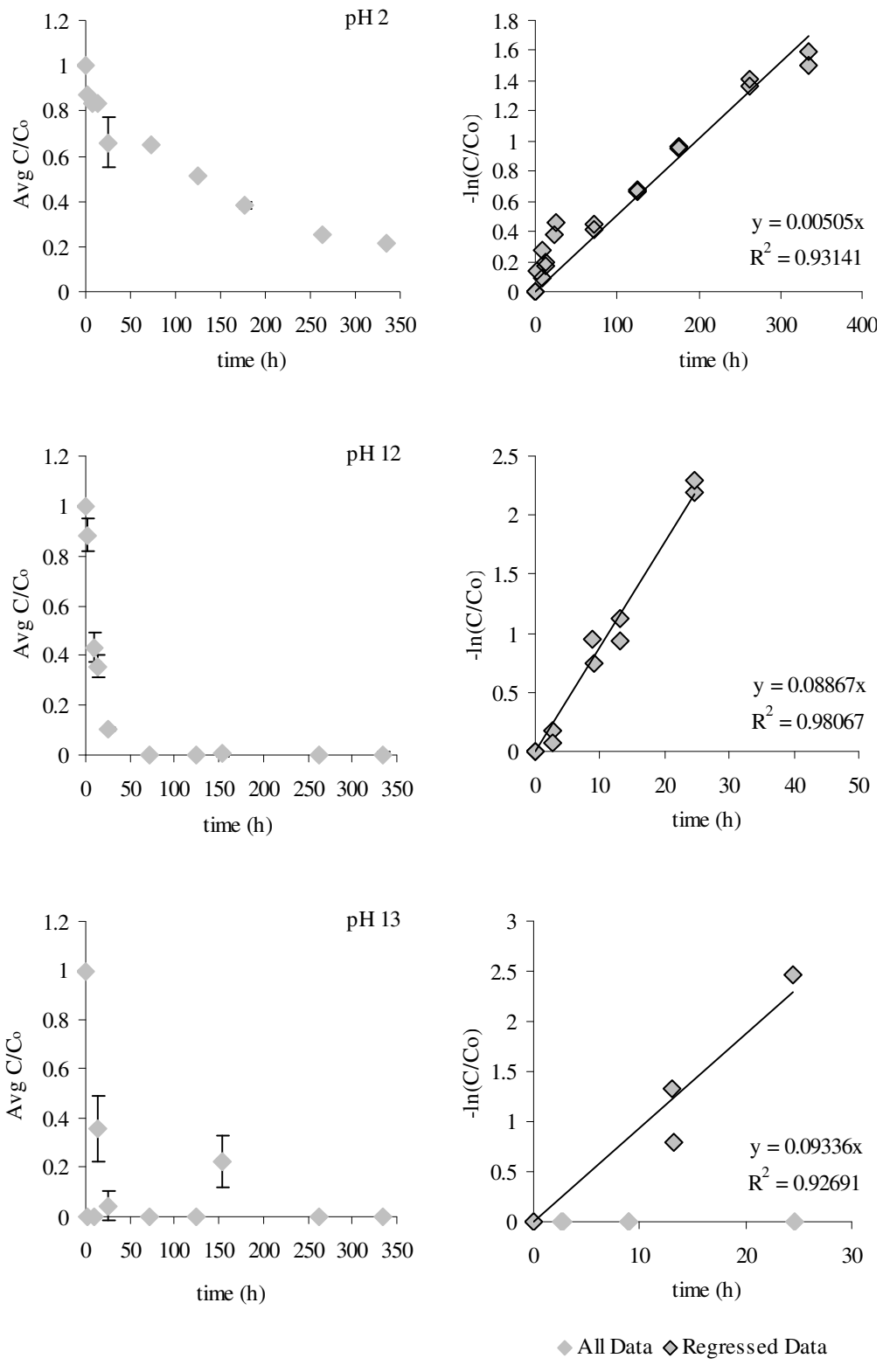


Figure 4.13 Linearly regressed first order behavior of metribuzin at pH levels 2 (top), 12 (middle), and 13 (bottom). (Solid shapes represent all data; unfilled shapes represent data included in regression.)

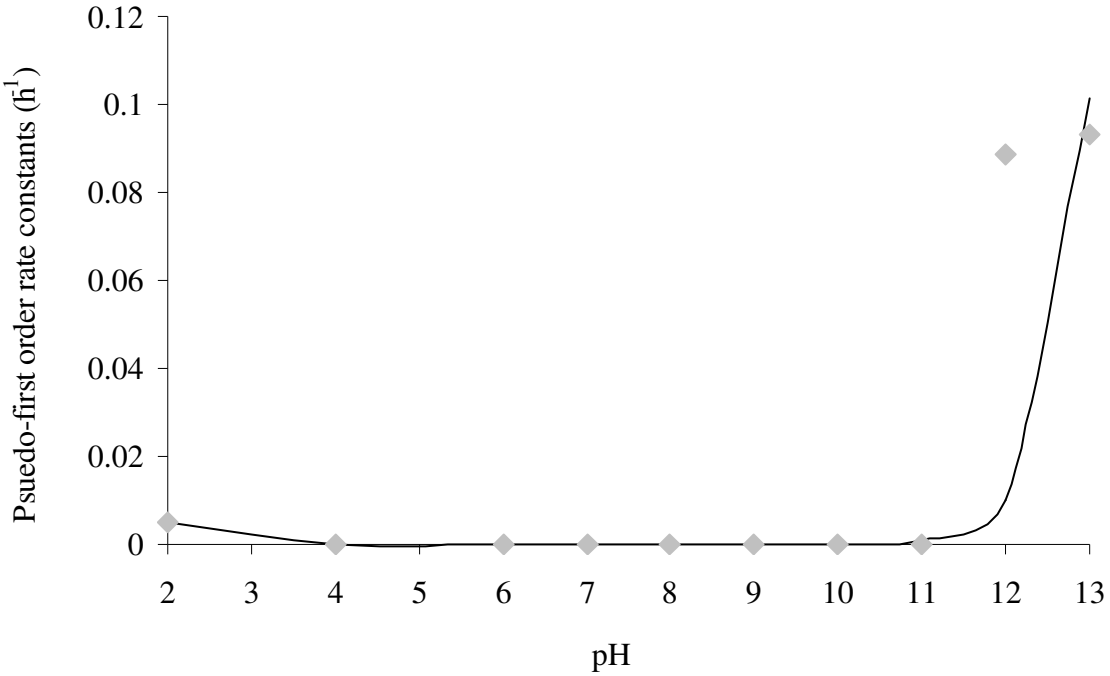


Figure 4.14 Non-linearly regressed pseudo-first order hydrolysis model for metribuzin. (Solid shapes represent experimental data, line represents model.)

The pseudo-first order model does not appear to fit metribuzin experimental data at the basic pH levels, although the acidic portion does map well. It should be noted that this discrepancy at pH 12 was also observed with non-linear regression of the second order representation of the data. It is proposed that the rate of hydrolysis at pH 13 cannot actually be determined in this study because of rapid degradation of metribuzin in solution at pH 13. In fact, such rapid hydrolysis was observed that the average initial concentration was measured as 0.88 µg/L. It is suggested that if the rate of hydrolysis of metribuzin at pH 13 could be measured, it would be much faster than is shown in Figure 4.11, and the model would go through the data point at pH 12. On average, the process of spiking, mixing, and extracting initial samples from the reactors took 5 minutes. Since the initial concentrations of metribuzin in the basic pH levels were near the detection limit, accuracy of the experimental data is not expected. The overall non-linearly regressed acid and base rate constants for etridiazole were determined to be 0.506 L mol^{-1} h^{-1} and 1.103 L mol^{-1} h^{-1}, respectively, fit by minimizing the difference of the

squares of the experimental and model rate constants. No neutral hydrolysis was observed.

4.2.2.3 Diazinon. Figures 4.15 and 4.16 show the pseudo-first order behavior of diazinon resulting from degradation of the parent compound in the average concentration versus reaction time plot and, subsequently, Figure 4.17 shows the pseudo-first order model applied as rate constants versus pH. As shown in Figure 4.16, the data only appear to follow a linear relationship up to a certain reaction time point. This deviation from linearity is assumed to be because the pesticide concentrations approach the detection limit at the end of the experiment. Near the MDL, the experimental and analytical errors are exaggerated. For pH 2, linearity is observed above 3% of initial C/C_o, at which point the cut-off point is set. For pH 11, the concentrations leveled out at 20% of C/C_o, and so confidence is lost and data past 168 h excluded. For pH 12, data up through 24 h is included. Confidence was lost and excluded in subsequent extractions because etridiazole concentrations were not detected in one of the duplicate reactors. For pH 13, rapid hydrolysis was observed such that only two data points were included. The pesticide concentrations reached the detection limit by the third sampling event (6 hours), and thus were not detectable.

The pseudo-first order model also appears to fit the diazinon experimental data. The non-linearly regressed acid and base rate constants for diazinon were determined to be 30.964 L mol^{-1} h^{-1} and 15.926 L mol^{-1} h^{-1}, respectively, fit by minimizing the difference of the squares of the experimental and model rate constants.

The pseudo-first order rate constants from the negative natural logarithm of C/C_o versus reaction time appear to be consistent with the estimated published studies that use a two species pseudo-first order model at acidic pH levels. He et al. (*64*) reports a hydrolysis rate constant value of 0.28 h^{-1} at pH 2 by non-linear regression of pseudo-first order represented data, and no observed hydrolysis at pH 4. Ku et al. (*62*) predicts pseudo-first order hydrolysis rate constants equal to 0.33 h^{-1} at pH 2, and 0.12 h^{-1} at pH 3, and no hydrolysis observed at pH levels 4 and greater based on a non-linear regression of pseudo-first order represented data, and 0.36 h^{-1} at pH 2, and 0.15 h^{-1} at pH 3 for linear regression of data. Gomaa et al. (*59*) reports a rate constant of 0.0589 h^{-1} at pH 3.1 based

on linear regression of first order data. These values compare favorably to values obtained during this study of 0.31 h^{-1} at pH 2, and 0.03 h^{-1} at pH 3.

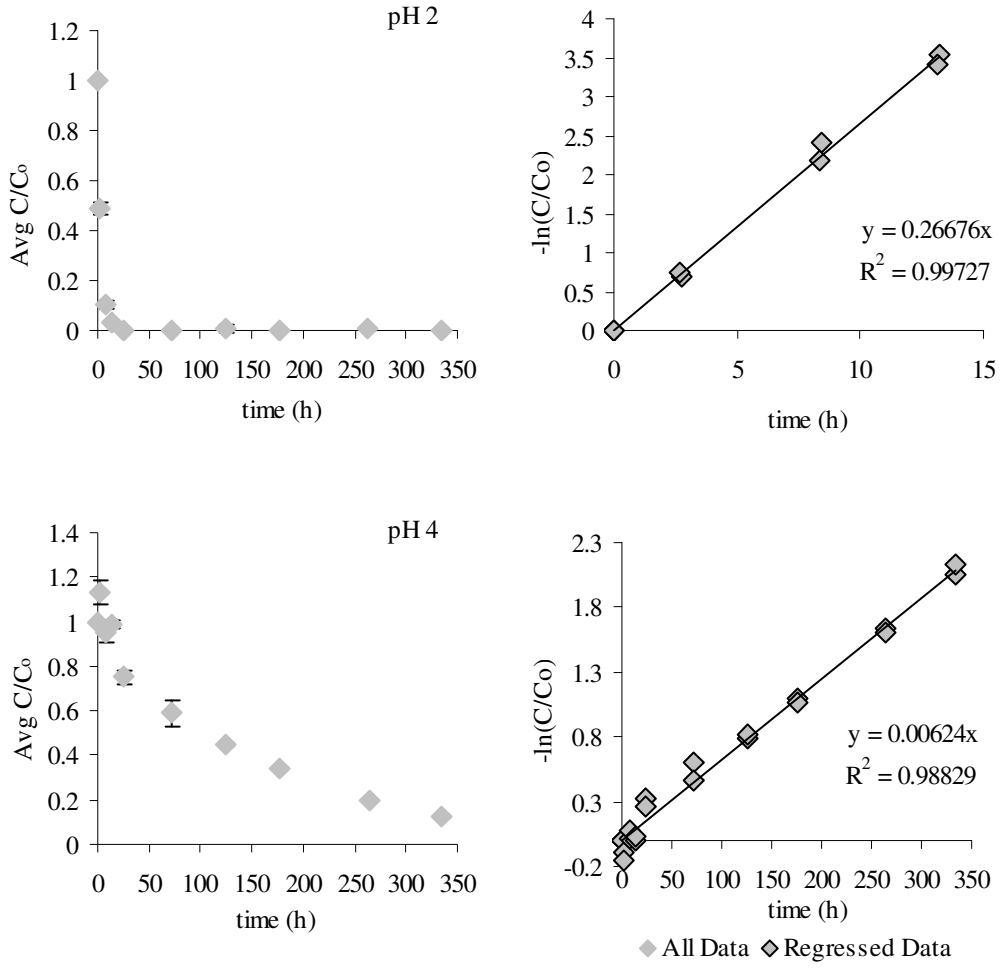


Figure 4.15 Linearly regressed first order behavior of diazinon at pH 2 (top), pH 4 (bottom). (Solid shapes represent all data; unfilled shapes represent data included in regression.)

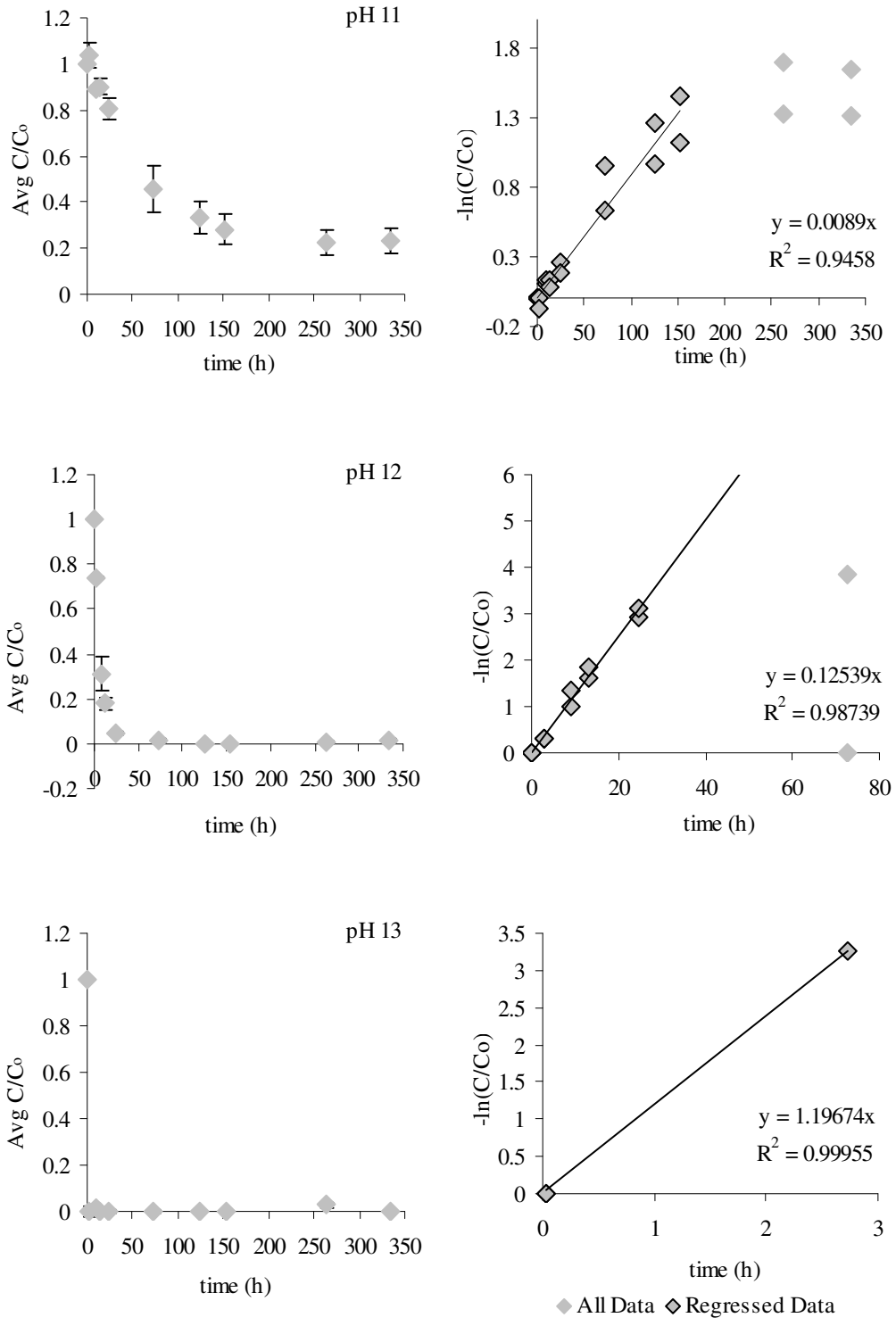


Figure 4.16 Linearly regressed first order behavior of diazinon at pH 11 (top), 12 (middle), 13 (bottom). (Solid shapes represent all data; unfilled shapes represent data included in regression.)

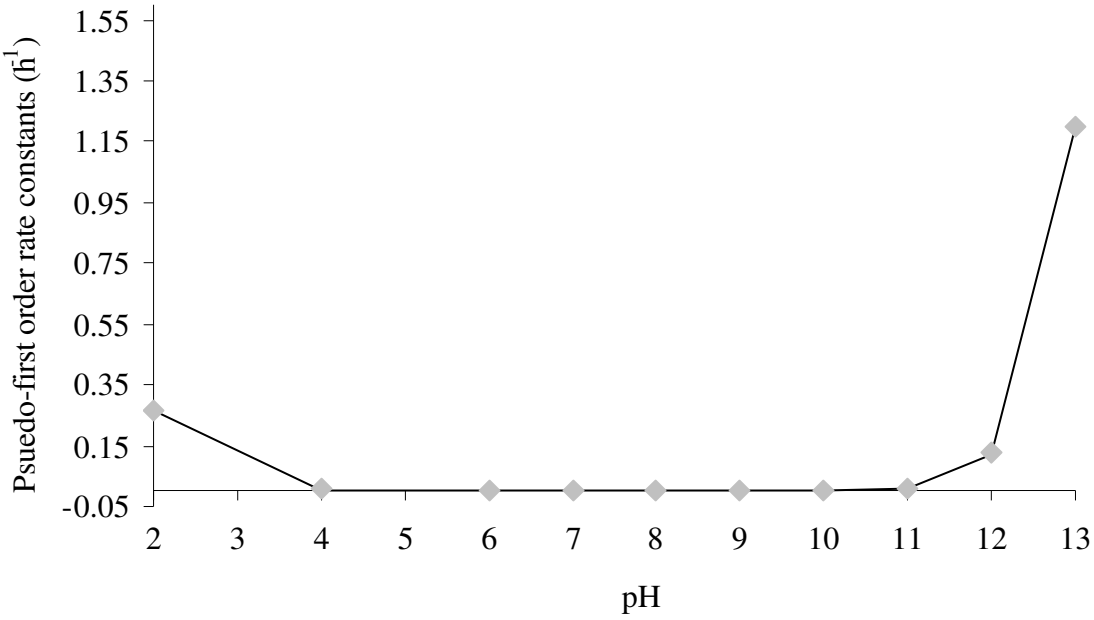


Figure 4.17 Non-linearly regressed pseudo-first order hydrolysis model for diazinon. (Solid shapes represent experimental data; line represents model.)

4.2.2.4 Pseudo-first order summary. Table 4.2 is a summary of the overall acidic, neutral, and basic rate constants as fitted parameters from the non-linear regression of the pseudo-first order model data, and Table 4.3 is a summary of the linearly regressed pseudo-first order rate constants.

Table 4.2 Non-linearly regressed overall rate constants from a pseudo-first order model.

	k_{Acid} (L mol^{-1} h^{-1})	k_{Base} (L mol^{-1} h^{-1})
Etridiazole	---	12.87
Metribuzin	0.51	2.7
Diazinon	30.96	15.93

Table 4.3 Pseudo-first order rate constants.

	pH	LR: k' (h^{-1})	NLR: k' (h^{-1})
Etridiazole	11	2.70E-3	1.29E-2
	12	4.04E-2	1.29E-1
	13	1.50	1.29
Metribuzin	2	5.05E-3	5.06E-3
	12	8.89E-2	1.10E-2
	13	9.34E-2	1.10E-1
Diazinon	2	2.67E-1	0.31
	4	6.24E-3	3.10E-3
	11	8.90E-3	1.59E-2
	12	1.25 E-1	1.59E-1
	13	1.20	1.59

4.2.3. Model Comparisons. Values from the linearly regressed first order, non-linearly regressed pseudo-first order, and non-linearly regressed second order models from this study can be compared, and compared with estimated published data when available. These comparisons are shown in Table 4.4 for etridiazole and metribuzin, and Table 4.5 for diazinon.

Table 4.4 Model derived rate constants for etridiazole and metribuzin.

pH	Etridiazole			Metribuzin		
	LR: psuedo-1st order model at each pH 22°C (h^{-1})	NLR: psuedo-1st order model over all pH 22°C (h^{-1})	NLR: 2nd order model over all pH 22°C (h^{-1})	LR: psuedo-1st order model at each pH 22°C (h^{-1})	NLR: psuedo-1st order model over all pH 22°C (h^{-1})	NLR: 2nd order model over all pH 22°C (h^{-1})
acid			---		0.51 ($L\ mol^{-1}h^{-1}$)	0.72 ($L\ mol^{-1}h^{-1}$)
2	---	1.29E-11	---	5.06E-03	5.06E-03	7.18E-03
3	---	1.29E-10	---	---	5.06E-04	7.18E-04
4	---	1.29E-09	---	---	5.06E-05	7.18E-05
5	---	1.29E-08	---	---	5.06E-06	
6	---	1.29E-07	---	---	5.17E-07	
7	---	1.29E-06	---	---	1.61E-07	
8	---	1.29E-05	---	---	1.11E-06	
9	---	1.29E-04	---	---	1.10E-05	
10	---	1.29E-03	4.32E-04	---	1.10E-04	3.50E-04
11	2.0E-03	1.29E-02	4.32E-03	---	1.10E-03	3.50E-03
12	3.13E-02	0.13	4.32E-02	8.89E-02	1.10E-02	3.50E-02
13	1.30	1.29	0.43	0.10	0.11	0.35
base		12.87 ($L\ mol^{-1}h^{-1}$)	4.32 ($L\ mol^{-1}h^{-1}$)		1.10 ($L\ mol^{-1}h^{-1}$)	3.50 ($L\ mol^{-1}h^{-1}$)
Independent variable	time	pH	pH	time	pH	pH
Dependent variable	$-\ln(C/C_o)$	k' (h^{-1})	C/C_o	$-\ln(C/C_o)$	k' (h^{-1})	C/C_o
Regression	Linear	Non-linear	Non-linear	Linear	Non-linear	Non-linear

Overall, the values between both the etridiazole and metribuzin models compare favorably and within one magnitude of each other. In general, the second order models predict slower hydrolysis rates. Lack of published rate constants makes it hard to benchmark these values, however the fact that multiple models appear to agree provides some credibility to this data and the modeling approaches used.

Table 4.5 Various model-derived hydrolysis rate constants for diazinon.

pH	Ku, et al. (*62*)		Gomaa, et al. (*59*)	He, et al. (*64*)		this work		
	LR: psuedo-1st order model at each pH	NLR: psuedo-1st order model over all pH	LR: psuedo-1st order model at each pH	LR: psuedo-1st order model at each pH	NLR: psuedo-1st order model over all pH	LR: psuedo-1st order model at each pH	NLR: psuedo-1st order model over all pH	NLR: 2nd order model over all pH
	25℃ (h^{-1})	25°C (h^{-1})	20°C (h^{-1})	25°C (h^{-1})	25°C (h^{-1})	22°C (h^{-1})	22°C (h^{-1})	22°C (h^{-1})
acid							30.96 (L $mol^{-1}h^{-1}$)	100.20 (L $mol^{-1}h^{-1}$)
2	0.36	0.33			0.28	0.31	0.31	1.00
3	0.15	0.12	0.06		0.10	6.51E-03	0.03	0.10
4		---		1.35E-02	1.25E-02	---	3.10E-03	1.00E-02
5		---	9.36E-04	2.0E-03	---	---	3.10E-04	
6	---	---		5.0E-04	---	---	3.11E-05	
7		---	1.56E-04	5.0E-04		---	4.69E-06	
8		---		5.0E-04		---	1.62E-05	
9	---	---	2.12E-04	6.0E-04		---	1.59E-04	
10		---	4.78E-04	2.0E-03		---	1.59E-03	1.33E-03
11						9.20E-03	1.59E-02	1.33E-02
12						0.14	0.16	0.13
13						1.59	1.59	1.33
base							15.93 (L $mol^{-1}h^{-1}$)	13.32 (L $mol^{-1}h^{-1}$)
Independent variable	time	pH	time	time	pH	time	pH	pH
Dependent variable	-ln(C/C_o)	k' (h^{-1})	-ln(C/C_o)	-ln(C/C_o)	C/C_o	-ln(C/C_o)	k' (h^{-1})	C/C_o
Regression	Linear	Non-linear	Linear	Linear	Non-linear	Linear	Non-linear	Non-linear

Comparing all the various models from this study, it appears that the models are within an order of magnitude of each other at acidic pH levels, however deviation is observed at basic pH levels. This discrepancy at alkaline hydrolysis can be attributed to the large rate constant values at high rates of hydrolysis such that any small error in pH measurements results in large changes in the associated rate constants. Essentially, pH meters and probes have error associated with them, and even two probes with the same calibration curve can give differing pH measurements of the same sample. Additionally, the averages of the measured experimental pH values were utilized in calculating the model k-values. It is anticipated that this deviation is observed when such rapid hydrolysis is observed at these extreme pH levels. It must also be noted that a first order model is entirely dependent on the initial concentrations chosen because the model holds in excess and, thus, negates, the concentration of protons or hydroxide ions in solution. A second order model accounts for all of these parameters

The values at specific pH levels from the studies on diazinon from this work can be compared to values found in literature. Overall, the rate constants were found to be reasonable and within one order of magnitude of published studies. The pH range of literature comparison is from pH 2 – 10. At pH 10, some discrepancy is observed if comparing the non-linearly regressed second order data to the literature values. As a whole, the published literature supports the data presented in this study.

5. CONCLUSIONS

5.1. CONCLUSIONS

Of the three pesticides included in this study, diazinon was most susceptible to hydrolysis and was susceptible at the widest range of pH levels. All of the pesticides studied underwent hydrolysis. Etridiazole experienced only base-catalyzed hydrolysis, while metribuzin and diazinon experienced both acid- and base-catalyzed hydrolysis, though only at extreme pH values (e.g., pH 2 for acid-catalyzed and pH 11 – 13 for base-catalyzed hydrolysis). No neutral hydrolysis was observed. The data and models suggest that degradation of these three pesticides in drinking water facilities is not a concern since the lime softening process generally raises inlet water to a maximum pH level of 10 (calcium removal) or 11 (magnesium removal). Only diazinon exhibits a moderate hydrolysis rate ($k = 0.11\ h^{-1}$) at pH 11 and therefore, merits further study. It should also be noted, however, that the time frame of 2 weeks is not representative of a drinking water lime softening contact time. The rate constant values from the various models constructed in this study to literature hydrolysis rate constant values generally agree to within one order of magnitude. This adds confidence to the data obtained in this study and the modeling approaches utilized.

5.2. FUTURE RECOMMENDATIONS

The comprehensive screening study by Chamberlain et al. listed 20 pesticides as highly reactive. A broader suite of pesticides could be studied to compare hydrolysis rate constants and kinetic models. General conclusions suggesting hydrolysis as a concern or not in drinking water plants based on classes of pesticides could be drawn with a broader scope. In general, the literature lacks data on base-catalyzed hydrolysis for many pesticides in use. Since lime softening is a common water softening practice, basic hydrolysis can be a very important mechanism for degradation of pesticides and other source water contaminants. Depending on the parent compound, degradation of pesticides in drinking water plants could be helpful or harmful to human health.

Compounds that are present in drinking water source waters should be examined with respect to their degradability as a function of water pH and time.

Additionally, this study only looked at batch hydrolysis in laboratory waters. Validation of models in surface and ground water is also warranted.

APPENDIX A.
HYDROLYSIS EXPERIMENTAL METHODS

STANDARD OPERATING PROCEDURE (SOP) FOR HYDROLYSIS EXPERIMENTS

Preparation:

1. Wash all bottles, beakers, and other glassware used with soap and water.
2. Rinse three times with distilled water and a final rinse with MQ; let dry.
3. Label containers and autosampler vials for experiment.
4. Dry salt at approximately 110 C in oven for at least overnight, then store in a tightly sealed bottle.

Chemicals/Solutions:

1. 5mM and 10mM sodium phosphate buffered MQ water (pH 2, 3, 4, 6, 7, 8, 9, 10, 11, 12, 13), (See MM07-04)
2. NaOH (low, med, high conc.)/Phosphoric acid (low, med, high conc.) for pH adjustment
3. Diazinon (CAS: 333-41-5, Formula: $C_{12}H_{21}N_2O_3PS$, MW: 304.35)
    a. 99.0% pure 250 mg oil
    b. Cat # 45428, Lot # 4110X
4. Etridiazole (CAS: 2593-15-9, Formula: $C_5H_5C_{l3}N_2OS$, MW: 247.53)
    a. 95+% pure 100 mg powder
    b. US-PST-1770
5. Metribuzin (CAS: 21087-64-9, Formula: $C_8H_{14}N_4O$ S, MW: 214.29)
    a. 99.3% pure 100 mg powder
    b. Cat# 36165, Lot# 3139X
6. 2,4,5,6-tetrachloroxylene (TCX) 2000 mg/L stock (IS)
7. Chlorpyrifos (CPY) 5mg/L (See MM08-14) (SUR)
8. Sodium Sulfate, Anhydrous 10-60 Mesh for LLE salting out (CAS: 7757-82-6, Formula: $NaSO_4$)

Procedure:

Section 1: Prepare and Validate Stock Solutions

1. Create 2000 mg/L Diazinon stock solution in 8mL MeOH.
    a. Weigh out 16 mg of Diazinon into 10 mL amber glass vial.
    b. Actually weighed: see Table.
    c. Actual volume of MeOH to add: see Table 1.
    d. Mix well by hand shaking. If necessary, sonicate for 15 min. or until powder dissolved.

Table A1: Weights of compounds

	Compound	Weighed (g)	V_{MeOH} (mL)	Conc. (mg/L)
1	Diazinon	0.01489	7.5	1912.5
2	Etridiazole	0.01447	2.894	5000
3	Metribuzin	0.01530	8.0	1985.3

2. Repeat steps a-d of step 1 for Etridiazole and Metribuzin.
3. Validate each stock solution by injection on the GC-ECD using the MM-MIX08 and MM-MIX08 methods after dilution.
    a. Dilute each 2000 mg/L pesticide stock solutions to 10 mg/L substock solutions in hexane.
        i. Add 1 mL hexane to each 2 mL screw-top amber glass vials.
        ii. Add 5 µL of 2000 mg/L pesticide stock solutions.
        iii. Cap and mix well, taking care not to over tighten cap, as it will break glass threads of vial.
    b. Dilute each 10 mg/L pesticide substock solutions to 0.1 mg/L in hexane for injection on the GC-ECD.
        i. Add 1 mL hexane to 6 of 2 mL GC amber glass vials.
        ii. Add 10 µL of the 3, 10 mg/L pesticide substock solutions each to 2 vials.
        iii. Add 10 µL of 2 mg/L substock internal standard solution (TCX) into all 6 vials.
        iv. Cap and mix well.

v. Inject on GC-ECD.

Section 2: Create and Validate Reaction Media

1. Create reaction media at 800 mg/L reaction media in hexane.
    a. Put appropriate volume from Table of pesticide stock solutions into a screw-top 2 mL amber glass vial.
    b. Mix well by hand shaking.

Table A2: Solution calculations

	C1	V1	C1	V1	Vsolv
	mg/L	mL	mg/L	mL	mL
DIZ	1985.3	0.604	800	1.5	0.028
ETZ	5000	0.240	800	1.5	=28 uL
MET	1912.5	0.627	800	1.5	

2. Create reaction media substock at 10 mg/L in MeOH.
    a. Put in 1 mL hexane in a screw-top 2 mL amber glass vial.
    b. Add in 13 uL of 800 mg/L reaction media stock solution.
3. Validate mix directly by injection on the GC-ECD using MM-Mix08 method after dilution.
    a. Dilute each 10 mg/L pesticide substock solutions to 0.1 mg/L in hexane for injection on the GC-ECD.
        i. Add 1 mL hexane to 2 mL amber glass autosampler vial.
        ii. Add 10 µL of the 10 mg/L reaction media substock solution.
        iii. Add 10 µL of 2 mg/L substock internal standard solution (TCX).
        iv. Cap and mix well.
        v. Inject on GC-ECD.

Table A3: Dilution calculations

Dilute Mix08 to Substock					
	C1	V1	C1	V1	Vsolv
	mg/L	mL	mg/L	mL	mL
MIX08	800	0.013	10	1	0.988

Dilute Mix08 substock to inject on GC-ECD					
	C1	V1	C1	V1	Vsolv
	mg/L	mL	mg/L	mL	mL
MIX08	10	0.010	0.1	1	0.990

4. Validate mix by injection after LLE extraction on the GC-ECD using MM-MIX08 method.
    a. Take 35 mL unbuffered and pH 2, 7 and 13 5mM sodium phosphate buffered MQ water into 40-mL extraction vials using 50-mL glass serological pipettes.
    b. Spike in 50µL of 5 mg/L substock surrogate solution (CPY) into each.
    c. Salt out: add approximately 6 g Na_2SO_4 solid into each vial.
        i. Weight out 6 g into a test tube, mark level and measure in Na_2SO_4 into each tube to this mark.
        ii. Shake until all salt dissolved.
    d. Add 2 mL Hexane to each vial using a pre-wetted pipette tip.
        iii. Shake vigorously for 1 min.
        iv. Let vials sit for 1 - 5 min to separate.
    e. Pipette off 1 mL of Hexane into an autosampler vial.
    f. Spike in 10 µL of 2 mg/L substock internal standard solution (TCX) into vial, cap and mix well.
    g. Inject on GC-ECD.
    h. Allow remaining hexane to evaporate off in fume hood, and discard remaining water sample.

Section 3: Perform Hydrolysis

1. Add 400 mL of each buffered pH water (pH=2, 4, 6, 7, 8, 9, 10, 11, 12, 13) into 500-mL labeled amber glass bottle reactors, two sets for spiking with pesticide reaction media, and 3 bottles (pH=2, 7, 13) as blank controls (total of 23 reactor bottles).
2. Create 5 µg/L reaction media (pesticide concentrations) in hydrolysis reactor bottles.
    a. Spike in 20 µL of 100 mg/L reaction media substock (use syringe).
    b. Cap and mix well by hand shaking.
3. Take initial samples (t»0) of 35 mL into 40-mL vials using a 50-mL glass pipette for each reactor, and perform LLE as described below in Section 4.
4. Clean each glass pipette (one pipette for each pH) by first rinsing with distilled water, second with acetone, and final rinse with distilled water.
5. Cap reactors very tightly and place in tumblers in temperature control room (CE 311) at 22ºC and begin tumbling.

Section 4: Perform LLE (hexane)

1. Check pH of reaction media using two pH probes and meters, calibrated with at least a 98% calibration curve using buffer standards pH 4 and 10 and checked in buffer standard pH 7.
2. Take 35 mL samples into a 40-mL extraction vials using a 50-mL glass pipette (same as above), 2 bottles (each set of duplicates) at a time.
3. Spike in 50µL of 5 mg/L substock surrogate solution (CPY) into each.
    a. Add approximately 6 g Na_2SO_4 solid into each vial.
    b. Weight out 6 g into a test tube, mark level and measure in $N_{a2}S_{O4}$ into each tube to this mark ahead of time and capped.
    c. Shake until all salt dissolved.
4. Add 2 mL Hexane to each vial using a pre-wetted pipette tip.
    a. Shake vigorously for 1 min.
    b. Let vials sit for 1 - 5 min to separate.
5. Pipette off 1 mL of Hexane into a pre-labeled autosampler vial.
6. Spike in 10 µL of 2 mg/L substock internal standard solution (TCX) into vial, cap and mix well.
7. Inject samples on GC-ECD and analyze.
8. Allow remaining hexane to evaporate off in fume hood, and discard remaining water sample.
9. At t = 2 h, 6 h, 12 h, 1 d, 3 d, 5 d, 7 d, 11 d, 14 d, take samples and extract as described in steps 1-8.

EXTRACTION EFFICIENCIES

Table A4: Extraction efficiencies

Compound	% Extracted
Etridiazole	84
Diazinon	109
Metribuzin	70
Chlorpyrifos	73

METHOD DETECTION LEVELS

Table A5: Method diction levels

Compound	MDL µg/L
Etridiazole	0.04
Diazinon	0.04
Metribuzin	0.09

STANDARD CURVES

DIAZINON

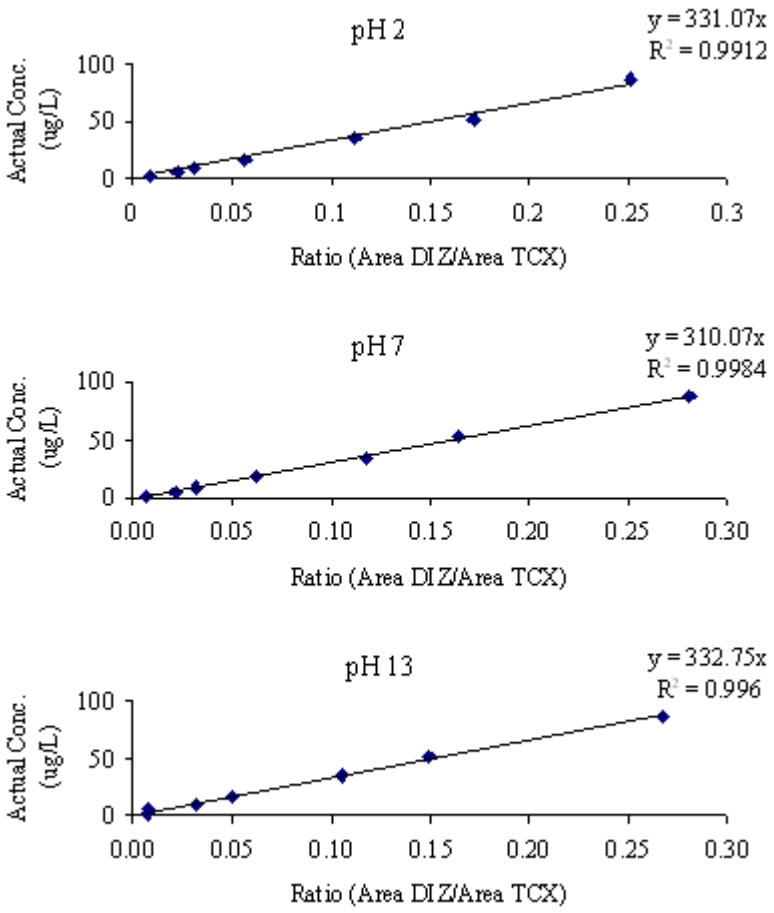


Figure A1: Diazinon standard curves

ETRIDIAZOLE

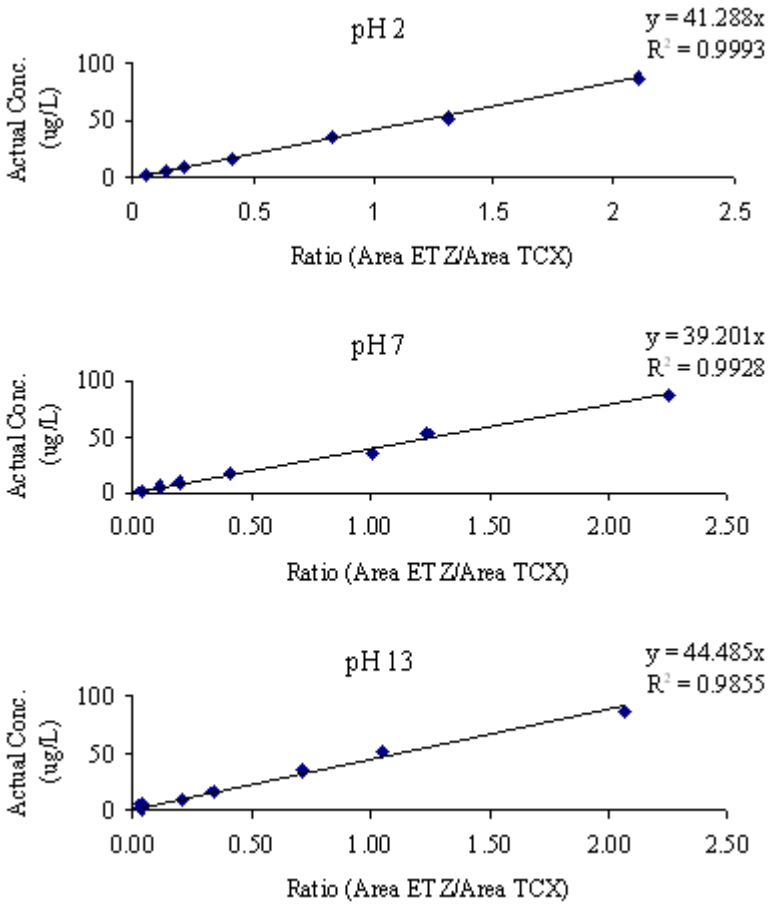


Figure A2: Etridiazole standard curves

METRIBUZIN

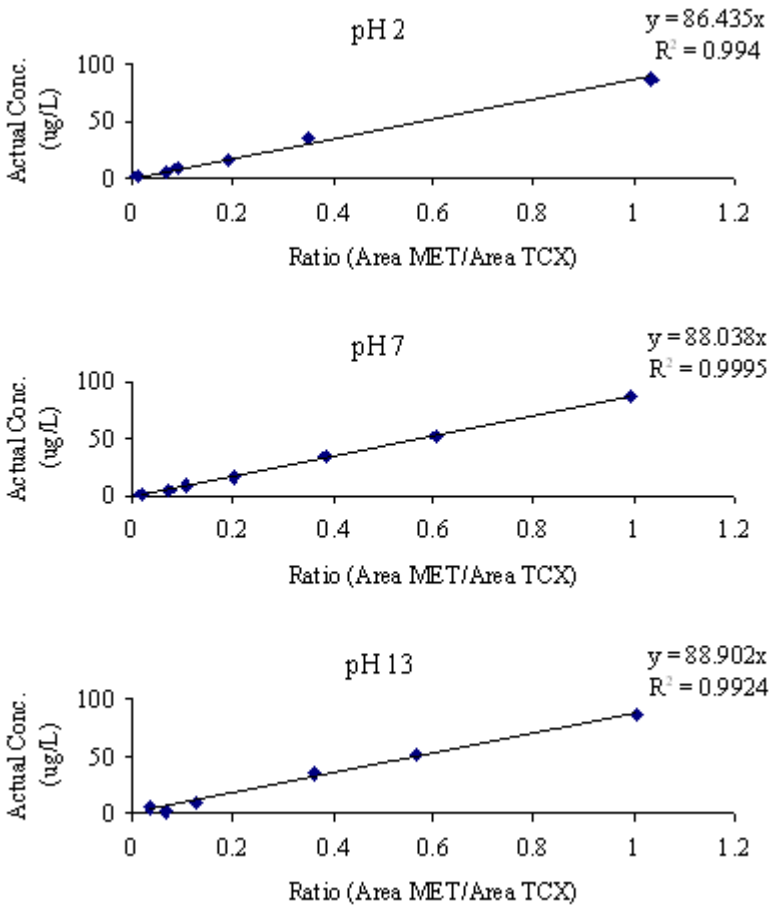


Figure A3: Metribuzin standard curves

STANDARD CURVES COMPARISONS

Table A6: Standard curves comparisons

Compound	pH	Ratio	C (µg/L)	Avg. C (µg/L)	s	%RSD
DIZ	2	0.1	33.11	32.46	1.26	3.89
	7	0.1	31.01			
	13	0.1	33.28			
ETZ	2	0.8	33.03	33.33	2.13	6.39
	7	0.8	31.36			
	13	0.8	35.59			
MET	2	0.35	30.25	30.73	0.44	1.43
	7	0.35	30.81			
	13	0.35	31.12			

EXPERIMENTAL STANDARDS

Table A7: Diazinon experimental standards

DIAZINON STANDARDS					
#	Day	Peak Area Std	Peak Area TCX	C (µg/L)	Avg. C (µg/L)
1	0	2.20E+03	14372.8	47.186	45.79
2	0	2.18E+03	13481.3	49.9365	
3	1	1.83E+03	12671.5	44.5493	s
4	3	1.78E+03	12893.9	42.4596	2.47
5	5	1854.26	13123.2	43.5711	
6	7	1841.48	12800.4	44.3812	%RSD
7	11	2015.20	13085.7	47.5838	5.39
8	14	2074.37671	13725.2	46.6792	

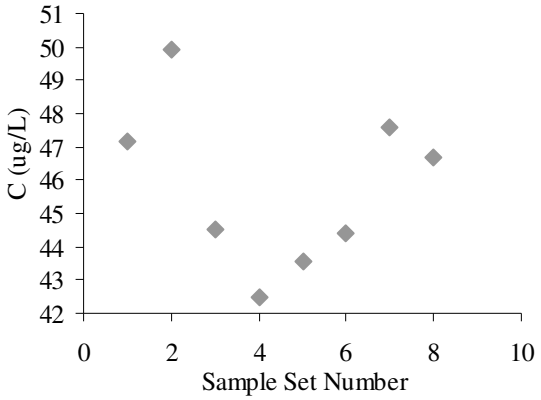


Figure A4: Experimental standards

Table A8: Metribuzin experimental standards

METRIBUZIN STANDARDS					
#	Day	Peak Area Std	Peak Area TCX	C (µg/L)	Avg. C (µg/L)
1	0	2.06E+04	14372.8	99.2295	91.75
2	0	1.92E+04	13481.3	98.4118	
3	1	1.54E+04	12671.5	84.1361	s
4	3	1.70E+04	12893.9	90.9125	5.83
5	5	1.58E+04	13123.2	83.1908	
6	7	17344.30	12800.4	93.5855	%RSD
7	11	17654.00	13085.7	93.1776	6.35
8	14	1.82E+04	13725.2	91.3922	

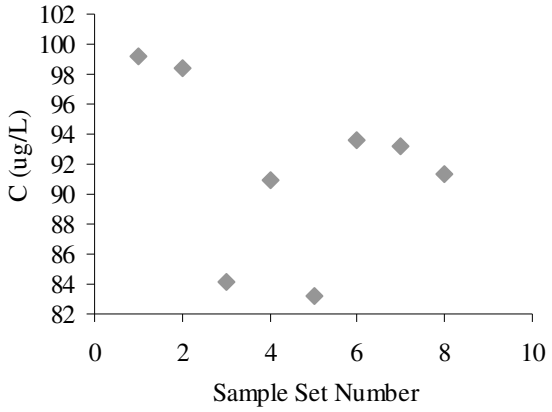


Figure A5: Metribuzin experimental standards

Table A9: Etridiazole experimental standards

ETRIDIAZOLE STANDARDS				
#	Day	Peak Area Std	Peak Area TCX	C (µg/L)
0	1.91E+04	1.44E+04	52.13	52.47
0	1.84E+04	1.35E+04	53.6073	
1	1.71E+04	1.27E+04	52.9537	s
3	1.64E+04	1.29E+04	50.086	2.24387
5	1.65E+04	1.31E+04	49.4672	
7	16828.90	12800.4	51.6413	%RSD
11	18909.00	13085.7	56.6716	4.27632
14	1.86E+04	1.37E+04	53.2194	

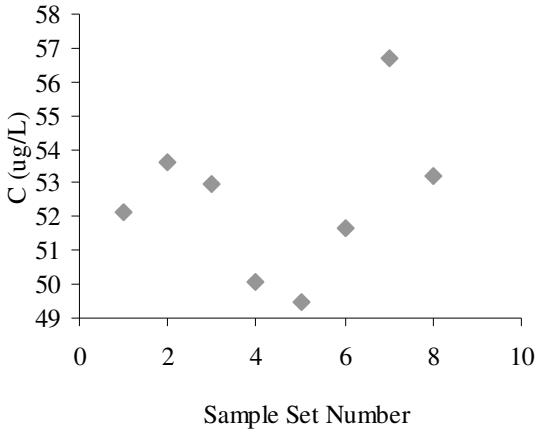


Figure A6: Etridiazole experimental standards

APPENDIX B.
GC-ECD ANALYTICAL METHODS

INSTRUMENTATION

Agilent Technologies 6890N Series gas chromatograph equipped with a μ-ECD and 7683 Series Injector (Palo Alto, CA, USA). EPA Method 505 with slight modifications was followed for analysis of samples.

METHOD SPECIFICS

Carrier Gas: in-house nitrogen production

Carrier Gas Flow Rate: 2 mL/min

Column: Agilent HP-5 capillary column Model 19091J-413, 5% Phenyl Methyl Siloxane (30 m · 320 μm · 0.25 μm)

Column Inlets: splitless mode, 20 psi pressure, and 25.8 mL/min total flow

Injections: 280 C injector temperature, 1 μL injection volume,

Detector: 300 C detector temperature, 30 mL/min detector flow

OVEN TEMPERATURE GRADIENTS

Table B1: Oven temperature gradients

	Ramp (°C/min)	Oven temp. (next °C)	Hold time (min)	Run time (min)
Initial	0	50	1	1
Ramp 1	20	120	0	4.5
Ramp 2	5	185	1	18.5
Ramp 3	15	220	6	26.83
Postrun	0	50	0	26.83

RETENTION TIMES

Table B2: Retention times

Compound Name	RT (min)
Etridiazole	11.4
TCX (Internal Standard)	14.9
Diazinon	18.9
Metribuzin	20.2
Chloropyrifos (Surrogate)	21.9

CHROMATOGRAM

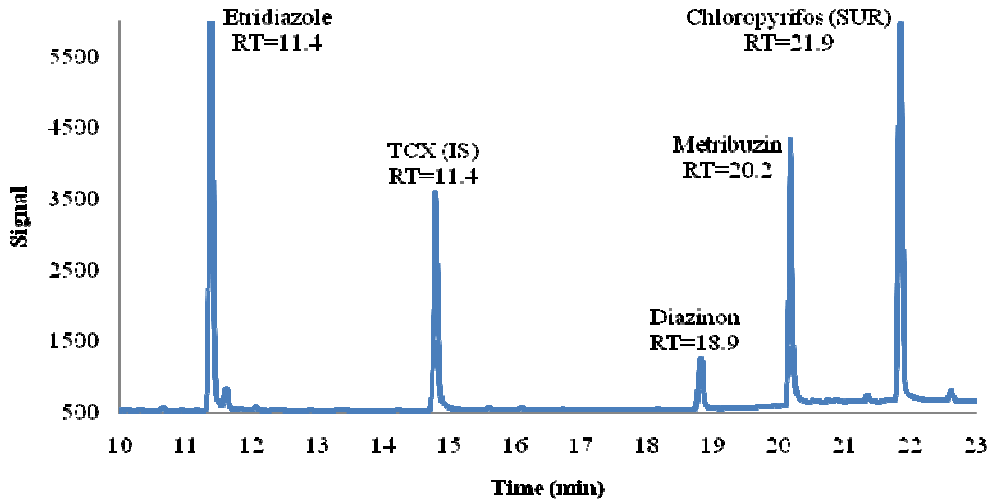


Figure B1: Chromatogram

APPENDIX C.
TABLED EXPERIMENTAL DATA

Table C1: Diazinon tabled experimental data

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
2	0.03	2813.96558	13114	66.534		1.000	0.000		
	0.03	2684.40918	12905.8	64.495	65.514	1.000	0.000	0.000	0.000
	2.73	1470.6593	13622.3	33.475		0.503	0.687		
	2.67	1510.74463	15404.7	30.409	31.942	0.471	0.752	0.022	0.070
	8.42	277.02213	14304.7	6.005		0.090	2.405		
	8.35	328.02243	13866.8	7.335	6.670	0.114	2.174	0.017	0.249
	13.22	98.11425	15852.7	1.919		0.029	3.546		
	13.15	100.38127	14747.9	2.110	2.015	0.033	3.420	0.003	0.136
	24.37		14848.8						
	24.30		15052.6						
	72.72		13793.5						
	72.65		14112.7						
	125.32		14225.3						
	125.25		14092.8						
	176.32		13575.2						
	176.25		15333.1						
	263.42		14047.8						
	263.35		14221						
	334.80		13796.5						
	334.73		14538.4						
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
4	0.03	3347.53589	14696.2	70.628		1.000	0.000		
	0.05	3240.28076	14688.5	68.401	69.515	1.000	0.000	0.000	0.000
	2.75	3963.53564	15889.3	77.346		1.095	-0.091		
	2.70	3662.52246	14220.9	79.857	78.601	1.167	-0.155	0.051	0.065
	8.47	3576.80957	15900.5	69.750		0.988	0.013		
	8.42	3391.36475	16667.4	63.091	66.420	0.922	0.081	0.046	0.069
	13.25	3655.37061	16103.4	70.384		0.997	0.003		
	13.20	3506.83496	16295.2	66.729	68.557	0.976	0.025	0.015	0.022
	24.43	2375.94312	14337.5	51.383		0.728	0.318		
	24.38	2422.33105	14197.5	52.903	52.143	0.773	0.257	0.032	0.062
	72.77	2124.16846	16988.6	38.770		0.549	0.600		
	72.72	1982.34	14313.6	42.943	40.856	0.628	0.466	0.056	0.137
	125.17	1389.89844	13412.3	32.132		0.455	0.788		
	125.12	1517.89258	15587.5	30.194	31.163	0.441	0.818	0.010	0.031
	176.17	1167.97351	15235.5	23.770		0.337	1.089		
	176.12	1145.96594	15164.5	23.432	23.601	0.343	1.071	0.004	0.018
	263.50	638.84717	14377.5	13.778		0.195	1.634		
	263.45	644.90131	14515.5	13.776	13.777	0.201	1.602	0.004	0.032
	334.83	449.24417	15257.6	9.130		0.129	2.046		
	334.78	385.15341	14731.9	8.107	8.618	0.119	2.133	0.008	0.088

Table C1: Diazinon tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
6	0.03	3324.03638	13872.8	74.295		1.000	0.000		
	0.03	3058.02734	15821.3	59.932	67.114	1.000	0.000	0.000	0.000
	2.72	3452.15967	16003.34	66.887		0.900			
	2.65				66.887	0.000			
	8.32	3792.76562	14352.7	81.937		1.103			
	8.25				81.937	0.000			
	13.10	3614.48755	15101.8	74.213		0.999			
	13.03				74.213	0.000			
	24.28	2594.23462	13892.5	57.901		0.779			
	24.22				57.901	0.000			
	72.62	3275.06885	15406	65.916		0.887			
	72.55				65.916	0.000			
	125.15	2929.89624	14079	64.527		0.869			
	125.08				64.527	0.000			
	176.22	3104.09	15272.5	63.021		0.848			
	176.15				63.021	0.000			
	263.35	3109.27686	14237.7	67.714		0.911			
	263.28				67.714	0.000			
	334.68	3016.9	13128.9	71.251		0.959			
	334.62				71.251	0.000			

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
7	0.03	3.25E+03	14152.5	71.189		1.000			
	0.03	3459.71997	13758.2	77.972	74.580	1.000	0.000	0.000	0.000
	2.65	3209.57666	14604.3	68.144		0.957			
	2.60	3587.04468	14652.1	75.910	72.027	0.974	0.027	0.012	0.016
	8.30	3492.79639	13941.3	77.684		1.091			
	8.25	3780.80615	14350.3	81.693	79.688	1.048	-0.047	0.031	0.039
	13.10	3640.61084	14959.9	75.458		1.060			
	13.05	4169.51172	15036.7	85.979	80.719	1.103	-0.098	0.030	0.037
	24.27	2632.10181	14509.2	56.250		0.790			
	24.22	2747.62964	14218.9	59.917	58.083	0.768	0.263	0.015	0.026
	72.55	2956.02734	13408.4	68.358		0.960			
	72.50	3426.06226	13849.8	76.703	72.531	0.984	0.016	0.017	0.023
	124.93	3026.38672	15913	58.970		0.828			
	124.88	3250.5942	15730.9	64.072	61.521	0.822	0.196	0.005	0.008
	176.00	3164.52393	15115.5	64.915		0.912			
	175.95	3340.12	15195.3	68.157	66.536	0.874	0.135	0.027	0.040
	263.32	3034.10352							
	263.27	3347.86	14400.5	72.086	72.086	0.925	0.078		
	334.58	2870.4209	13544.9	65.710		0.923			
	334.53	2918.87988	13265.9	68.224	66.967	0.875	0.134	0.034	0.051

Table C1: Diazinon tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
8	0.03	3.33E+03	13781.2	74.901		1.000			
	0.02	3.54E+03	14219.2	77.257	76.079	1.000	0.000	0.000	0.000
	2.65	3348.08472	13652.6	76.040		1.015			
	2.58	3390.75952	14043.4	74.866	75.453	0.969	0.031	0.033	0.043
	8.37	3833.20288	14965.6	79.420		1.060			
	8.30	3720.13794	14509.9	79.498	79.459	1.029	-0.029	0.022	0.028
	13.10	3805.94971	17071.8	69.126		0.923			
	13.03	4152.21924	15294.6	84.179	76.652	1.090	-0.086	0.118	0.154
	24.53	2863.76001	1.45E+04	61.064		0.815			
	24.47	3305.36621	14835.6	69.083	65.074	0.894	0.112	0.056	0.086
	72.58	3151.24634	16385.3	59.633		0.796			
	72.52	3345.07227	14095	73.587	66.610	0.952	0.049	0.111	0.166
	124.98	2994.43188	14462.4	64.200		0.857			
	124.92	3097.00415	14246.2	67.407	65.803	0.873	0.136	0.011	0.017
	175.10	3020.73169	14982.3	62.516		0.835			
	175.03	3429.61426	14956.1	71.103	66.810	0.920	0.083	0.061	0.091
	263.33	2986.93	14326.9	64.645		0.863			
	263.27	3247.32	14842.6	67.838	66.241	0.878	0.130	0.011	0.016
	334.57	3099.26904	14853.1	64.700		0.864			
	334.50	3021.42798	13831.8	67.732	66.216	0.877	0.132	0.009	0.014
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
9	0.03	3414.64771	14909.5	71.014		1.000			
	0.02	3197.85107	15460.4	64.135	67.575	1.000	0.000	0.000	0.000
	2.77	3333.46851	14185.2	72.865		1.026			
	2.70	3485.23291	16402	65.886	69.376	1.027	-0.027	0.001	0.001
	8.98	3530.81958	14818.1	73.883		1.040			
	8.92	3543.55	14668.2	74.907	74.395	1.168	-0.155	0.090	0.121
	13.12	4031.5686	15150.6	82.510		1.162			
	13.05	3511.95947	15397.2	70.724	76.617	1.103	-0.098	0.042	0.055
	24.55	3254.89233	14773.1	68.316		0.962			
	24.48	3500.34326	16395.1	66.200	67.258	1.032	-0.032	0.050	0.074
	72.60	3244.68359	14511.6	69.329		0.976			
	72.53	3381.29907	14518.2	72.216	70.772	1.126	-0.119	0.106	0.150
	124.87	3697.67651	14133.5	81.122		1.142			
	124.80	3114.09863	14455.58	66.797	73.959	1.042	-0.041	0.071	0.096
	174.98	3106.50781	15506.2	62.119		0.875			
	174.92	3,235	14802.1	67.767	64.943	1.057	-0.055	0.129	0.198
	263.35	3032.19	14952.4	62.879		0.885			
	263.28	2981.12	15064.9	61.358	62.119	0.957	0.044	0.050	0.081
	334.57	2965.8313	15047.2	61.115		0.861			
	334.50	2888.76782	13793.5	64.938	63.027	1.013	-0.012	0.107	0.170

Table C1: Diazinon tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
10	0.03	3197.85107	14344.2	69.126		1.000	0.000		
	0.03	3761.03711	14026.1	83.144	76.135	1.000	0.000	0.000	0.000
	2.65	3472.52563	16016.8	67.225		0.972	0.028		
	2.58	3513.19971	16377.7	66.513	66.869	0.962	0.039	0.007	0.011
	9.03	3338.60986	15830	65.395		0.946	0.055		
	8.97	3365.65015	14619.8	71.382	68.388	1.033	-0.032	0.061	0.090
	13.15	3447.02979	16869.7	63.357		0.917	0.087		
	13.08	3174.47266	14825.8	66.392	64.875	0.960	0.040	0.031	0.048
	24.57	3511.42871	16262.1	66.953		0.969	0.032		
	24.50	3451.16089	14505.7	73.771	70.362	1.067	-0.065	0.070	0.099
	72.60	3302.67944	14532.6	70.467		1.019	-0.019		
	72.53	3221.6853	16568.2	60.293	65.380	0.872	0.137	0.104	0.159
	125.00	2964.44141	14543.6	63.202		0.914	0.090		
	124.93	2948.75391	14426.6	63.377	63.290	0.917	0.087	0.002	0.003
	152.15	3.13E+03	15570.9	62.268		0.901	0.104		
	152.08	2747.33203	14203.8	59.974	61.121	0.868	0.142	0.023	0.038
	263.35	3201.41064	15448.2	64.257		0.930	0.073		
	263.28	2853.8	15025.8	58.891	61.574	0.852	0.160	0.055	0.089
	334.57	2794.64307	15043	57.604		0.833	0.182		
	334.50	2617.9729	15052.5	53.928	55.766	0.780	0.248	0.038	0.067
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
11	0.03	3560.97241	15433.8	71.541		1.000	0.000		
	0.02	3351.30933	15461.1	67.210	69.376	1.000	0.000	0.000	0.000
	2.78	3344.6355	14532.3	71.363		0.998	0.002		
	2.70	3452.88916	14804.7	72.317	71.840	1.076	-0.073	0.055	0.077
	9.02	3060.79712	14757.5	64.310		0.899	0.107		
	8.93	2913.41187	15321	58.962	61.636	0.877	0.131	0.015	0.025
	13.15	3017.92822	14902.6	62.792		0.878	0.130		
	13.07	3049.29858	15210.6	62.160	62.476	0.925	0.078	0.033	0.053
	24.55	2710.18	15236.1	55.155		0.771	0.260		
	24.47	2652.25244	14640.2	56.173	55.664	0.836	0.179	0.046	0.082
	72.57	1479.30042	16662.1	27.529		0.385	0.955		
	72.48	1756.77393	15267.5	35.679	31.604	0.531	0.633	0.103	0.327
	124.85	918.41089	13988.6	20.357		0.285	1.257		
	124.77	1216.31201	14773	25.529	22.943	0.380	0.968	0.067	0.294
	152.00	845.69818	15604.4	16.805		0.235	1.449		
	151.92	1106.6025	15530.5	22.094	19.449	0.329	1.113	0.066	0.341
	263.35	618.67767	14602.9	13.137		0.184	1.695		
	263.27	882.8252	15347.5	17.836	15.486	0.265	1.327	0.058	0.373
	334.52	587.718	13153.1	13.855		0.194	1.642		
	334.43	886.78662	15193.1	18.098	15.976	0.269	1.312	0.053	0.335

Table C1: Diazinon tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
12	0.03	3351.30933	15461.1	67.210		1.000	0.000		
	0.03	3468.18872	15666.3	68.643	67.926	1.000	0.000	0.000	0.000
	2.77	2515.13403	15699.6	49.674		0.739	0.302		
	2.72	2419.15601	14708.4	50.999	50.336	0.743	0.297	0.003	0.005
	9.00	1126.23	14237.9	24.527		0.365	1.008		
	8.95	926.41467	16283.5	17.641	21.084	0.257	1.359	0.076	0.362
	13.17	651.59253	15059.1	13.416		0.200	1.611		
	13.12	510.31738	14696.8	10.767	12.091	0.157	1.852	0.030	0.250
	24.60	193.46109	16522.7	3.631		0.054	2.918		
	24.55	156.26126	16032.8	3.022	3.326	0.044	3.123	0.007	0.212
	72.57	74.92258	16255.2	1.429		0.021	3.851		
	72.52	23.97937	15714.8	0.473	0.951	0.007	0.000	0.010	1.068
	124.85		15015.6						
	124.80		16028.8						
	153.20		9212.88						
	153.15		1						
	263.35		15231.3						
	263.30		15965.6						
	334.50		15529.3						
	334.45		15127.9						
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
13	0.03	2.07E+03	15711	40.838		1.000	0.000		
	0.03	2417.36133	15699.6	47.743	44.291	1.000	0.000	0.000	0.000
	2.73	7.47E+01	14948	1.549		0.038	3.272		
	2.67		15956						
	8.98		16052.3						
	8.92		14434.8						
	13.17		15189						
	13.10		16603.4						
	24.58		14756.2						
	24.52		14415.3						
	72.55		15961.2						
	72.48		15787.4						
	124.70		15790.5						
	124.63		13489.9						
	153.05		15567.7						
	152.98		14214.8						
	263.33		15498						
	263.27		14918.2						
	334.48		15046.4						
	334.42		13665.3						

Table C2: Etridiazole tabled experimental data

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
2	0.03	2.57E+04	1.31E+04	76.791		1.000	0.000		
	0.03	2.56E+04	1.29E+04	77.629	77.210	1.000	0.000	0.000	0.000
	2.73	2.56E+04	1.36E+04	73.772		0.961	0.040		
	2.67	2.52E+04	1.54E+04	64.094	68.933	0.826	0.192	0.095	0.139
	8.42	2.54E+04	1.43E+04	69.478		0.905	0.100		
	8.35	2.82E+04	1.39E+04	79.787	74.633	1.028	-0.027	0.087	0.117
	13.22	3.06E+04	1.59E+04	75.672		0.985	0.015		
	13.15	3.09E+04	1.47E+04	82.004	78.838	1.056	-0.055	0.050	0.064
	24.37	2.48E+04	1.48E+04	65.556		0.854	0.158		
	24.30	2.52E+04	1.51E+04	65.710	65.633	0.846	0.167	0.005	0.008
	72.72	2.62E+04	1.38E+04	74.412		0.969	0.031		
	72.65	2.56E+04	1.41E+04	70.972	72.692	0.914	0.090	0.039	0.053
	125.32	2.58E+04	1.42E+04	71.079		0.926	0.077		
	125.25	2.36E+04	1.41E+04	65.529	68.304	0.844	0.169	0.058	0.084
	176.32	2.47E+04	1.36E+04	71.208		0.927	0.075		
	176.25	2.53E+04	1.53E+04	64.560	67.884	0.832	0.184	0.068	0.100
	263.42	2.65E+04	1.40E+04	73.974		0.963	0.037		
	263.35	2.43E+04	1.42E+04	67.065	70.519	0.864	0.146	0.070	0.100
	334.80	2.24E+04	1.38E+04	63.625		0.829	0.188		
	334.73	2.45E+04	1.45E+04	66.101	67.691	0.851	0.161	0.016	0.024
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
4	0.03	2.70E+04	1.47E+04	72.054		1.000	0.000		
	0.05	2.83E+04	1.47E+04	75.531	73.793	1.000	0.000	0.000	0.000
	2.75	3.07E+04	1.59E+04	75.805		1.052	-0.051		
	2.70	2.78E+04	1.42E+04	76.532	76.169	1.013	-0.013	0.027	0.036
	8.47	2.91E+04	1.59E+04	71.806		0.997	0.003		
	8.42	2.76E+04	1.67E+04	64.945	68.375	0.860	0.151	0.097	0.141
	13.25	3.13E+04	1.61E+04	76.224		1.058	-0.056		
	13.20	3.12E+04	1.63E+04	74.974	75.599	0.993	0.007	0.046	0.061
	24.43	2.57E+04	1.43E+04	70.253		0.975	0.025		
	24.38	2.50E+04	1.42E+04	68.976	69.614	0.913	0.091	0.044	0.063
	72.77	2.90E+04	1.70E+04	66.916		0.929	0.074		
	72.72	2.68E+04	1.43E+04	73.455	70.186	0.973	0.028	0.031	0.044
	125.17	2.56E+04	1.34E+04	74.890		1.039	-0.039		
	125.12	2.88E+04	1.56E+04	72.357	73.623	0.958	0.043	0.058	0.078
	176.17	2.27E+04	1.52E+04	58.425		0.811	0.210		
	176.12	2.82E+04	1.52E+04	72.823	65.624	0.964	0.037	0.108	0.165
	263.50	2.57E+04	1.44E+04	70.205		0.974	0.026		
	263.45	2.72E+04	1.45E+04	73.323	71.764	0.971	0.030	0.003	0.004
	334.83	2.66E+04	1.53E+04	68.384		0.949	0.052		
	334.78	2.61E+04	1.47E+04	69.448	68.916	0.919	0.084	0.021	0.030

Table C2: Etridiazole tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
6	0.03	2.85E+04	1.39E+04	80.652		1.000	0.000		
	0.03	2.64E+04	1.58E+04	65.501	73.077	1.000	0.000	0.000	0.000
	2.72	2.80E+04	1.60E+04	68.508		0.849	0.163		
	2.65				68.508				
	8.32	3.02E+04	1.44E+04	82.414		1.022	-0.022		
	8.25				82.414				
	13.10	3.28E+04	1.51E+04	85.194		1.056	-0.055		
	13.03				85.194				
	24.28	2.62E+04	1.39E+04	73.994		0.917	0.086		
	24.22				73.994				
	72.62	2.98E+04	1.54E+04	75.836		0.940	0.062		
	72.55				75.836				
	125.15	2.63E+04	1.41E+04	73.090		0.906	0.098		
	125.08				73.090				
	176.22	2.71E+04	1.53E+04	69.576		0.863	0.148		
	176.15				69.576				
	263.35	2.66E+04	1.42E+04	73.332		0.909	0.095		
	263.28				73.332				
	334.68	2.64E+04	1.31E+04	78.945		0.979	0.021		
	334.62				78.945				0.000
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
7	0.03	2.95E+04	1.42E+04	81.651		1.000			
	0.03	2.96E+04	1.38E+04	84.311	82.981	1.000	0.000	0.000	0.000
	2.65	2.66E+04	1.46E+04	71.394		0.874			
	2.60	2.86E+04	1.47E+04	76.395	73.894	0.906	0.099	0.022	0.030
	8.30	2.91E+04	1.39E+04	81.911		1.003			
	8.25	2.96E+04	1.44E+04	80.863	81.387	0.959	0.042	0.031	0.038
	13.10	3.31E+04	1.50E+04	86.774		1.063			
	13.05	3.53E+04	1.50E+04	92.155	89.465	1.093	-0.089	0.021	0.024
	24.27	2.67E+04	1.45E+04	72.245		0.885			
	24.22	2.53E+04	1.42E+04	69.774	71.009	0.828	0.189	0.040	0.057
	72.55	2.80E+04	1.34E+04	81.901		1.003			
	72.50	2.97E+04	1.38E+04	83.986	82.943	0.996	0.004	0.005	0.006
	124.93	2.71E+04	1.59E+04	66.733		0.817			
	124.88	2.80E+04	1.57E+04	69.726	68.230	0.827	0.190	0.007	0.010
	176.00	2.79E+04	1.51E+04	72.486		0.888			
	175.95	2.84E+04	1.52E+04	73.206	72.846	0.868	0.141	0.014	0.019
	263.32	2.62E+04							
	263.27	2.89E+04	1.44E+04	78.668	78.668	0.933	0.069		
	334.58	2.46E+04	1.35E+04	71.312		0.873			
	334.53	2.49E+04	1.33E+04	73.520	72.416	0.872	0.137	0.001	0.001

Table C2: Etridiazole tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
8	0.03	3.04E+04	1.38E+04	86.561		1.000			
	0.02	3.03E+04	1.42E+04	83.499	85.030	1.000	0.000	0.000	0.000
	2.65	2.81E+04	1.37E+04	80.555		0.931			
	2.58	2.92E+04	1.40E+04	81.386	80.971	0.975	0.026	0.031	0.038
	8.37	3.23E+04	1.50E+04	84.584		0.977			
	8.30	3.11E+04	1.45E+04	83.997	84.290	1.006	-0.006	0.020	0.024
	13.10	3.39E+04	1.71E+04	77.757		0.898			
	13.03	3.51E+04	1.53E+04	89.927	83.842	1.077	-0.074	0.126	0.151
	24.53	2.94E+04	1.45E+04	79.186		0.915			
	24.47	2.88E+04	1.48E+04	76.063	77.624	0.911	0.093	0.003	0.004
	72.58	2.86E+04	1.64E+04	68.439		0.791			
	72.52	3.00E+04	1.41E+04	83.537	75.988	1.000	0.000	0.148	0.195
	124.98	2.66E+04	1.45E+04	72.042		0.832			
	124.92	2.87E+04	1.42E+04	79.067	75.554	0.947	0.055	0.081	0.107
	175.10	2.68E+04	1.50E+04	70.059		0.809			
	175.03	3.00E+04	1.50E+04	78.756	74.407	0.943	0.058	0.095	0.127
	263.33	2.65E+04	1.43E+04	72.419		0.837			
	263.27	2.84E+04	1.48E+04	75.022	73.720	0.898	0.107	0.044	0.059
	334.57	2.66E+04	1.49E+04	70.257		0.812			
	334.50	2.59E+04	1.38E+04	73.513	71.885	0.880	0.127	0.049	0.068
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
9	0.03	2.98E+04	1.49E+04	78.322		1.000			
	0.02	2.80E+04	1.55E+04	71.036	74.679	1.000	0.000	0.000	0.000
	2.77	2.87E+04	1.42E+04	79.301		1.013			
	2.70	2.85E+04	1.64E+04	68.092	73.696	0.959	0.042	0.038	0.052
	8.98	2.96E+04	1.48E+04	78.405		1.001			
	8.92	3.00E+04	1.47E+04	80.098	79.252	1.128	-0.120	0.089	0.113
	13.12	3.57E+04	1.52E+04	92.474		1.181			
	13.05	3.19E+04	1.54E+04	81.270	86.872	1.144	-0.135	0.026	0.030
	24.55	2.97E+04	1.48E+04	78.776		1.006			
	24.48	3.05E+04	1.64E+04	72.991	75.884	1.028	-0.027	0.015	0.020
	72.60	2.99E+04	1.45E+04	80.769		1.031			
	72.53	3.06E+04	1.45E+04	82.684	81.727	1.164	-0.152	0.094	0.115
	124.87	3.33E+04	1.41E+04	92.331		1.179			
	124.80	2.81E+04	1.45E+04	76.165	84.248	1.072	-0.070	0.075	0.090
	174.98	2.75E+04	1.55E+04	69.647		0.889			
	174.92	2.93E+04	1.48E+04	77.511	73.579	1.091	-0.087	0.143	0.194
	263.35	2.72E+04	1.50E+04	71.212		0.909			
	263.28	2.70E+04	1.51E+04	70.277	70.745	0.989	0.011	0.057	0.080
	334.57	2.59E+04	1.50E+04	67.527		0.862			
	334.50	2.52E+04	1.38E+04	71.752	69.640	1.010	-0.010	0.105	0.150

Table C2: Etridiazole tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
10	0.03	2.80E+04	1.43E+04	76.621		1.000			
	0.03	3.48E+04	1.40E+04	97.367	86.994	1.000	0.000	0.000	0.000
	2.65	2.91E+04	1.60E+04	71.169		0.929			
	2.58	2.87E+04	1.64E+04	68.805	69.987	0.707	0.347	0.157	0.224
	9.03	2.82E+04	1.58E+04	69.935		0.913			
	8.97	2.78E+04	1.46E+04	74.622	72.278	0.766	0.266	0.103	0.143
	13.15	3.28E+04	1.69E+04	76.148		0.994			
	13.08	2.87E+04	1.48E+04	75.835	75.992	0.779	0.250	0.152	0.200
	24.57	3.06E+04	1.63E+04	73.794		0.963			
	24.50	2.96E+04	1.45E+04	80.060	76.927	0.822	0.196	0.100	0.129
	72.60	3.08E+04	1.45E+04	83.034		1.084			
	72.53	2.90E+04	1.66E+04	68.630	75.832	0.705	0.350	0.268	0.353
	125.00	2.85E+04	1.45E+04	76.803		1.002			
	124.93	2.72E+04	1.44E+04	73.916	75.359	0.759	0.276	0.172	0.228
	152.15	2.96E+04	1.56E+04	74.457		0.972			
	152.08	2.53E+04	1.42E+04	69.761	72.109	0.716	0.333	0.181	0.250
	263.35	2.94E+04	1.54E+04	74.614		0.974			
	263.28	2.66E+04	1.50E+04	69.320	71.967	0.712	0.340	0.185	0.257
	334.57	2.58E+04	1.50E+04	67.212		0.877			
	334.50	2.40E+04	1.51E+04	62.618	64.915	0.643	0.441	0.166	0.255
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
11	0.03	3.01E+04	1.54E+04	76.477		1.000	0.000		
	0.02	2.94E+04	1.55E+04	74.480	75.479	1.000	0.000	0.000	0.000
	2.78	2.87E+04	1.45E+04	77.413		1.012	-0.012		
	2.70	3.03E+04	1.48E+04	80.336	78.875	1.079	-0.076	0.047	0.060
	9.02	2.85E+04	1.48E+04	75.687		0.990	0.010		
	8.93	2.94E+04	1.53E+04	75.297	75.492	1.011	-0.011	0.015	0.020
	13.15	3.16E+04	1.49E+04	83.099		1.087	-0.083		
	13.07	3.17E+04	1.52E+04	81.591	82.345	1.095	-0.091	0.006	0.008
	24.55	2.87E+04	1.52E+04	73.882		0.966	0.035		
	24.47	2.76E+04	1.46E+04	73.871	73.877	0.992	0.008	0.018	0.025
	72.57	2.34E+04	1.67E+04	55.156		0.721	0.327		
	72.48	2.44E+04	1.53E+04	62.648	58.902	0.841	0.173	0.085	0.144
	124.85	1.88E+04	1.40E+04	52.723		0.689	0.372		
	124.77	2.03E+04	1.48E+04	53.847	53.285	0.723	0.324	0.024	0.045
	152.00	1.99E+04	1.56E+04	49.905		0.653	0.427		
	151.92	2.03E+04	1.55E+04	51.333	50.619	0.689	0.372	0.026	0.051
	263.35	1.76E+04	1.46E+04	47.224		0.617	0.482		
	263.27	1.78E+04	1.53E+04	45.455	46.340	0.610	0.494	0.005	0.011
	334.52	1.71E+04	1.32E+04	50.964		0.666	0.406		
	334.43	1.79E+04	1.52E+04	46.083	48.523	0.619	0.480	0.034	0.069

Table C2: Etridiazole tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
12	0.03	2.94E+04	1.55E+04	74.480		1.000	0.000		
	0.03	3.15E+04	1.57E+04	78.824	76.652	1.000	0.000	0.000	0.000
	2.77	2.61E+04	1.57E+04	65.054		0.873	0.135		
	2.72	2.64E+04	1.47E+04	70.485	67.769	0.894	0.112	0.015	0.022
	9.00	1.94E+04	1.42E+04	53.403		0.717	0.333		
	8.95	2.07E+04	1.63E+04	49.940	51.671	0.634	0.456	0.059	0.114
	13.17	1.83E+04	1.51E+04	47.630		0.640	0.447		
	13.12	1.85E+04	1.47E+04	49.459	48.545	0.627	0.466	0.009	0.018
	24.60	1.02E+04	1.65E+04	24.242		0.325	1.122		
	24.55	1.05E+04	1.60E+04	25.582	24.912	0.325	1.125	0.001	0.003
	72.57	1.36E+03	1.63E+04	3.289		0.044	3.120		
	72.52	1.37E+03	1.57E+04	3.426	3.358	0.043	3.136	0.000	0.015
	124.85	1.93E+02	1.50E+04	0.505		0.007	4.994		
	124.80	1.92E+02	1.60E+04	0.469	0.487	0.006	5.124	0.001	0.119
	153.20	5.51E+01	9.21E+03	0.234		0.003	5.761		
	153.15		1.00E+00						
	263.35	2.00E+01	1.52E+04	0.051		0.001	7.279		
	263.30	5.30E+01	1.60E+04	0.130	0.051	0.002	6.406	0.001	1.324
	334.50	2.04E+01	1.55E+04	0.051		0.001	7.278		
	334.45		1.51E+04						
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
13	0.03	2.53E+04	1.57E+04	63.012		1.000	0.000		
	0.03	3.01E+04	1.57E+04	75.074	69.043	1.000	0.000	0.000	0.000
	2.73	4.37E+02	1.49E+04	1.147		0.018	4.007		
	2.67	5.09E+02	1.60E+04	1.251	1.199	0.017	4.094	0.001	0.090
	8.98								
	8.92								
	13.17								
	13.10								
	24.58								
	24.52								
	72.55								
	72.48								
	124.70								
	124.63								
	153.05								
	152.98								
	263.33								
	263.27								
	334.48								
	334.42								

Table C3: Metribuzin tabled experimental data

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
2	0.03	7.97E+03	1.31E+04	53.527		1.000	0.000		
	0.03	1.09E+04	1.29E+04	74.404	63.966	1.000	0.000	0.000	0.000
	2.73	7.20E+03	1.36E+04	46.562		0.870	0.139		
	2.67	3.39E+03	1.54E+04	19.383	46.562				0.000
	8.42	6.59E+03	1.43E+04	40.532		0.757	0.278		
	8.35	1.07E+04	1.39E+04	67.903	54.218	0.913	0.091	0.110	0.203
	13.22	8.10E+03	1.59E+04	44.979		0.840	0.174		
	13.15	1.02E+04	1.47E+04	61.157	53.068	0.822	0.196	0.013	0.024
	24.37	5.71E+03	1.48E+04	33.872		0.633	0.458		
	24.30	8.74E+03	1.51E+04	51.109	42.490	0.687	0.376	0.038	0.090
	72.72	5.54E+03	1.38E+04	35.345		0.660	0.415		
	72.65	7.64E+03	1.41E+04	47.639	41.492	0.640	0.446	0.014	0.034
	125.32	4.41E+03	1.42E+04	27.284		0.510	0.674		
	125.25	6.09E+03	1.41E+04	38.048	32.666	0.511	0.671	0.001	0.004
	176.32	3.17E+03	1.36E+04	20.555		0.384	0.957		
	176.25	4.96E+03	1.53E+04	28.468	24.511	0.383	0.961	0.001	0.004
	263.42	2.18E+03	1.40E+04	13.673		0.255	1.365		
	263.35	2.93E+03	1.42E+04	18.108	15.890	0.243	1.413	0.009	0.054
	334.80	1.86E+03	1.38E+04	11.854		0.221	1.507		
	334.73	2.49E+03	1.45E+04	15.067	13.461	0.203	1.597	0.013	0.100
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
4	0.03	2.02E+04	1.47E+04	120.784		1.000			
	0.05	1.91E+04	1.47E+04	114.378	117.581	1.000	0.000	0.000	0.000
	2.75	2.25E+04	1.59E+04	124.774		1.033			
	2.70	1.85E+04	1.42E+04	114.518	119.646	1.001	-0.001	0.022	0.019
	8.47	2.08E+04	1.59E+04	115.058		0.953			
	8.42	1.70E+04	1.67E+04	89.674	102.366	0.784	0.243	0.119	0.116
	13.25	2.43E+04	1.61E+04	132.787		1.099			
	13.20	2.02E+04	1.63E+04	109.156	120.971	0.954	0.047	0.103	0.085
	24.43	2.05E+04	1.43E+04	125.924		1.043			
	24.38	1.76E+04	1.42E+04	108.934	117.429	0.952	0.049	0.064	0.054
	72.77	2.36E+04	1.70E+04	122.468		1.014			
	72.72	1.83E+04	1.43E+04	112.265	117.366	0.982	0.019	0.023	0.020
	125.17	2.35E+04	1.34E+04	154.320		1.278			
	125.12	1.83E+04	1.56E+04	103.122	128.721	0.902	0.104	0.266	0.207
	176.17	2.28E+04	1.52E+04	131.656		1.090			
	176.12	1.68E+04	1.52E+04	97.673	114.665	0.854	0.158	0.167	0.146
	263.50	2.62E+04	1.44E+04	160.417		1.328			
	263.45	2.04E+04	1.45E+04	123.427	141.922	1.079	-0.076	0.176	0.124
	334.83	2.39E+04	1.53E+04	138.142		1.144			
	334.78	1.83E+04	1.47E+04	109.299	123.720	0.956	0.045	0.133	0.108

Table C3: Metribuzin tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
6	0.03	1.22E+04	1.39E+04	77.713		1.000			
	0.03	1.08E+04	1.58E+04	59.959	68.836	1.000	0.000		0.000
	2.72	1.12E+04	1.60E+04	61.876		0.796			
	2.65				61.876				
	8.32	1.58E+04	1.44E+04	97.122		1.250			
	8.25				97.122				
	13.10	1.43E+04	1.51E+04	83.231		1.071			
	13.03				83.231				
	24.28	1.14E+04	1.39E+04	72.259		0.930			
	24.22				72.259				
	72.62	1.27E+04	1.54E+04	72.536		0.933			
	72.55				72.536				
	125.15	1.19E+04	1.41E+04	74.379		0.957			
	125.08				74.379				
	176.22	1.26E+04	1.53E+04	72.354		0.931			
	176.15				72.354				
	263.35	1.34E+04	1.42E+04	82.746		1.065			
	263.28				82.746				
	334.68	1.24E+04	1.31E+04	83.253		1.071			
	334.62				83.253				
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
7	0.03	1.03E+04	1.42E+04	63.949		1.000			
	0.03	1.39E+04	1.38E+04	89.258	76.604	1.000	0.000	0.000	0.000
	2.65	9.73E+03	1.46E+04	58.634		0.917			
	2.60	1.34E+04	1.47E+04	80.629	69.631	0.903	0.102	0.010	0.014
	8.30	1.10E+04	1.39E+04	69.760		1.091			
	8.25	1.26E+04	1.44E+04	77.112	73.436	0.864	0.146	0.160	0.219
	13.10	1.01E+04	1.50E+04	59.564		0.931			
	13.05	1.54E+04	1.50E+04	89.889	74.727	1.007	-0.007	0.053	0.072
	24.27	9.08E+03	1.45E+04	55.098		0.862			
	24.22	1.29E+04	1.42E+04	80.015	67.556	0.896	0.109	0.025	0.036
	72.55	8.52E+03	1.34E+04	55.963		0.875			
	72.50	1.39E+04	1.38E+04	88.361	72.162	0.990	0.010	0.081	0.113
	124.93	1.11E+04	1.59E+04	61.525		0.962			
	124.88	1.04E+04	1.57E+04	58.154	59.840	0.652	0.428	0.220	0.367
	176.00	1.04E+04	1.51E+04	60.522		0.946			
	175.95	1.39E+04	1.52E+04	80.605	70.563	0.903	0.102	0.031	0.043
	263.32	1.01E+04							
	263.27	1.35E+04	1.44E+04	82.651	82.651	0.926	0.077		
	334.58	9.60E+03	1.35E+04	62.387		0.976			
	334.53	1.37E+04	1.33E+04	91.051	76.719	1.020	-0.020	0.031	0.041

Table C3: Metribuzin tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
8	0.03	9.79E+03	1.38E+04	62.560		1.000			
	0.02	1.14E+04	1.42E+04	70.535	66.548	1.000	0.000	0.000	0.000
	2.65	9.58E+03	1.37E+04	61.758		0.987			
	2.58	1.20E+04	1.40E+04	75.242	68.500	1.067	-0.065	0.056	0.082
	8.37	1.04E+04	1.50E+04	60.992		0.975			
	8.30	1.08E+04	1.45E+04	65.288	63.140	0.926	0.077	0.035	0.055
	13.10	1.08E+04	1.71E+04	55.586		0.889			
	13.03	1.11E+04	1.53E+04	63.746	59.666	0.904	0.101	0.011	0.018
	24.53	9.50E+03	1.45E+04	57.531		0.920			
	24.47	9.93E+03	1.48E+04	58.947	58.239	0.836	0.179	0.059	0.102
	72.58	9.79E+03	1.64E+04	52.597		0.841			
	72.52	1.14E+04	1.41E+04	70.987	61.792	1.006	-0.006	0.117	0.190
	124.98	1.13E+04	1.45E+04	68.744		1.099			
	124.92	1.19E+04	1.42E+04	73.461	71.102	1.041	-0.041	0.041	0.057
	175.10	9.78E+03	1.50E+04	57.495		0.919			
	175.03	1.13E+04	1.50E+04	66.568	62.031	0.944	0.058	0.017	0.028
	263.33	1.09E+04	1.43E+04	67.232		1.075			
	263.27	1.20E+04	1.48E+04	71.039	69.136	1.007	-0.007	0.048	0.069
	334.57	1.06E+04	1.49E+04	62.851		1.005			
	334.50	1.17E+04	1.38E+04	74.779	68.815	1.060	-0.058	0.039	0.057
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
9	0.03	1.08E+04	1.49E+04	64.053		1.000			
	0.02	9.71E+03	1.55E+04	55.293	59.673	1.000	0.000	0.000	0.000
	2.77	9.90E+03	1.42E+04	61.433		0.959			
	2.70	1.07E+04	1.64E+04	57.526	59.479	1.040	-0.040	0.057	0.097
	8.98	1.00E+04	1.48E+04	59.626		0.931			
	8.92	1.03E+04	1.47E+04	61.859	60.743	1.119	-0.112	0.133	0.219
	13.12	1.15E+04	1.52E+04	66.879		1.044			
	13.05	9.89E+03	1.54E+04	56.548	61.713	1.023	-0.022	0.015	0.025
	24.55	1.04E+04	1.48E+04	61.994		0.968			
	24.48	9.92E+03	1.64E+04	53.251	57.622	0.963	0.038	0.003	0.006
	72.60	1.03E+04	1.45E+04	62.449		0.975			
	72.53	1.11E+04	1.45E+04	67.573	65.011	1.222	-0.201	0.175	0.269
	124.87	1.16E+04	1.41E+04	72.424		1.131			
	124.80	1.10E+04	1.45E+04	66.918	69.671	1.210	-0.191	0.056	0.081
	174.98	1.08E+04	1.55E+04	61.214		0.956			
	174.92	1.10E+04	1.48E+04	65.646	63.430	1.187	-0.172	0.164	0.258
	263.35	9.62E+03	1.50E+04	56.645		0.884			
	263.28	1.05E+04	1.51E+04	61.303	58.974	1.109	-0.103	0.159	0.269
	334.57	1.13E+04	1.50E+04	66.294		1.035			
	334.50	1.26E+04	1.38E+04	80.557	73.426	1.457	-0.376	0.298	0.406

Table C3: Metribuzin tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
10	0.03	1.20E+04	1.43E+04	73.814		1.000			
	0.03	9.08E+03	1.40E+04	56.990	65.402	1.000	0.000	0.000	0.000
	2.65	9.85E+03	1.60E+04	54.159		0.734			
	2.58	1.11E+04	1.64E+04	59.644	56.902	1.047	-0.046	0.221	0.389
	9.03	1.01E+04	1.58E+04	56.102		0.760			
	8.97	1.06E+04	1.46E+04	63.907	60.005	1.121	-0.115	0.255	0.426
	13.15	9.54E+03	1.69E+04	49.773		0.674			
	13.08	1.19E+04	1.48E+04	70.773	60.273	1.242	-0.217	0.401	0.666
	24.57	9.58E+03	1.63E+04	51.889		0.703			
	24.50	1.10E+04	1.45E+04	66.568	59.228	1.168	-0.155	0.329	0.555
	72.60	9.95E+03	1.45E+04	60.262		0.816			
	72.53	1.21E+04	1.66E+04	64.506	62.384	1.132	-0.124	0.223	0.358
	125.00	1.02E+04	1.45E+04	61.620		0.835			
	124.93	1.17E+04	1.44E+04	71.168	66.394	1.249	-0.222	0.293	0.441
	152.15	9.25E+03	1.56E+04	52.298		0.709			
	152.08	9.04E+03	1.42E+04	56.020	54.159	0.983	0.017	0.194	0.358
	263.35	1.00E+04	1.54E+04	57.239		0.775			
	263.28	1.04E+04	1.50E+04	60.664	58.951	1.064	-0.062	0.204	0.347
	334.57	1.06E+04	1.50E+04	62.190		0.843			
	334.50	1.18E+04	1.51E+04	69.230	65.710	1.215	-0.195	0.263	0.401
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
11	0.03	8.05E+03	1.54E+04	45.926		1.000			
	0.02	6.86E+03	1.55E+04	39.086	42.506	1.000	0.000	0.000	0.000
	2.78	7.79E+03	1.45E+04	47.164		1.027			
	2.70	7.58E+03	1.48E+04	45.057	46.110	1.153	-0.142	0.089	0.193
	9.02	7.97E+03	1.48E+04	47.558		1.036			
	8.93	7.11E+03	1.53E+04	40.851	44.205	1.045	-0.044	0.007	0.015
	13.15	8.45E+03	1.49E+04	49.903		1.087			
	13.07	7.44E+03	1.52E+04	43.046	46.474	1.101	-0.097	0.010	0.022
	24.55	7.92E+03	1.52E+04	45.743		0.996			
	24.47	6.80E+03	1.46E+04	40.871	43.307	1.046	-0.045	0.035	0.081
	72.57	8.15E+03	1.67E+04	43.049		0.937			
	72.48	7.36E+03	1.53E+04	42.430	42.740	1.086	-0.082	0.105	0.245
	124.85	7.46E+03	1.40E+04	46.939		1.022			
	124.77	7.42E+03	1.48E+04	44.225	45.582	1.131	-0.124	0.077	0.170
	152.00	6.76E+03	1.56E+04	38.119		0.830			
	151.92	5.47E+03	1.55E+04	31.034	34.576	0.794	0.231	0.025	0.074
	263.35	6.01E+03	1.46E+04	36.252		0.789			
	263.27	6.96E+03	1.53E+04	39.948	38.100	1.022	-0.022	0.165	0.432
	334.52	8.49E+03	1.32E+04	56.836		1.238			
	334.43	7.50E+03	1.52E+04	43.481	50.159	1.112	-0.107	0.088	0.176

Table C3: Metribuzin tabled experimental data continued

pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
12	0.03	6.86E+03	1.55E+04	39.086		1.000	0.000		
	0.03	7.69E+03	1.57E+04	43.230	41.158	1.000	0.000	0.000	0.000
	2.77	5.82E+03	1.57E+04	32.645		0.835	0.180		
	2.72	6.72E+03	1.47E+04	40.241	36.443	0.931	0.072	0.068	0.186
	9.00	2.99E+03	1.42E+04	18.466		0.472	0.750		
	8.95	3.11E+03	1.63E+04	16.819	17.643	0.389	0.944	0.059	0.334
	13.17	2.61E+03	1.51E+04	15.274		0.391	0.940		
	13.12	2.33E+03	1.47E+04	13.962	14.618	0.323	1.130	0.048	0.328
	24.60	8.22E+02	1.65E+04	4.378		0.112	2.189		
	24.55	7.91E+02	1.60E+04	4.345	4.362	0.101	2.298	0.008	0.187
	72.57		1.63E+04						
	72.52		1.57E+04						
	124.85		1.50E+04						
	124.80		1.60E+04						
	153.20		9.21E+03						
	153.15		1.00E+00						
	263.35		1.52E+04						
	263.30		1.60E+04						
	334.50		1.55E+04						
	334.45		1.51E+04						
pH	Time (h)	DIZ Area	TCX Area	C exp	Ave C	C/Co	-ln(C/Co)	s	%RSD
13	0.03	1.70E+02	1.57E+04	0.952		1.000	0.000		
	0.03	2.15E+02	1.57E+04	1.205	1.078	1.000	0.000	0.000	0.000
	2.73		1.49E+04						
	2.67		1.60E+04						
	8.98		0.00E+00						
	8.92		0.00E+00						
	13.17		0.00E+00						
	13.10		0.00E+00						
	24.58		0.00E+00						
	24.52		0.00E+00						
	72.55		0.00E+00						
	72.48		0.00E+00						
	124.70		0.00E+00						
	124.63		0.00E+00						
	153.05		0.00E+00						
	152.98		0.00E+00						
	263.33		0.00E+00						
	263.27		0.00E+00						
	334.48		0.00E+00						
	334.42		0.00E+00						

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VITA

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