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Pesticide Partitioning In Louisiana Wetland Aand Ricefield Sediment

Brendan Michael Marsh

Louisiana State University and Agricultural and Mechanical College

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PESTICIDE PARTITIONING IN LOUISIANA WETLAND AND RICEFIELD SEDIMENT

A Thesis

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

in

The Department of Environmental Science

by

Brendan Michael Marsh
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ABSTRACT

Pesticides are used globally and are often found within bodies of water. The EPA investigates the potential environmental impact through computer modeling in order to help mitigate some of the regulatory burden of pesticide fate investigation. Currently when pesticides enter a water body, the Exposure Analysis Modeling System (EXAMS) estimates partitioning depth as 5 cm and assumes equal distribution. This assumption was tested with a wide variety of pesticides with varying K_{oc} ranges and water solubilities. Savillex 150 ml Teflon tubes were filled with wetland and ricefield sediments with fresh and seawater as the aqueous phase. The seven pesticides tested included, quinclorac, bentazon, 2,4-D, atrazine, dicloran, flutolanil, and trifluralin had reported K_{oc} ranges as low as 20 and as high as 15800. Pesticides were sprayed onto the top layer of water and allowed to partition over 24 hours. Once suspended, 0.5 cm segments were sonicated and analyzed by Agilent 1260 Infinity High Performance Liquid Chromatography. Normalized applied mass percentages were calculated by comparison to pesticide standards that ran simultaneously with all samples. The majority of pesticides were found in the overlying water layer and within the first 0.5 cm of sediment. Salinity of the aqueous phase was shown to increase pesticide sediment concentration, but did not increase partitioning depth.

CHAPTER 1: INTRODUCTION

The United States Environmental Protection Agency (USEPA) is charged with regulating the use of pesticides within the United States. The transport of pesticides to non target locations is of great regulatory importance for the EPA. Highly mobile pesticides such as quinclorac and bentazon are a continual source of concern for ground and surface water contamination. The state of California banned the use of the rice herbicide bentazon, Trade name Basagran[®], because it was found in well water of ten counties in the northern and central parts of the central valley of California. The pesticide levels in the ground water were below 20 ppb, but the pesticide was still banned even though it was not a health concern. The Sacramento Valley, which is in the northern section of the central valley and where the major acreage of rice is located, contained the largest amount of contamination [1]. As new pesticides are introduced, pressure has mounted on regulatory agencies to develop ways of testing and evaluating the fate and transport of each pesticide. Testing of a new pesticide often includes laboratory leaching studies to determine the potential impact of a pesticide in terrestrial and aquatic system [2].

The EPA currently uses computer models to estimate pesticide behavior under differing environmental conditions. A tiered approach is used to determine the potential impact of a pesticide in aquatic ecosystems. The Exposure Analysis Modeling System (EXAMS) is commonly used to estimate the environmental distribution and overall persistence and fate in aquatic ecosystems. Currently EPA simulates pesticide behavior using a standard pond scenario in EXAMS based upon a 5 cm sediment partitioning depth [3]. This 5 cm depth was rather arbitrarily selected and not based upon any measurements. It may not be accurate for pesticides with lower mobility, higher soil affinity, and higher K_{oc} values. It would be more intuitive that a

strongly sorbed pesticide, such as the pyrethroid insecticide bifenthrin, would adsorb strongly to the soil, and remain closer to the water-sediment boundary layer. Pesticide exposure to benthic organism such as crawfish and other benthic dwelling aquatic organisms may be much higher than predicted if pesticides remain within the first 0.5 cm of sediment rather than even distributing over 5 cm.

The purpose of this investigation was to determine if a 5 cm depth is an appropriate depth estimation, or if a shallower depth is more accurate. Additionally salinity has been shown to impact pesticide physical-chemical properties (REF), with chemicals exhibiting decreased solubility and higher partitioning behavior into non-polar solvents in seawater vs freshwater. This could also impact a chemicals soil sorption and could be significant for chemicals entering coastal estuarine ecosystems. Thus an additional goal of this work was to estimate the impacts of seawater vs freshwater on pesticide partitioning to sediment.

CHAPTER 2: LITERATURE REVIEW

2.1 Regulatory History

Modern agricultural is dependent on the use of pesticides for sufficient agricultural production, which is essential to adequately feed the earth's growing population. The agricultural industry spends 8 billion dollars annually on pesticides, accounting for 70 percent of the United States pesticide usage. Pesticide use has increased dramatically over the last 60 years and currently ranges between 700 and 780 million pounds annually. Agricultural and residential usage accounts for the majority of the agrochemical market and pesticides are used extensively on high value crops such as cotton, soy, or rice. The US accounts for 32 percent of the global pesticide market with annual spending of approximately 12.5 billion dollars [4].

At the end of the 19th century environmental concern about chemical use was low as the chemical revolution took hold in agriculture. The earliest laws were designed to protect the consumer from products that made fraudulent claims of efficacy; they insured the products people were purchasing contained the actual pesticide chemicals at the levels stated on the label. Products such as lead arsenate that were very efficacious yet highly toxic to humans were heavily used during this period. When DDT was first introduced in the early 1940s it was declared safe for humans if used according to the label, but had disastrous environmental effects on avian populations, particular raptor species. As a result, environmental awareness became more mainstream as books such as *Silent Spring* grew in popularity. This resulted in the first laws in the late 1960s that required pesticides to be tested for environmental behavior and to be registered for use by the US EPA prior to their sale. However these early regulations were found not to be sufficient as methods of detecting the concentrations of organochlorine insecticides were developed and these chemicals were found in surface water and groundwater in the 1960's.

This early chemical testing confirmed that pesticides were transported from the site of application through water runoff and other mechanisms to non-target aquatic systems. Bioaccumulation of organochlorine insecticide residues in bird tissue were also present at detectable levels at that time, and provided proof that widespread pesticide usage had unintended consequences.[5]

A focus on surface water and groundwater contamination began in earnest in 1979. The EPA began to monitor ground water, and 38 states reported suspected groundwater contamination due to agricultural pesticide use in 1985. Atrazine, a herbicide, was found to be a significant source of groundwater contamination between 1980 and 1990. As environmental protections and human health concerns developed, laws such as the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) were amended to require more stringent testing for pesticide registration [6]. The new requirements forced manufactures to perform environmental assessments in order to continue to sell their products within the United States. These changes helped turn environmental protection mechanisms from reactionary measures, to preventive measures.

2.2 Pesticide Transport

Pesticides are often transported to non-target areas, which is problematic when trying to mitigate environmental impact. Major mechanisms for transport include volatilization, runoff, leaching, and drift. The extent of transport is affected by a pesticide's properties such as soil adsorption affinity, water solubility, vapor pressure, and degradation rates.

Volatilization occurs when the pesticide undergoes a phase change to gas. Pesticides with low vapor pressures are more susceptible to volatilization than pesticides with higher vapor

pressures. Runoff is the horizontal movement of water over land and occurs when the water holding capacity of the soil is exceeded. The holding capacity of soil depends on several factors such as soil type, texture, and the local terrain. As water moves over land, dissolved or adsorbed pesticides in water or sorbed onto soil particles, are transported to water bodies. Leaching is the vertical movement of water through soil. Groundwater contamination can occur for highly water soluble pesticides that do not easily adhere to soil particles.

Soil characteristics influence pesticide transport also. These properties include pH, soil moisture holding capacity, organic content, and texture. Soils with higher clay content have more surface area for pesticide adsorption. Coarser soils with high sand content are more permeable and encourage percolation. Pesticides soil penetration increases as water moves downward. Surface runoff near time of pesticide application can account for approximately 70% of pesticide loss [7,8].

Soil properties are an important factor in determining the strength of pesticide adsorption. The pH of the soil can either encourage or discourage the adsorption of the pesticide by changing the equilibrium between the protonated or deprotonated form [9]. Sediment adsorption is strongly influenced by functional groups of the pesticide. Cationic functional groups help bind the pesticide to the soil, while anionic functional groups cause the pesticide to be poorly bound by sediment unless positively charged colloids are present. Neutral functional groups lead to weakly bound pesticides that often concentrate near the sediment surface [10].

2.3 Degradation

Degradation occurs when pesticides are broken down from their parent compound into various products. This process can take place via several different abiotic and biotic mechanisms. The three main pathways include, chemical, microbial, and photochemical degradation [11]. Chemical degradation includes hydrolysis, oxidation, and reduction of the parent compound without the aid of microbial organisms. Microbial degradation can be similar to chemical degradation, but the oxidation and reduction occurs via microbial metabolism of the parent compound [12].

2.3.1 Fate in Aquatic Systems

Many non-target species are exposed to pesticide residues transported from the site of application by runoff water. When introduced into an aquatic system either indirectly or intentionally as in the case of aquatic use pesticides (e.g. rice herbicides), pesticides partition between sediment and water based upon the pesticide's soil adsorption distribution coefficient (K_d). This term is often corrected to the soil's organic matter or organic carbon content (K_{oc}). The concentration of pesticide that resides in the sediment versus the water is determined by complex factors unique to each soil/sediment such as its pH, cation exchange capacity, moisture, and soil type as well as others characteristics. Generally, a pesticide with a higher organic carbon adsorption coefficient (K_{oc}) will be more hydrophobic and adsorb into the soil more readily, primarily through van der Waals and other non-polar, non-covalent forces. However ionizable compounds can bind through ionic interactions. Soil organic matter is dominated by acidic functional groups and thus has an overall negative charge. Anionic compounds such as phenols and carboxylic acids will be repelled by these and bind less strongly than cationic compounds such as quaternary ammonium herbicides.

2.4. The Soil Sorption Coefficient/Distribution Constant

Pesticide fate is determined in the sediment after it has been applied to crops. Partitioning occurs between the solid and aqueous phases of the sediment once pesticides are transported. How a pesticide partitions in the soil is vital to determining its environmental persistence, ability to transport, and how effective the chemical is as a pesticide. Pesticide partitioning has been studied for many years with varying amounts of success [13,14]. Accurately calculating a pesticides distribution is not readily estimated due to the myriad of interactions between the gels, biota, and solutes of the aqueous phases and the varying particles types and sizes of the solid phases. Therefore an empirical measurement must be made for each soil type to determine its K_d [15,16].

The sorption coefficient that describes pesticide partitioning in sediment is denoted as K_d , with d as distribution. K_d is measured in a batch slurry containing the sediment and an aqueous phase, usually water, and may contain CaCl_2 in order to prevent mineral imbalance. The flask is gently shaken and allowed to sit between 2 and 48 hours. The aqueous phase is then analyzed in order to determine the K_d . The sediment can also be analyzed in order to ensure mass balance. K_d follows the equation $K_d = \frac{x/ms}{C_e}$ [17].

Pesticides with a high K_d value tend to be hydrophobic, non-polar, and bioconcentrated, suggesting that organic matter is the main absorbent in sediment. The organic matter in soil is not directly measured. The organic carbon in the soil is measured through combustion or digestion techniques. This value is known as the K_{oc} and is the organic carbon coefficient. K_d

and K_{oc} are related via the following equation: $K_{oc} = \frac{K_d}{F_{oc}}$. The K_{oc} value is a coefficient that allows for the calculation of K_d of any soil by knowing its organic carbon fraction (F_{oc}) [18, 19, 20].

2.4.1 K_{oc} and Salinity

The K_{oc} is a measurement of the soil/sediment solubility of a particular chemical; little research has been done to determine if K_{oc} is affected by salinity. Other published works have shown that the octanol water coefficient (K_{ow}) may be influenced by salinity, but these studies have not been done for K_{oc} [21,22,23]. Current computer models are specific to freshwater systems, and do not take into account estuarine environments that are highly susceptible to agricultural pollutants. K_{oc} and K_{ow} are correlated by the equation:

$$\log K_{oc} (L\ kg^{-1}) = 0.8679 \log K_{ow} - 0.0004 \quad [24]$$

Biphenol A (BPA) was shown to have an increase in K_{ow} as salinity increased. Bioaccumulation of BPA also increased as salinity was increased in the aqueous phases [25]. It stands to reason that K_{oc} would also increase since the two measurements are correlated. This increase in K_{ow} would greatly affect the environmental persistence and degradation rates of pesticides as greater concentrations would be found within sediment and marine organisms.

2.5 Exposure Analysis Modeling System

The Environmental Protection Agency (EPA) has an obligation to protect the environment of the United States of America. Pesticides are regulated by EPA through the Office of Pesticide Programs and Toxic Substances (OPPTS) and the environmental assessments of pesticide environmental fate data submitted by pesticide registrants in support of their registration or reregistration are conducted by the Environmental Fate and Effects Division

(EFED) of EPA. This division (EFED) uses several exposure simulation models to help predict the effects of various pollutants during the regulatory risk assessment analysis process [3]. While restoration of damaged environments is important, prevention and mitigation can often be more beneficial and practical.

The EFED has several different computational models that combine physical and chemical data to predict exposure. Not all pesticides require the same amount of regulatory oversight. In order to determine what model is appropriate and eliminate undue regulatory burden, the EFED has developed a tiered system for modeling. If a pesticide passes the first tier, then further regulatory investigation is not required. Failing a tier does not necessarily mean that a pesticide will fail registration, but rather there is more environmental concern, and more investigation is required [3]. The EFED uses GENEEC2 [26] and FIRST for Tier I analysis of pesticides. Tier I models are more simplistic and more conservative in the exposure estimates in order to screen pesticides for further analysis. If a pesticide fails Tier I analysis, then Tier II analysis takes place.

One model used by the EPA to predict synthetic organic chemical fate, transport, exposure, and concentration is the Exposure Analysis Modeling System (EXAMS). EXAMS is a Tier II exposure model that simulates pesticide concentration and exposure in surface water and aquatic ecosystems. The EXAMS exposure model is made up of process modules that estimate exposure by modeling fundamental chemical properties of the pesticide and combining them with limnological processes that control the fate and transport of chemicals in an aquatic environment [27, 28, 29]. EXAMS has been instrumental in preventing environmental disasters due to overexposure in vulnerable environments by modeling the complex interactions between a contaminant and the lithosphere, hydrosphere, and atmosphere.

The Pesticide Root Zone Model (PRZM) is a compartmental model that simulates pesticide movement through unsaturated soils such as an agricultural field. PRZM deals with the soil at the surface and extending down to through and just below the root zone [30, 31, 32], [Figure 2.1].

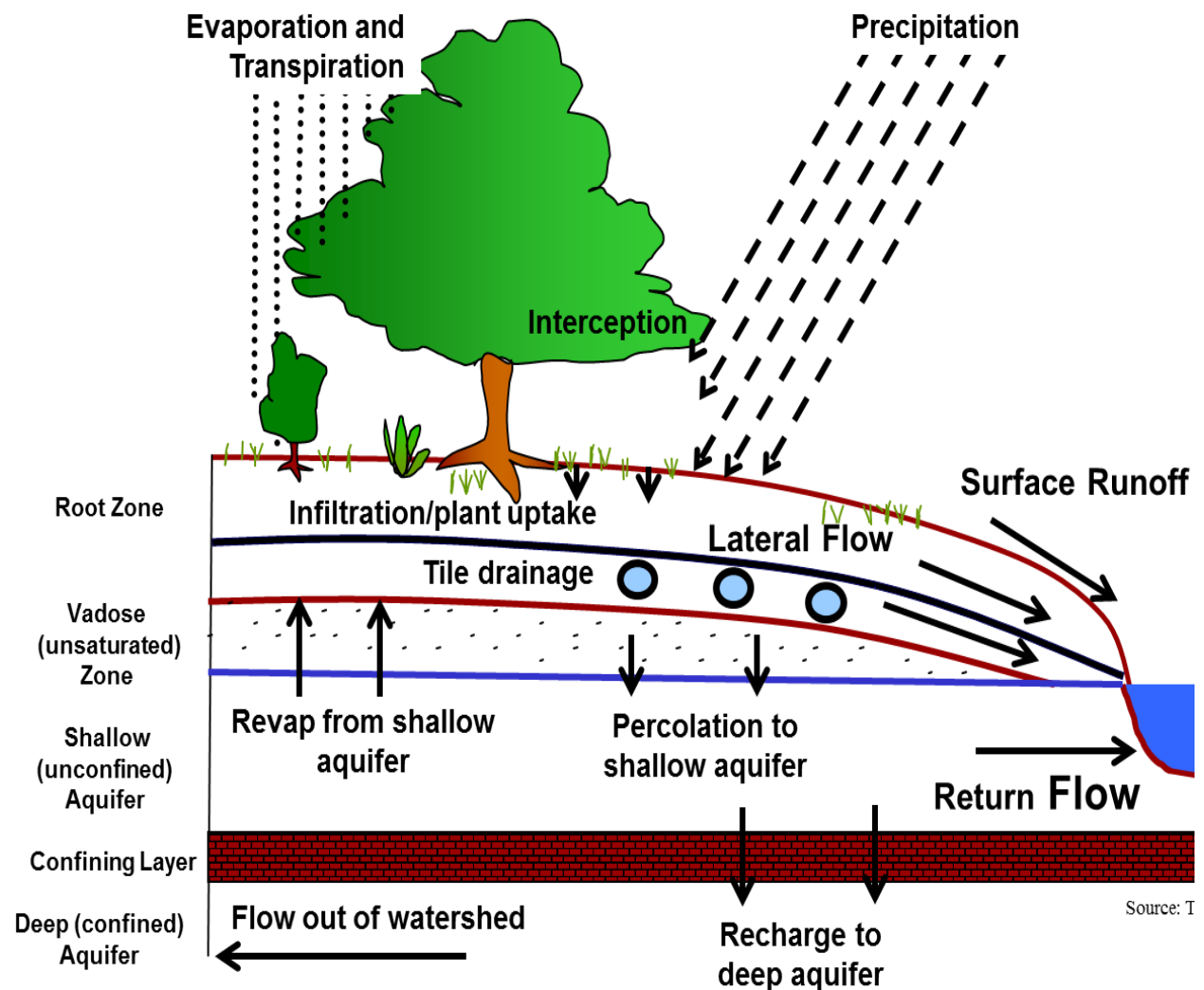


Figure 2.1. Conceptual model of run off from land into a water body. This is a similar scenario for the Express Shell composed of EXAMS and PRZM.

2.5.1 Standard Farm Pond Scenario

EXAMS and PRZM are combined in order to simulate an agricultural field that drains into a fresh water body. PRZM describes the pesticide transport from the agricultural field, while EXAMS determines the pesticide concentrations in the sediment and water based upon equilibrium and degradation processes in each phase after the water body is exposed to agricultural runoff [Figure 2.2]. The combination of the two modules is referred to as EXPRESS and often used in a standard farm pond scenario. This scenario simulates a farm pond surrounded by 10 hectares of crops. The pond is dosed with pesticides as residue is washed into the pond from simulated rain. The standard farm pond is assumed to have a one hectare area and a 2 meter water depth and a sediment depth of 5 centimeters. The standard farm pond scenario assumes that once equilibrium is achieved, pesticides will partition evenly down the 5 centimeter sediment depth. The assumptions of partitioning depth and concentration are not based on experimental data, but on sediment testing apparatus used during field studies. These assumptions are particularly absurd when accounting for the high variability of K_{oc} for pesticides. A low K_{oc} , highly mobile pesticide would not be expected to have the same partitioning as an immobile pesticide such as Trifluralin.

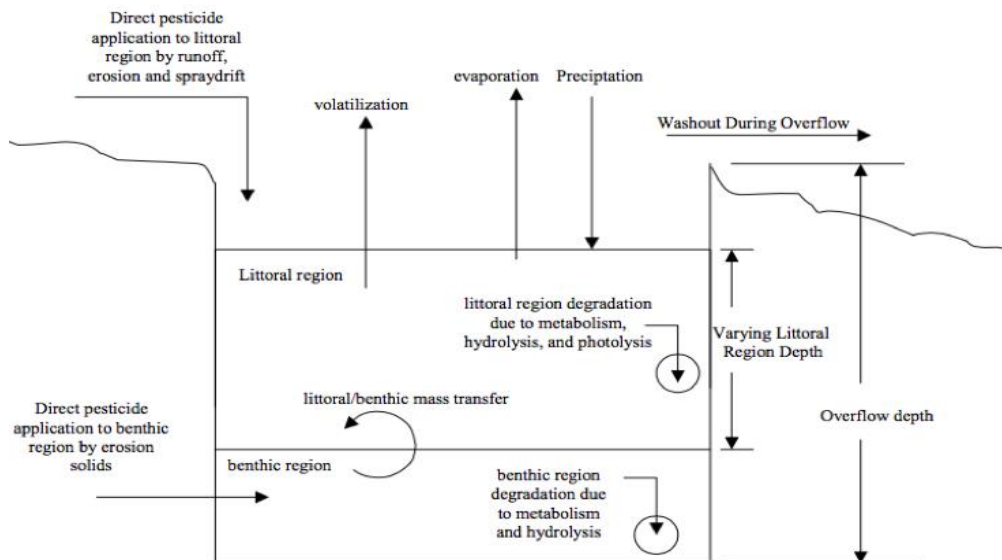


Figure 2.2. Complex environmental interactions EXAMS models to determine regulatory concern for a pesticide.

2.6 Pesticides

Pesticides were selected for this research based on a number of different criteria. A wide range of K_{oc} values were used in order to represent a range of sediment mobility. Another concern for selection was that the pesticides be sufficiently stable in order to last the duration of the experiment. Therefore half-lives of several days or longer were necessary for selection. The last criteria was that the pesticide have a strong response to UV detection during HPLC analysis.

2.6.1 Quinclorac

3,7-Dichloro-8-quinolinecarboxylic acid (Quinclorac) is a substituted quinolinecarboxylic acid that is used as an herbicide. Quinclorac acts as a synthetic auxin that is absorbed through the foliage where auxin activity inhibits cell wall activity. Often Quinclorac is used on rice fields to eliminate monocot and dicot weeds. It is used to control pre and post-soil emergent weeds in the agricultural sector since many crops such as rice, rapeseed oil, and wheat

are tolerant to Quinclorac. Quinclorac has a K_{oc} of 50 and a pK_a of 4.34 at 25°C [31, 32].

Quinclorac is highly water soluble and therefore can be extremely mobile in aquatic systems. In theory, in highly acidic conditions Quinclorac will protonate and become less water soluble, potentially limiting its mobility. However since most waters range from pH 6-9, it will likely exist predominately in its anionic ionized state which would be more polar and thus more water soluble than its anionic state.

2.6.2 Bentazon

3-Isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2- dioxide (Bentazon) belongs to the thiadiazine class of pesticides. It is known for its contamination of drinking water due to high mobility and water solubility. Bentazon degradation in aquatic systems heavily favors photolysis, while soil degradation occurs via oxidative mineralization through microbial processes with CO₂ as the end product. Residues can be incorporated into the soil by organic matter such as humic acids, humins, and fulvic acids [35]. Bentazon has a low affinity for sediments with a K_{oc} range 13.3 -176 with some reports of K_{oc} as low as 0.176. [33,34]

2.6.3 Atrazine

1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine (Atrazine) is a triazine pesticide that is one of the most widely used in the US. Atrazine is often applied to corn due to its potential to increase crop yields by 1 to 6 percent [36]. Atrazine was banned in Europe in 2004 due to persistent ground water contamination. As late as 2001, atrazine was the most commonly detected pesticide found in US watersheds. Atrazine degrades in sediments through microbial degradation. The hydrolysis of the carbon-chlorine bond is proceeded by hydrolysis of the

isopropyl group and ethyl groups, leaving behind cyanuric acid. Atrazine has a pKa of 1.7 and a K_{oc} range of 100-129.6. [33,34]

2.6.4 2,4-D

2,4-Dichlorophenoxy acetic acid (2,4-D) is a pesticide developed during World War II. The pesticide has garnered controversy as a component of Agent Orange during the Vietnam era. However the controversy surrounding Agent Orange was not with 2,4-D, but with trace amounts of dioxin, a compound linked to birth defects and cancer, which were traced back to a manufacturing impurity in the second component in Agent Orange, 2,4,5-T (2,4,5-trichlorophenoxyacetic acid). 2,4-D is a phenoxyacetic acid that is highly water soluble with a relatively low K_{oc} range of 19.6 to 109.1 and a pKa of 3.4 [33,34]. 2,4-D is a selective herbicide that is able to eliminate most broad leaf weeds, without impacting the growth of cereal crops and grasses. 2,4-D is an effective herbicide as it acts as a synthetic auxin, and creates uncontrolled cellular growth in affected plants. Soil degradation of 2,4-D is primarily driven by microbial metabolism, but mineralization, photolysis, and other mechanism have also been suggested [37]. Leaching of 2,4-D does not occur often, but has been reported to leach to a depth of 30 centimeters [37]. Degradation is unlikely once leaching has occurred because microbes responsible for 2,4-D metabolism become less abundant as depth increases.

2.6.5 Dicloran

2,6-dichloro-4-nitroaniline (Dicloran) is a substituted aniline used as a pre and post harvest fungicide. It is applied to multiple crops including lettuce, celery, and grapes. Dicloran (DCNA) has low mammalian toxicity, but a high toxicity for fish according to the EPA reregistration. DCNA may cause skin sensitivity for workers that are exposed to it. Over 200,000 pounds of

DCNA are applied annually in the United States [38]. DCNA is expected to have some persistence when released into the environment. Soil mobility is limited, and half lives are longer under aerobic conditions. Aerobic mineral soils were reported to have a half-life of 6 to 18 months, while anaerobic sandy soils were reported to have a half-life of 24 to 36 days. Dicloran has a mid-range K_{oc} of 380 with no reported disassociation [33,34].

2.6.6 Flutolanil

N-(3-propan-2-yloxyphenyl)-2-(trifluoromethyl)benzamide (Flutolanil) is an antifungal pesticide that inhibits Succinate Dehydrogenase (Complex II) in eukaryotic and prokaryotic organisms [39]. The inhibition of this enzyme results in a disruption of the tricarboxylic cyclic and mitochondrial electron transport chains leading to cell death. Flutolanil can have negative effects on wetland sediments by inhibiting denitrifying bacteria present in the soil [40]. Flutolanil is a highly non polar pesticide with a high K_{oc} range of 500-2000 [33,34]. No dissociation is reported for this pesticide.

2.6.7 Trifluralin

2,6-Dinitro-*N,N*-dipropyl-4-(trifluoromethyl)aniline (Trifluralin) is dintroaniline that is highly non-mobile and moderately persistent in the environment. It is a selective pre-emergence pesticide first registered in the United States in 1963. Trifluralin has a K_{oc} range of 3900-15800 and no reported dissociation [33,34]. Ground water issues associated with highly immobile, water insoluble pesticides such as this are less of a regulatory concern due to its high soil affinity. Trifluralin is non-toxic to birds and mammals at acute dosages. However, chronic dosages studies have shown to cause egg shell cracking in birds. Aquatic organisms are more susceptible to trifluralin with toxicity ranging from moderate to high. Some species of fish may

be at an even greater danger as toxicity studies did not account for sediment and water column equilibrium.

Trifluralin is usually persistent when released into the environment under anaerobic conditions. Trifluralin is not susceptible to leaching, but can move away from the target area via adsorption to particulates carried with runoff during a rainstorm event. Trifluralin is capable of degradation by Fe(II) as Fe(II) acts as an electron donor for the degradation of trifluralin. Degradation can also occur by photolysis and microbial action under anaerobic conditions by transforming the nitro groups into amines [41,42]. Degradation of trifluralin is reduced in the presence of oxygen and nitrates [43]. The manufacturer's label states that trifluralin should not be used on saturated anaerobic soils due to the inhibition of its herbicidal properties [44].

CHAPTER 3: MATERIALS AND METHODS

3.1 Materials

3.1.1. Chemical Reagents and Supplies

Analytical grade 3,7-Dichloro-8-quinolinecarboxylic acid (Quinclorac), 3-Isopropyl-1*H*-2,1,3-benzothiadiazin-4(3*H*)-one 2,2- dioxide (Bentazon), 1-Chloro-3-ethylamino-5-isopropylamino-2,4,6-triazine Atrazine, (2,4-Dichlorophenoxy)acetic acid (2,4-D), 2,6-dicloro-4-nitroaniline (Dicloran), N-(3-propan-2-yloxyphenyl)-2-(trifluoromethyl)benzamide (Flutolanil), and 2,6-Dinitro-*N,N*-dipropyl-4-(trifluoromethyl)aniline (Trifluralin) were purchased from Chem Service (West Chester, PA). High performance liquid chromatograph (HPLC) grade acetonitrile was purchased from Fisher Scientific (Pittsburgh, PA) and HPLC grade water was purchased from J. T. Baker (Center Valley, CA). Both were used as eluents for HPLC analysis.

Borosilicate clear glass vials (2 ml) were purchased from Agilent Technologies, and were used for all samples. Polytetraflourene (PTFE) filters were used on all samples to remove potentially harmful sediments before analysis. The filters were purchased from Cole-Parmer (Vernon Hills, IL). Teflon tubes (150 mL) were purchased from Savillex (Eden Prairie, MN). Instant Ocean (Blacksburg, VA) was used to make salt water at a concentration of 35 ppt and was purchased from local retailers.

3.1.2 Soils and Sediments

Soils used for partitioning experiments were obtained from locations around Louisiana. Wetland soil was obtained near the Dixon correctional facility (latitude 30 15'31.07 N, longitude, 91 02'57.70 W elevation 11ft). Rice field soil was obtained from a commercial field at Gueydan, LA (latitude 29.9926 N, longitude: -92.474738 W) during a fallow period after harvest and prior to field preparation for the next season. All sediment samples were characterized by Agvise

(Northwood, ND) using the Series I analysis methods. No sediments were sterilized during this experiment since all pesticides chosen had minimal degradation within a 24 hour period in both aerobic soil metabolism and aerobic aquatic metabolism studies submitted by pesticide registrants in support of their registration [45]. The two sediment types from a local wetland and rice field and were characterized by measuring clay, silt, sand, organic matter, pH, and cation exchange capacity [Table 3.1].

Table 3.1. Wetlands and Ricefield Soil Characteristics

Adsorbent	Texture	Clay%	Silt %	Sand %	O. M. %	pH	CEC
Wetlands	Clay	65	14	21	5.7	6.7	68.2
Ricefield	Loam	27	40	33	2	6.6	13.7

3.2 Methods

3.2.1. Pesticide Partitioning in Wetland and Rice Field Soils

The goal of this design was to determine if pesticides applied to water partitioned only within the top-most layer of underlying sediment or uniformly across a 5 cm depth as assumed by current regulatory exposure modeling scenarios. This type of situation occurs in the environment when a pesticide directly enters a water body as in the case of rice pesticides or runoff from a treated area into an aquatic ecosystem. In addition, chemical partitioning to sediment could be enhanced in a marine ecosystem as pesticide solubility could be reduced by salinity and thereby creating a driving force into sediment. Thus an additional goal was to determine if seawater would increase the amount of pesticide present in the sediment. Pesticides were injected into an upper layer of water and allowed to partition to underlying sediment in a

column with no downward movement over a 24 hour period. The pesticides were chosen to cover a range of soil sorptive properties and also on the basis of initial stability over a 24 hour period and water solubility.

Stock solutions (2000 ppm) of Quinclorac, Bentazon, Atrazine, 2,4-D, Flutolanil, and Trifluralin were used for all standards and pesticide partitioning experiments. A 1000 ppm stock solution was created within acetonitrile for Dicloran and was used in the same manner as the other stock solutions.

All sediment cores were created by saturating sediment with water for a 24 hour period prior to the addition of sediment to tubes. Approximately 130 ml of sediment with 20 ml of water on top of the sediment was placed into each Savillex 150 ml Teflon tube. Settling was allowed to occur over a 2 hour period, and then 100 μ g of each pesticide were added via a 50 μ l syringe. Each pesticide was injected onto the top water layer of each sediment core. Pesticides were present together in all cores. Trifluralin was run separately with atrazine since it was selected at a later date for its exceedingly high K_{oc} value. At these dosing levels, all chemicals other than trifluralin would be below their reported aqueous water solubility limits. The dosing limit for trifluralin in this experiment would have exceeded its reported aqueous water solubility by roughly an order or magnitude, however in this design it would have created a stronger driving force to sediment and would be a worst-case scenario for sediment partitioning. The sediment cores were capped and allowed to equilibrate for 24 hours. After this period, the sediment cores were placed into a freezer in order to suspend pesticide partitioning. Once the cores were completely frozen, 5 cm of sediment was then measured and cut into 0.5 cm segments starting from the water-sediment boundary. The water layer was also analyzed in order to account for mass balance.

Five sediment core replicates were used for both wetland and ricefield sediment saturated with fresh water. Trifluralin was run separately since it was selected at a later date. Atrazine was also run with all trifluralin samples which accounts for the 10 replicates for Atrazine. Both Trifluralin and Dicloran had one replicate where no pesticide appeared when analyzed, which is why only 4 replicates were included for those pesticides. Three replicates were run for wetland sediment that was saturated with 35 ppt Instant Ocean Solution in order to determine if the salinity of water would impact pesticide partitioning.

3.2.2. Pesticide Analysis

Each 0.5 cm segment was placed into a 100ml beaker and allowed to thaw. Each segment was not weighed since calculations were done by volume, but all segments had an approximate 10g mass of sediment. After thawing 40 ml of acetonitrile was added and the sediment/solvent mixture was sonicated for 30 minutes. All samples were allowed to settle approximately one hour or less depending of sediment type then 1 ml of acetonitrile was then filtered with 0.45 μ m PTFE syringe filters, and promptly analyzed by HPLC.

HPLC methods varied depending on which pesticides were analyzed. Pesticides with dissociative properties were particularly responsive to a 40% acetonitrile, 30 %HPLC grade water, and 30% HPLC grade water containing a 1% formic acid solution that decreased their water solubility. The 23 minutes analysis method increased to 60% acetonitrile, 20% HPLC grade water, and 20% HPLC grade water containing 1% formic acid. Pesticides analyzed with the use of formic acid were Quinclorac, Bentazon, 2,4-D, and Dicloran. This increased the analysis time significantly and provided better peak separation. Atrazine and Flutolanil were analyzed in a 40% acetonitrile, 60% HPLC grade water mobile phase. Separation occurred using a Zorbax Eclipse Plus C-18 4.6x150 mm 5 micron analytical column. Pesticides were detected

by using a photodiode array detector at wavelengths of 254 nm, 280 nm, and 380 nm.

Quinclorac, 2,4-D, and Flutolanil applied masses were calculated using the 280 nm wavelength while bentazon, atrazine, and trifluralin applied masses were calculated at 254 nm. Dicloran applied mass was calculated at 380 nm.

The efficiency of the extraction method was tested by adding 100 ug of each pesticide to a 0.5 cm segment of 10g wetland sediment. Calculations of applied mass were performed following the same procedure previously listed. Recovery Data is shown in Table 4.1.

3.3 Data Analysis

Data was analyzed using Agilent OpenLab software. Integration was performed automatically for the majority of peak areas; occasionally a manual integration was required in order to analyze smaller peaks. Peak areas were compared to pesticide 2.5 ppm standards that ran simultaneously with each sediment core. Linear response was shown for the Agilent 1260 Infinity for levels appropriate to the study. Pesticide concentrations and percentage of applied mass were calculated for each 0.5 cm segment of sediment core.

3.3.1 Statistical Analysis:

For each depth (water layer, 0.5cm, ...etc) a percent normalized applied mass was calculated and then averaged with other replicates for each individual pesticide. Applied mass percentages were then listed by depth for all sediment types and aqueous phases (Figures 4.1, 4.2, 4.3). The standard error was calculated for all values. Calculations were performed using Microsoft Excel 2016.

SAS version 9.4 was used for statistical analysis. A two sample t-test was performed to determine statistical significance for percent applied mass between each treatment pairs.

Treatments were water types and sediment types. Replicates within each pesticide dataset were determined whether or not to be outliers using a residual test.

CHAPTER 4: RESULTS

4.1 Recovery of Pesticides from Sediment

Pesticide recovery data was generated in order to validate extraction methods used during the experiment. Table 4.1 lists the pesticides with recovery percentages of applied mass. With the exception of quinclorac, all pesticides were recovered from sediment at greater than 75% efficiency. Quinclorac's recovery was slightly lower at 66% most due to the pesticide being mildly insoluble in acetonitrile since it was manufactured in salt form.

Table 4.1: Recovery data for each pesticide and the percentage of applied mass that was recovered.

Pesticide Recovery Data						
Quinclorac	2,4-D	Bentazon	Atrazine	Dicloran	Flutolanil	Trifluralin
66.31	76.96	95.41	97.39	99.38	93.62	84.94

4.2 Pesticide Partitioning in Wetland and Ricefield Sediment

In all cases the majority of applied mass was located within the water layer in all samples and pesticide partitioning was not observed below 2 centimeters. Of the applied mass that partitioned to sediment, the majority was found in the top 0.5 cm layer. Sporadically, certain pesticides such as dicloran would partition further than 0.5 cm, but this was not consistently observed in all sample replicates for a single pesticide..

As seen in figures 4.1 and 4.2 and 4.3, concentrations in sediment generally increased as K_{oc} increased. There was some variation in concentration that is readily explained with the wide

variations in reported K_{oc} . The relative percentage of pesticide applied to water that partitioned to sediment generally increased as the pesticide's K_{oc} increased. Organic matter in the sediment is known to be the main non-polar adsorbing surface and the data trends generally followed this assumption. Ricefield sediment had higher concentrations of polar, lower K_{oc} pesticides, while wetland sediment saw more adsorption of non-polar pesticides. The wetland sediment had approximately three times as much organic matter as the ricefield sediment. Trifluralin exhibited the strongest difference in adsorption between the two sediments.

K_{oc} is the soil adsorption coefficient (K_d) corrected for the organic carbon content of soil. It is recognized as an indicator of a pesticide's mobility in soil. The K_d value often positively correlates with soil organic matter content, but due to the complexity of sediment/pesticide interactions, it is not always linear. While there was some correlation in amounts of pesticides adsorbed to sediment as a function of their soil adsorption coefficient, there was no noticeable difference in partitioning depth. The majority of each compound remained in the top 0.5 cm layer or overlying water with each specific equilibrium varying by K_{oc} value.

Other factors may also influence pesticide sediment adsorption. Ligand interactions with pesticides are possible. Dicloran was consistently found in higher sediment concentrations than Flutolanil even though it has a lower average K_{oc} however each has reported ranges in K_{oc} values that do overlap. Dicloran has a K_{oc} range of 380 - 800, while Flutolanil is reported to have a K_{oc} range between 500 - 2000. These ranges show significant overlap and variability of K_{oc} values. For this reason it is not at all surprising that flutolanil may absorb less than dicloran.

Statistical analysis to determine significant differences between sediment types was performed for all pesticides, and only Bentazon was shown to have a significant difference in

percent applied mass in sediment. One replicate of the Bentazon sediment subset ($p=0.7512$, $\alpha=0.05$) was removed as an outlier after a test of residual. After removal of the replicate it became significantly different. There does appear to be a difference of percent applied mass between the sediment types based upon averages, but variability between replicates confounds any establishment of statistical significance.

Wetlands with Freshwater Normalized Applied Mass Percentage							
Depth	Quinclorac	Bentazon	Atrazine	2,4-D	Dicloran	Flutolanil	Trifluralin
	N=5	N=5	N=10	N=5	N=4	N=5	N=4
Water Layer	96.39 (2.39)	87.63 (5.60)	80.56 (7.45)	95.12 (3.15)	67.11 (7.35)	76.54 (8.22)	66.85 (5.40)
0.5 cm	3.61 (2.39)	10.04 (3.49)	14.38 (4.77)	4.88 (3.15)	28.45 (5.36)	20.70 (6.63)	33.15 (5.40)
1.0 cm	0	2.34 (2.34)	3.61 (1.96)	0	4.02 (2.17)	2.76 (1.69)	0
1.5 cm	0	0	1.44 (1.02)	0	0.42 (0.48)	0	0
2.0 cm	0	0	0	0	0	0	0

Figure 4.1. Wetlands/Fresh Water normalized applied mass percentage by pesticide and segment depth. N is the number of replicates performed for each pesticide. Standard error is given in parentheses below the applied mass percentage. Analysis was performed through 5 cm, but is not shown since no pesticides were observed.

Rice Fields with Freshwater

Normalized Applied Mass Percentages

Depth	Quinclorac	Bentazon	Atrazine	2,4-D	Dicloran	Flutolanil	Trifluralin
	N=5	N=5	N=10	N=5	N=5	N=5	N=5
Water Layer	96.54 (3.46)	80.08 (5.22)	81.07 (4.83)	91.64 (5.97)	67.12 (3.58)	71.21 (3.78)	84.63 (4.88)
0.5 cm	3.46 (3.46)	17.01 (4.53)	16.69 (3.97)	8.36 (5.97)	31.70 (2.99)	28.11 (3.78)	15.37 (4.88)
1.0 cm	0	1.82 (1.16)	2.24 (1.24)	0	1.17 (0.80)	0.68 (0.68)	0
1.5 cm	0	1.09 (1.09)	0	0	0	0	0
2.0 cm	0	0	0	0	0	0	0

Figure 4.2. Ricefield/Fresh Water normalized applied mass partitioning percentages for each pesticide and segment for ricefield sediment. N is the number of replicates for each pesticide and the standard error is given in parentheses. Analysis was performed through 5 cm, but is not shown since no pesticides were observed.

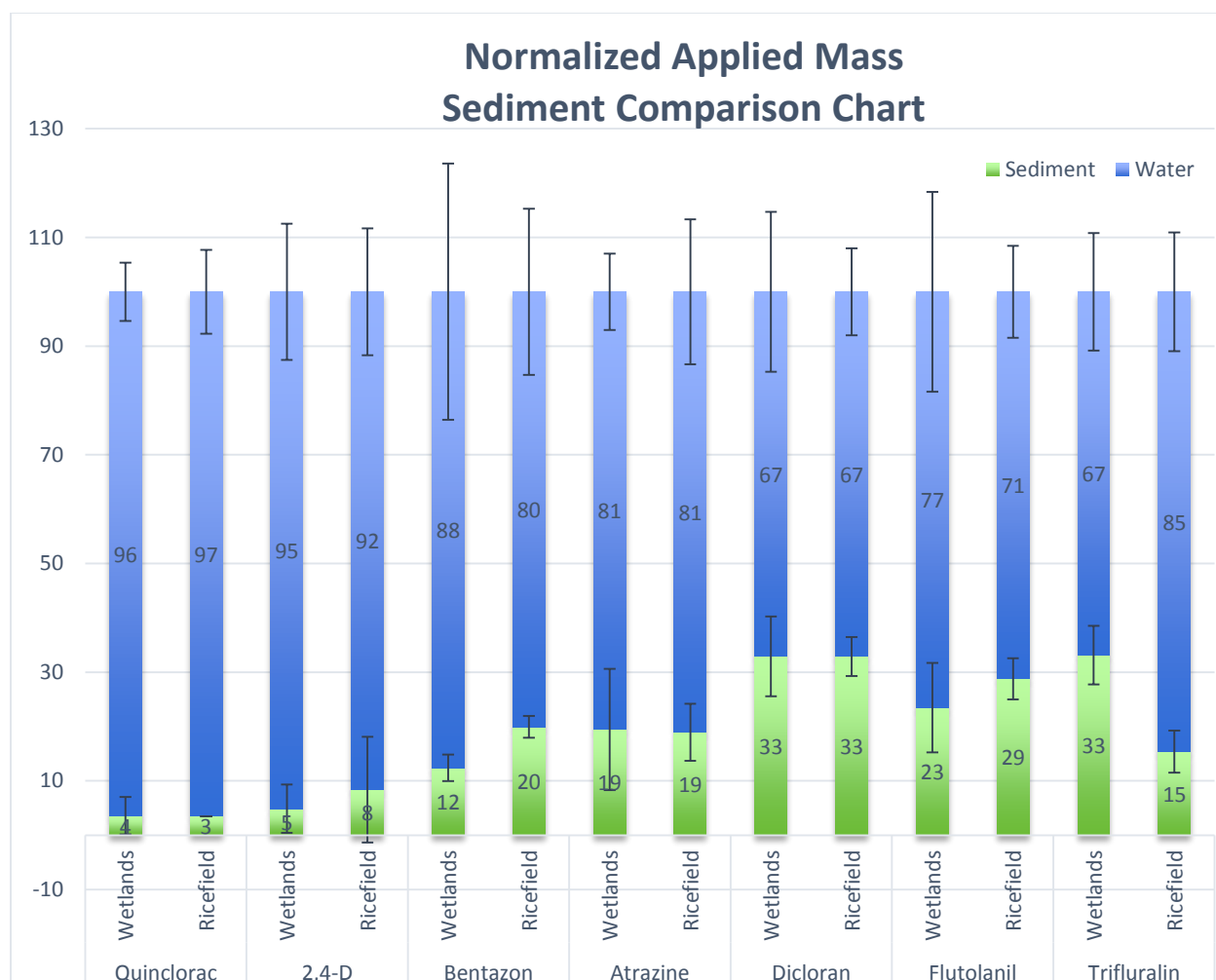


Figure 4.3. Normalized applied mass sediment comparison chart showing the normalized percent applied mass found in water and sediment for each sediment types. All segments are combined for each sediment type. There is slight variations between sediment, with the most pronounced variation from Trifluralin.

4.3 Impact of Seawater on Pesticide Partitioning in Wetland Sediment

Three replications were performed for each pesticide with seawater as the aqueous phase. As with the samples using freshwater, the overlying water contained the largest normalized applied mass percentages [Figures 4.4]. Salt water has a noticeable impact on the pesticide concentration found within the sediment [Figure 4.5]. All pesticides partitioned more into

sediment with overlying seawater, except for 2,4-D. No pesticide was observed to partition significantly beyond 0.5 cm.

The differences in percent applied mass were not significantly different for all pesticides except atrazine ($p=0.5853$, $\alpha=0.05$), which had one outlier of the water type subset removed by a test of residuals, and became significantly different afterwards. While there does appear to be a difference between aqueous phases, the variability in the replications likely makes statistical significance difficult to determine. More replications would likely allow for more detailed analysis.

Wetlands with Saltwater Normalized Applied Percentage							
Depth	Quinclorac	Bentazon	Atrazine	2,4-D	Dicloran	Flutolanil	Trifluralin
	N=3	N=3	N=6	N=3	N=3	N=3	N=3
Water Layer	85.81 (7.70)	76.63 (4.37)	71.53 (3.02)	100	65.48 (3.94)	76.15 (3.40)	50.37 (5.94)
0.5 cm	14.19 (7.70)	23.37 (4.37)	27.58 (3.34)	0	30.56 (3.82)	21.06 (4.76)	49.63 (5.94)
1.0 cm	0	0	0.89 (0.89)	0	3.96 (1.58)	2.79 (2.79)	0
1.5 cm	0	0	0	0	0	0	0
2.0 cm	0	0	0	0	0	0	0

Figure 4.4. Wetlands/Salt Water normalized applied mass percentages by pesticide and depth. Wetland sediment was used in order to best replicate an estuarine environment. N is the number of replicates and standard error is in parentheses. Analysis was performed through 5 cm, but is not shown since no pesticides were observed.

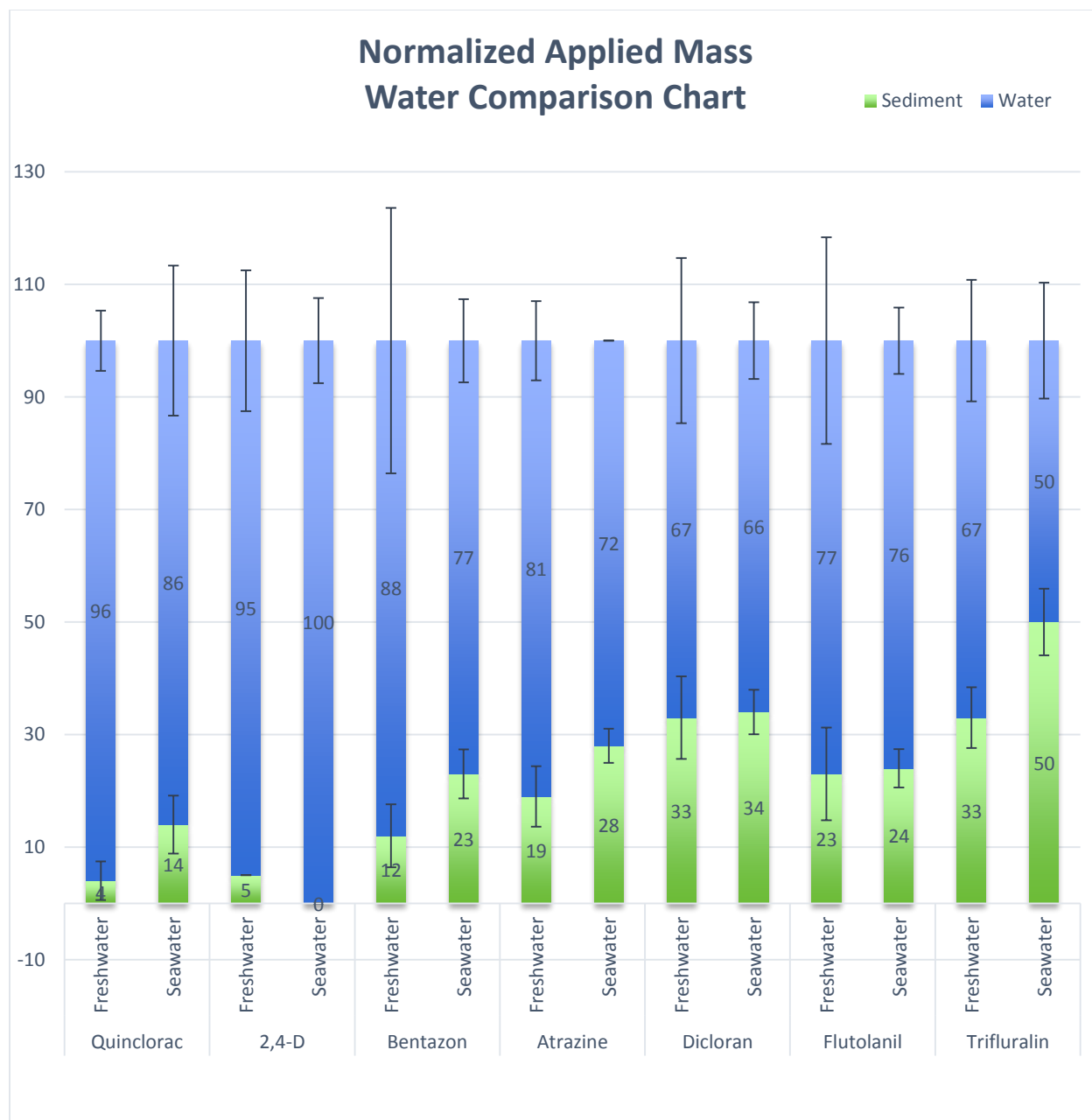


Figure 4.5. Aqueous phase comparison chart for fresh and sea water. Wetland sediment was used in all replicates. Concentrations for sediment were combined at all depth. This figure implies that sea water increases sediment forcing for pesticides.

Figure 4.6. suggests that seawater likely impacts soil absorptivity, however additional work would be needed to further explore this relationship. First, K_{oc} values would need to be measured in salt water for each pesticide since K_{oc} has wide variability even among soil/sediment types. Additional soils with varying characteristics, especially soil pH, organic carbon content and cation exchange capacity would need to be tested as well. Further research into this relationship would help to accurately model pesticide contamination in sensitive estuarine environments where mitigation and prevention are necessary.

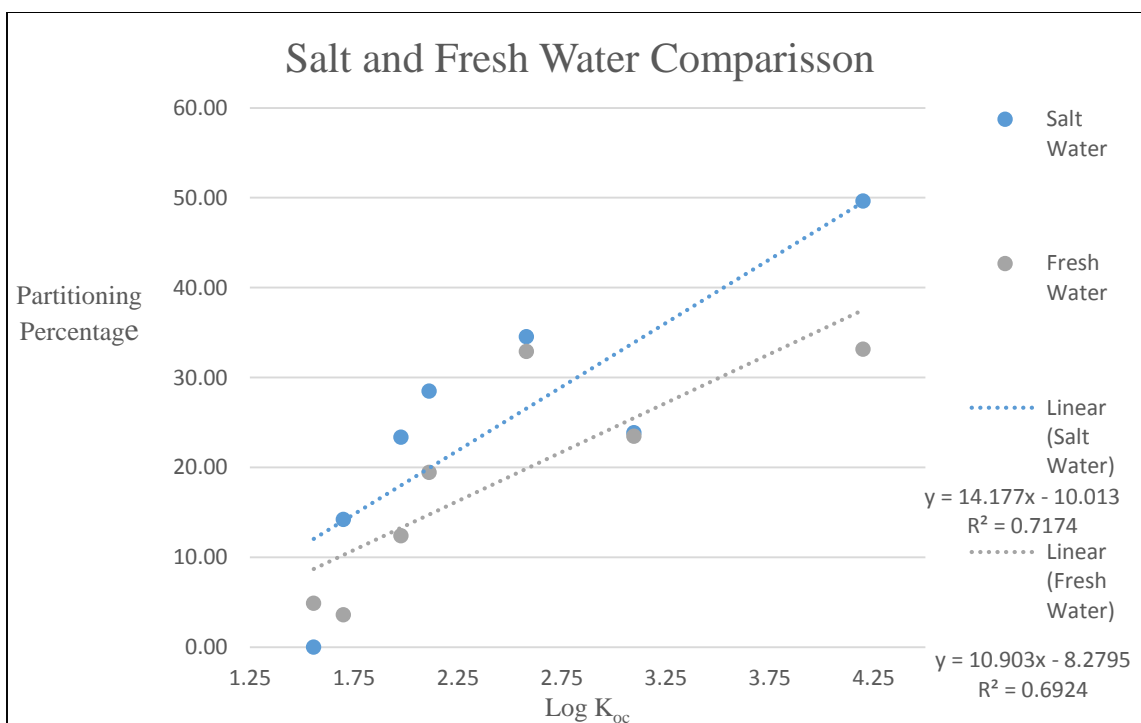


Figure 4.6. Aqueous phase scatter chart showing concentration for fresh and sea water. Sea water had an increase in pesticide concentration. All pesticides are plotted using literature K_{oc} values. Linear trend line equations and R^2 values are listed in the legend.

CHAPTER 5: CONCLUSION

The focus of this research was not to disprove that pesticides are able to migrate through soil, but rather to determine if pesticides partition only into the top most layers of sediment or uniformly across a 5 cm depth with a 24 hour period after application. . What has been shown through multiple sediment types and aqueous phases is that the assumption of even distribution over 5cm by current computer modeling is inaccurate. This inaccurate assumption can have significant impact on bioaccumulation, pesticide fate, and environmental persistence.

What has been shown is that the majority of pesticide mass partitions to the top most (0.5 cm) layer during the first 24 hours, and even the most polar compounds do not partition significantly below this depth.. Differing the sediment type and the aqueous phase did not impact partitioning within this time frame either. A correlation of increasing sediment concentration and salinity was shown, but further research into defining that relationship is necessary. K_{oc} measurements for different sediments in sea water will most likely be necessary in order to define how salinity effects pesticide concentration. Further refinement of EPA computer modeling will likely need more research into both partitioning depth and variations of the aqueous phase.

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APPENDIX – SUPPLEMENTAL DATA

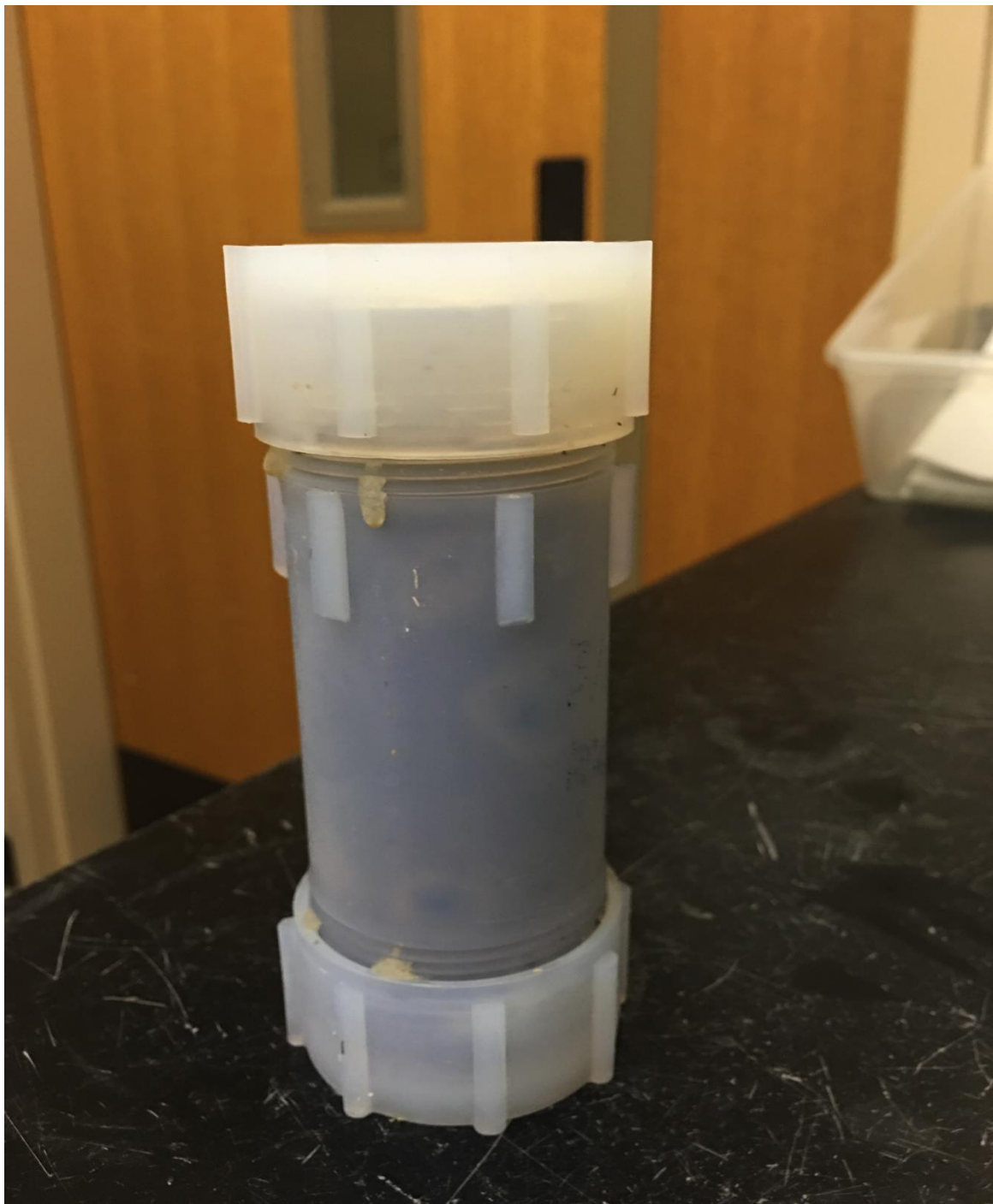


Figure A.1. Savillex sediment core in a 150 ml Teflon tube containing sediment and water.

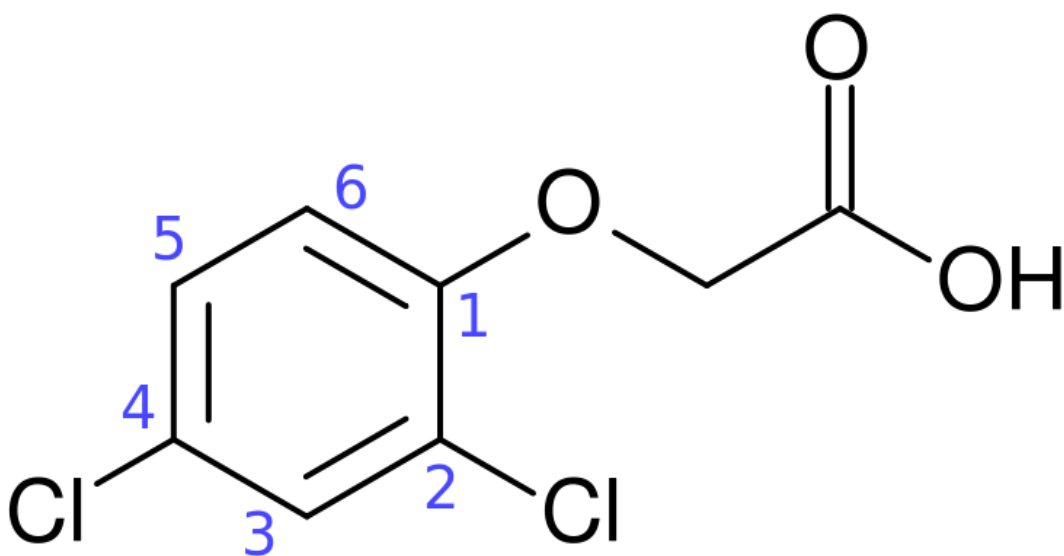


Figure A.2. 2,4-D Molecule

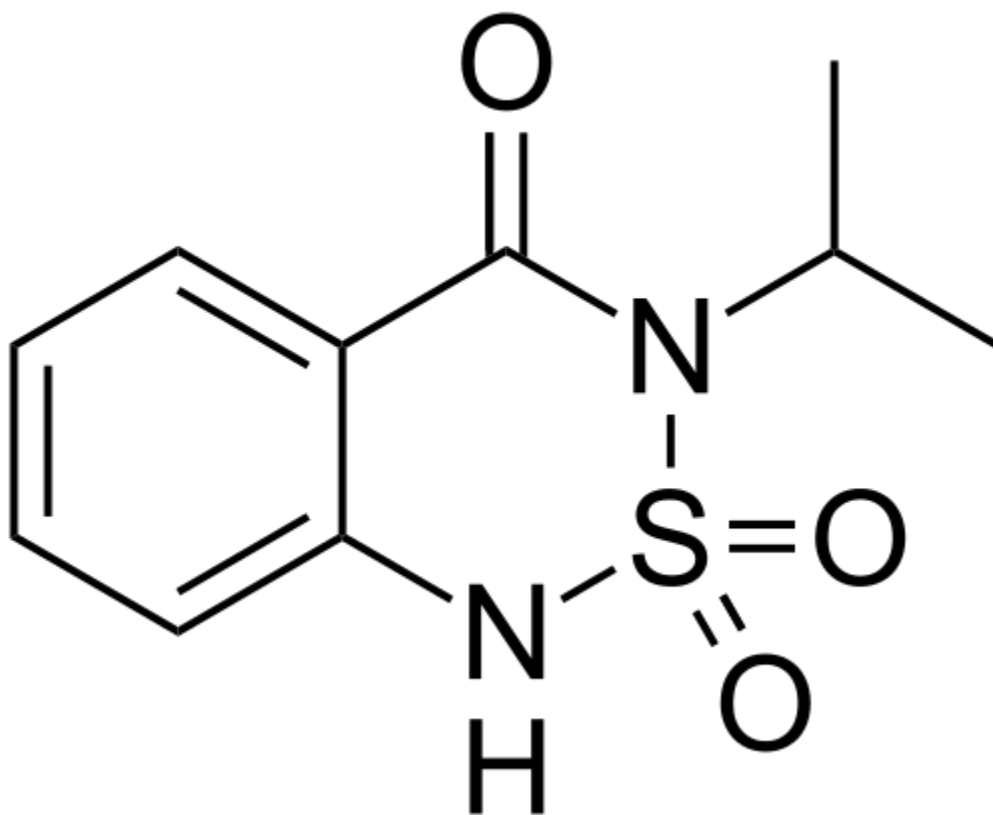


Figure A.3. Bentazon Molecule

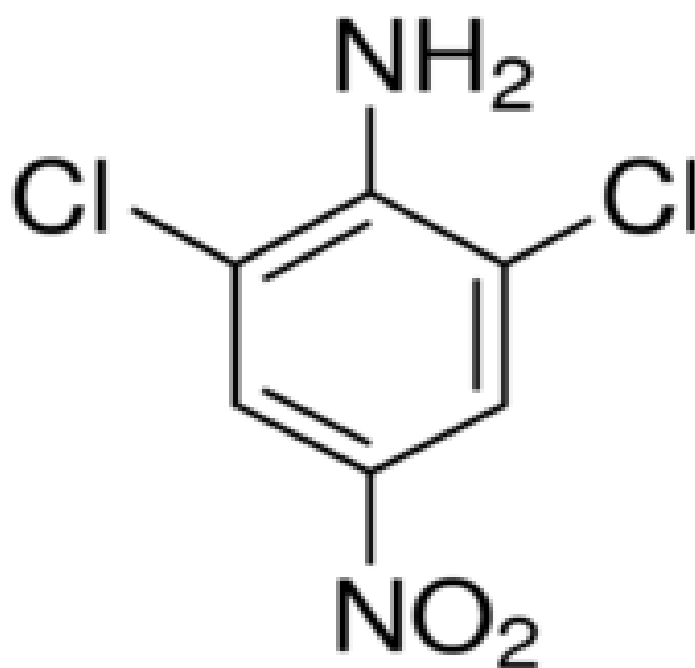


Figure A.4. Dicloran Molecule

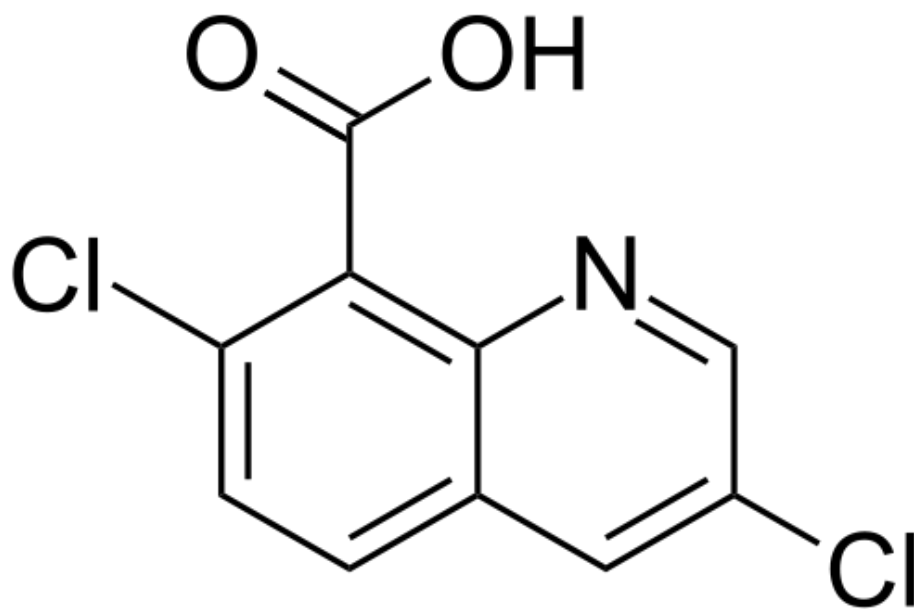


Figure A.5. Quinclorac Molecule

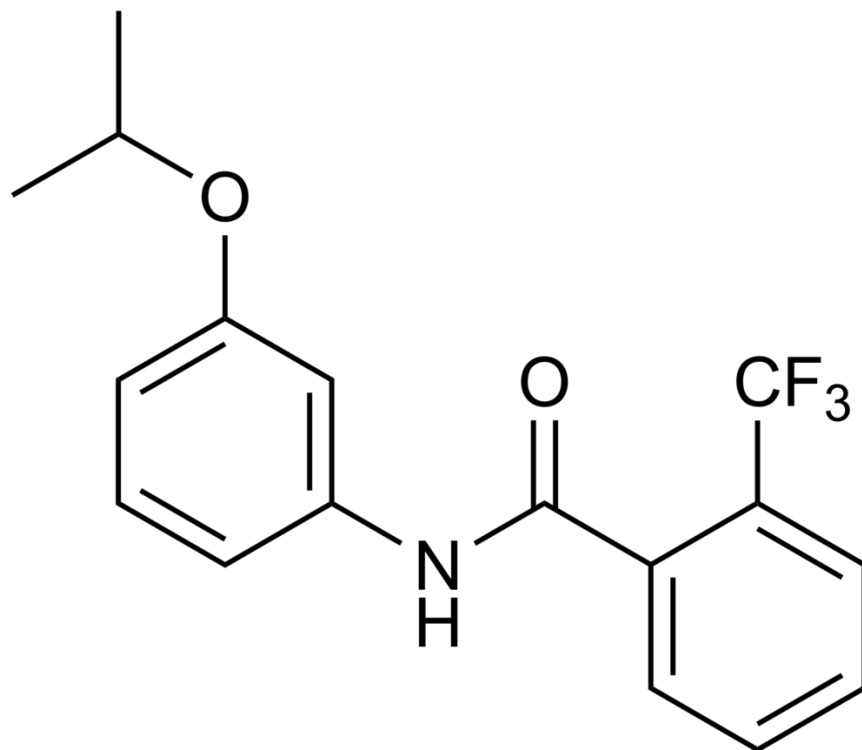


Figure A.6. Flutolanil Molecule

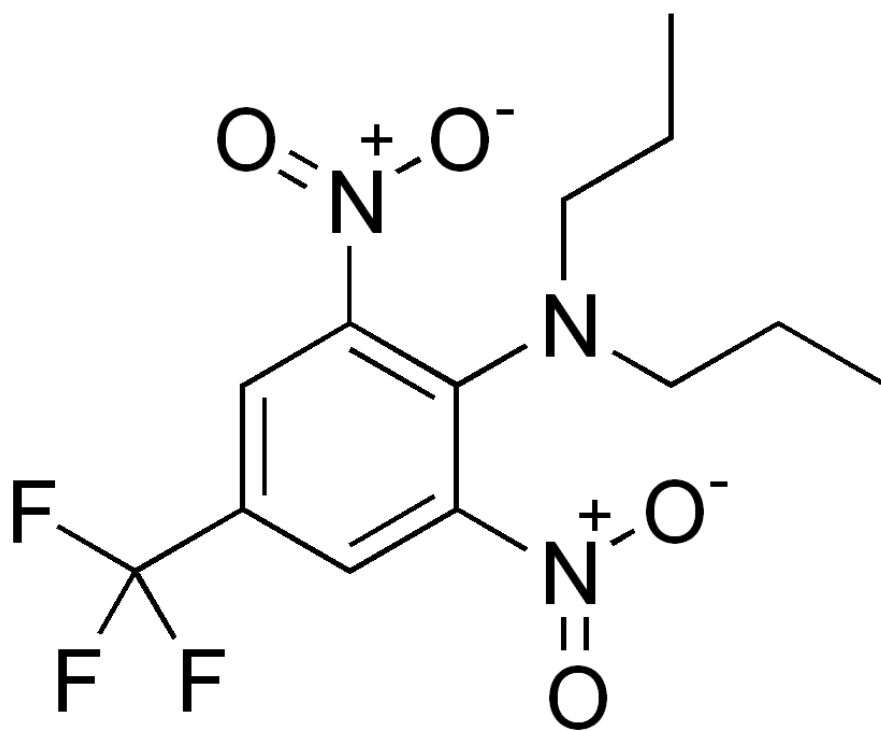


Figure A.7. Trifluralin Molecule

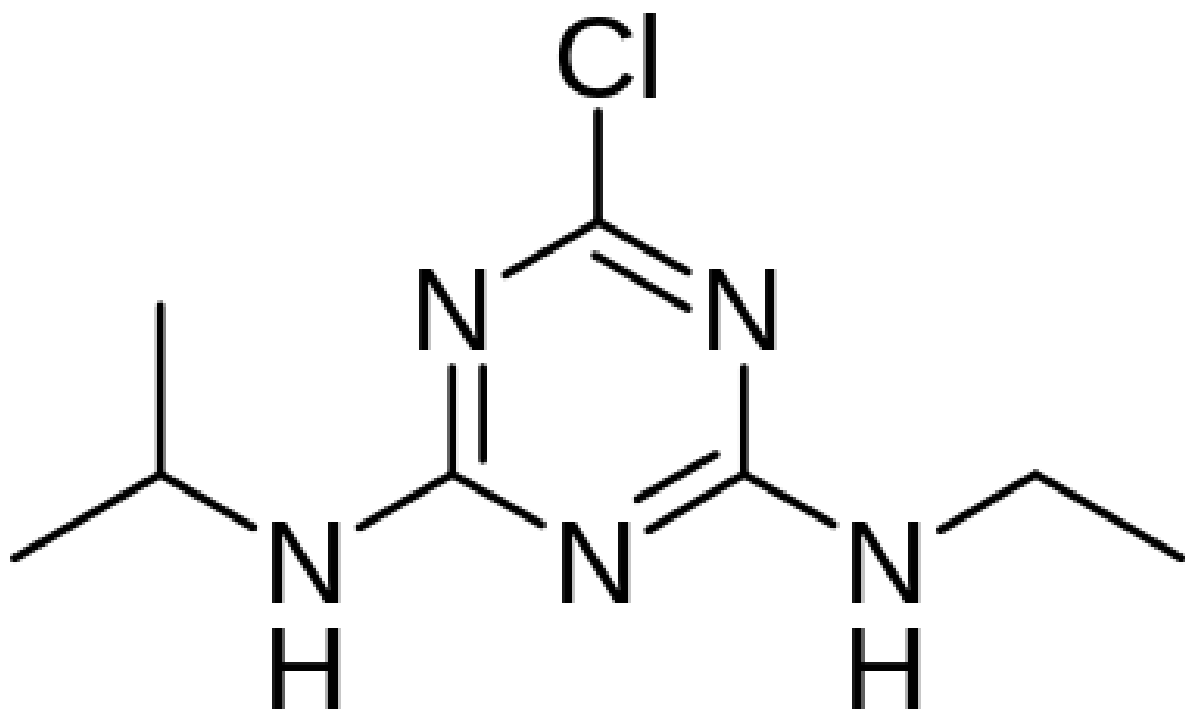


Figure A.8 Atrazine Molecule

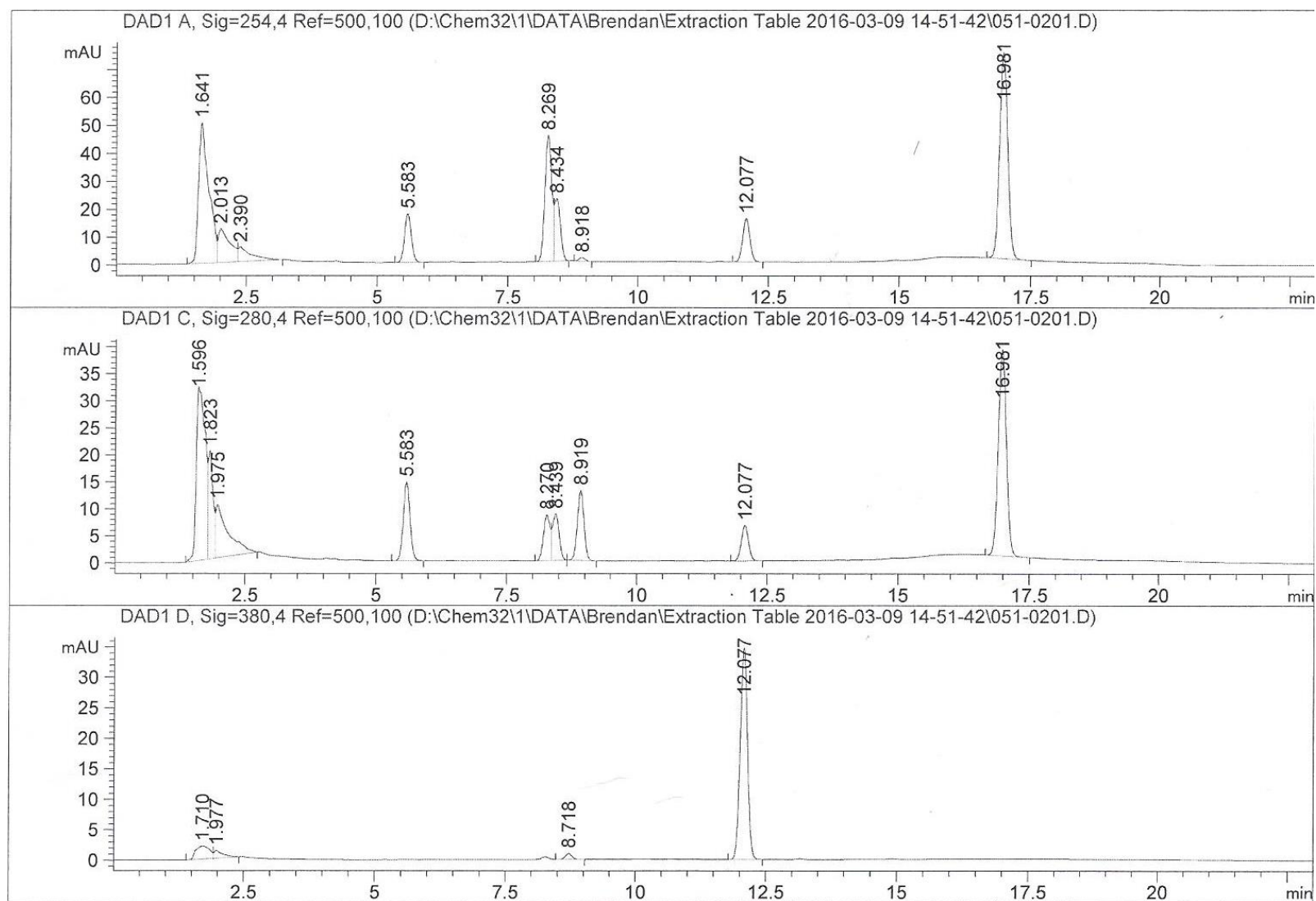


Figure A.9. The chromatograph of the water layer which contained the majority of pesticide mass.

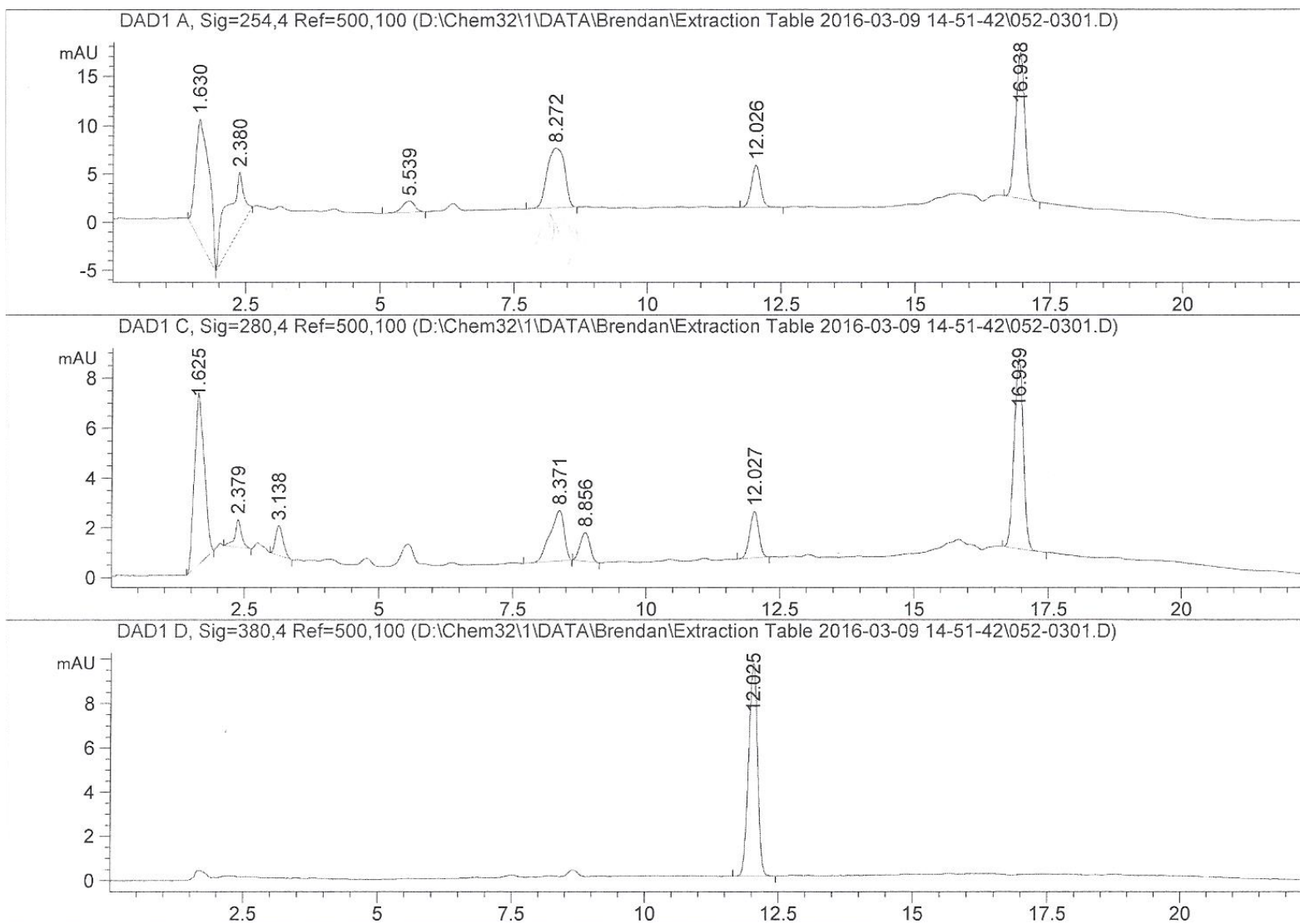


Figure A.10. First 0.5 cm of sediment core analysis. Contains the majority of sediment pesticide.

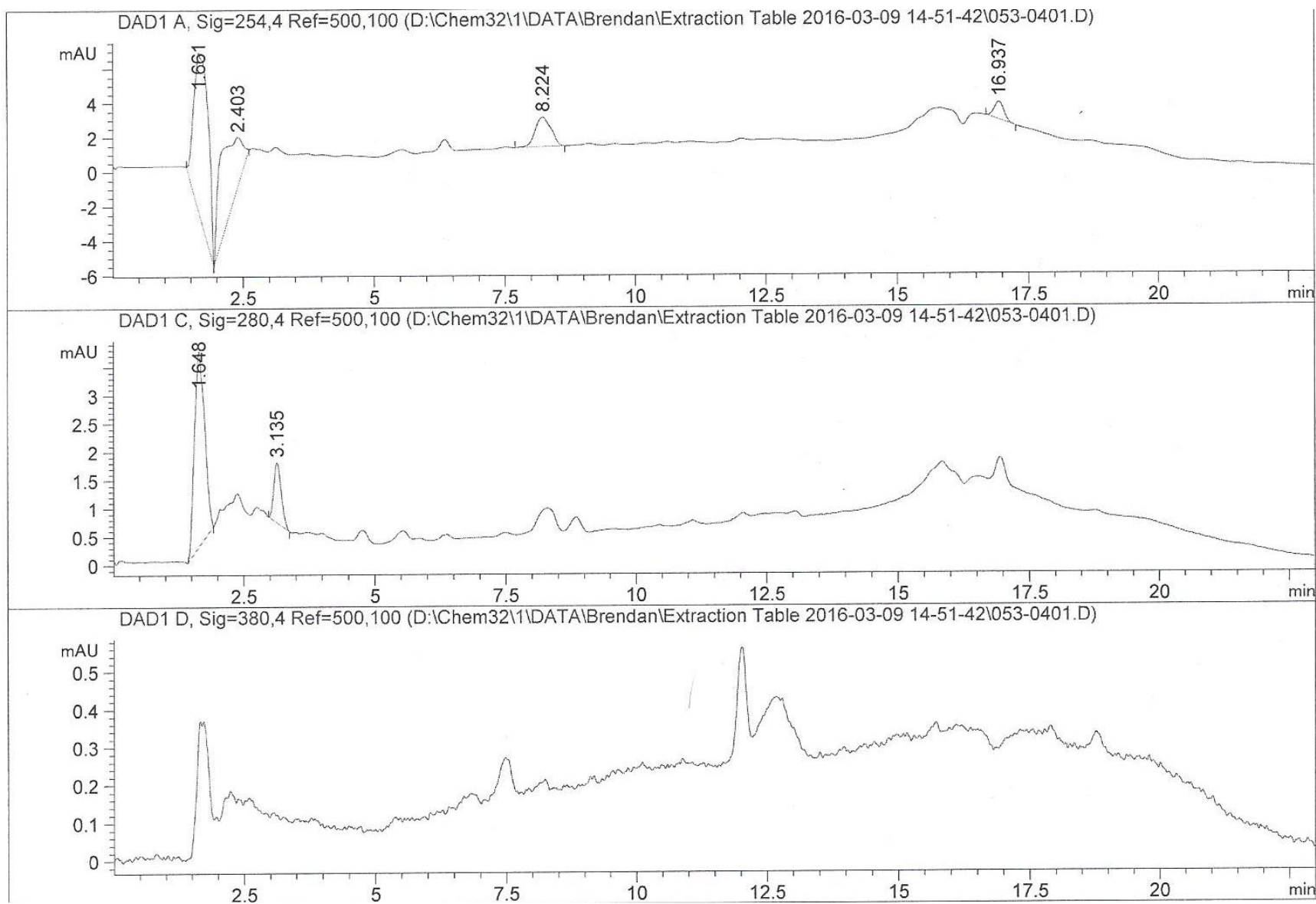


Figure A.11. 1.0 cm segment of sediment core. Most pesticides are now gone.

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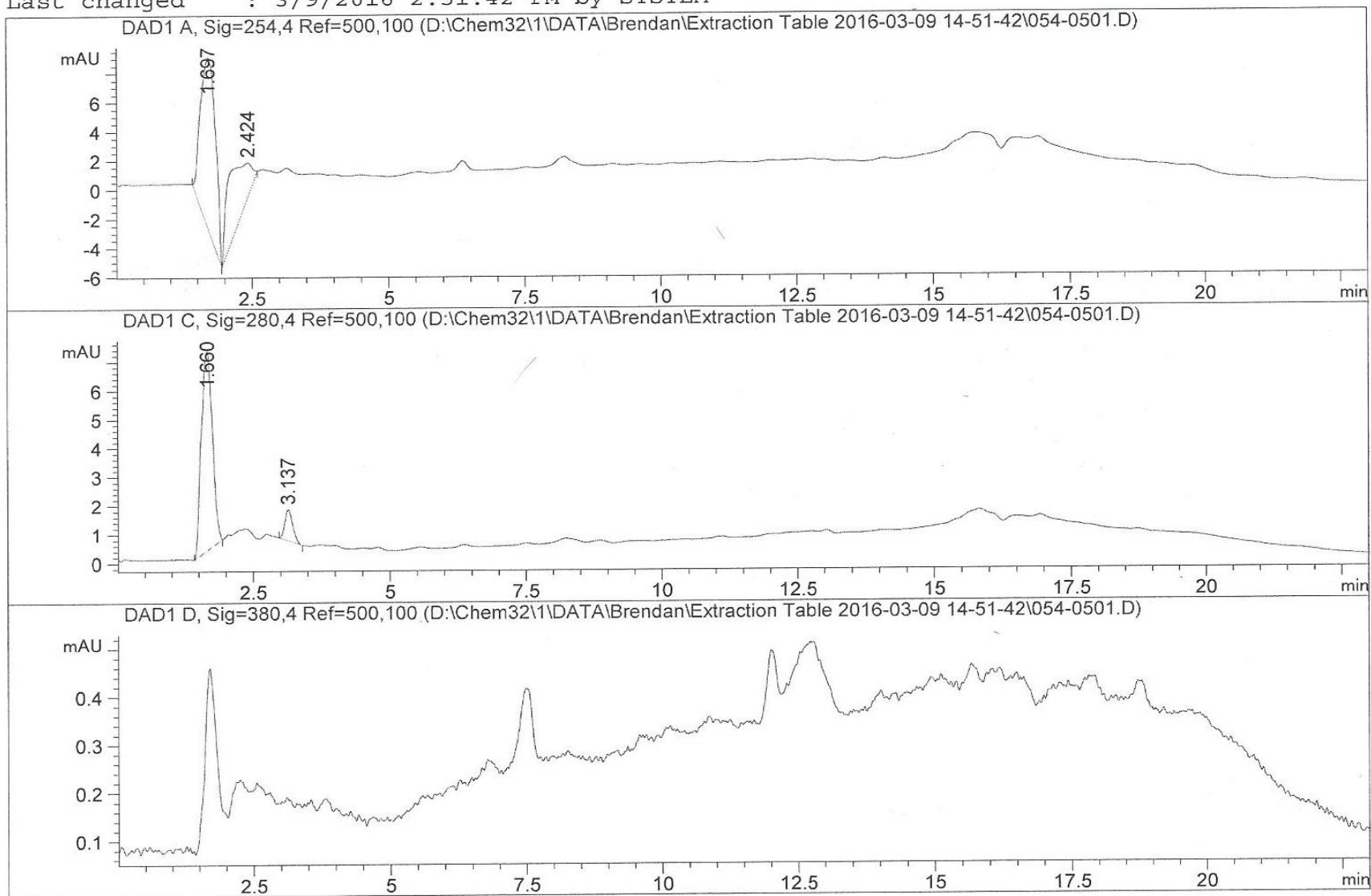


Figure A.12. 1.5 cm segment of sediment core. All pesticides are absent by 1.5 cm

		Atrazine			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
8/19/2015	100.00	0.00	0.00	0.00	0.00
8/27/2015	100.00	0.00	0.00	0.00	0.00
6/28/2016	42.77	35.69	14.31	7.22	0.00
6/28/2016	75.64	20.62	3.74	0.00	0.00
7/18/2016	84.42	15.58	0.00	0.00	0.00
7/21/2016	94.25	5.75	0.00	0.00	0.00
		Ricefield			
1/29/2016	59.99	36.20	3.81	0.00	0.00
3/8/2016	63.12	27.55	9.32	0.00	0.00
3/9/2016	76.10	23.90	0.00	0.00	0.00
4/1/2016	63.85	26.84	9.31	0.00	0.00
4/7/2016	74.96	25.04	0.00	0.00	0.00
7/27/2016	97.31	2.69	0.00	0.00	0.00
7/29/2016	90.19	9.81	0.00	0.00	0.00
8/3/2016	100.00	0.00	0.00	0.00	0.00
8/4/2016	93.97	6.03	0.00	0.00	0.00
		Sea Water			
4/15/2016	75.09	19.57	5.34	0.00	0.00
4/22/2016	57.23	42.77	0.00	0.00	0.00
4/25/2016	72.25	27.75	0.00	0.00	0.00
8/24/2016	77.04	22.96	0.00	0.00	0.00
8/25/2016	76.53	23.47	0.00	0.00	0.00
8/29/2016	71.04	28.96	0.00	0.00	0.00

Figure A.13. Atrazine normalized applied mass recovery by sample

		Quinclorac			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
8/19/2015	97.33	2.67	0.00	0.00	0.00
8/27/2015	97.50	2.50	0.00	0.00	0.00
12/11/2015	100.00	0.00	0.00	0.00	0.00
12/15/2015	100.00	0.00	0.00	0.00	0.00
3/10/2016	87.11	12.89	0.00	0.00	0.00
		Ricefield			
1/29/2016	100.00	0.00	0.00	0.00	0.00
3/8/2016	100.00	0.00	0.00	0.00	0.00
3/9/2016	100.00	0.00	0.00	0.00	0.00
4/1/2016	82.72	17.28	0.00	0.00	0.00
4/7/2016	100.00	0.00	0.00	0.00	0.00
		Sea Water			
4/15/2016	100.00	0.00	0.00	0.00	0.00
4/22/2016	73.55	26.45	0.00	0.00	0.00
4/25/2016	83.87	16.13	0.00	0.00	0.00

Figure A.14. Quinclorac normalized applied mass by sample

		Bentazon			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
8/19/2015	96.98	3.02	0.00	0.00	0.00
8/27/2015	96.88	3.12	0.00	0.00	0.00
12/11/2015	90.64	9.36	0.00	0.00	0.00
12/15/2015	87.08	12.92	0.00	0.00	0.00
3/10/2016	66.56	21.75	11.69	0.00	0.00
		Ricefield			
1/29/2016	78.66	15.72	5.63	0.00	0.00
3/8/2016	69.64	21.46	3.45	5.45	0.00
3/9/2016	74.68	25.32	0.00	0.00	0.00
4/1/2016	100.00	0.00	0.00	0.00	0.00
4/7/2016	77.43	22.57	0.00	0.00	0.00
		Sea Water			
4/15/2016	82.60	17.40	0.00	0.00	0.00
4/22/2016	68.12	31.88	0.00	0.00	0.00
4/25/2016	79.18	20.82	0.00	0.00	0.00

Figure A.15. Bentazon normalized applied mass by sample

		2,4-D			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
08/19/15	96.36	3.64	0.00	0.00	0.00
08/27/15	96.29	3.71	0.00	0.00	0.00
12/11/15	100.00	0.00	0.00	0.00	0.00
12/15/15	100.00	0.00	0.00	0.00	0.00
03/10/16	82.95	17.05	0.00	0.00	0.00
		Ricefield			
1/29/2016	69.38	30.62	0.00	0.00	0.00
3/8/2016	100.00	0.00	0.00	0.00	0.00
3/9/2016	88.81	11.19	0.00	0.00	0.00
4/1/2016	100.00	0.00	0.00	0.00	0.00
4/7/2016	100.00	0.00	0.00	0.00	0.00
		Sea Water			
04/15/16	100.00	0.00	0.00	0.00	0.00
04/22/16	100.00	0.00	0.00	0.00	0.00
04/25/16	100.00	0.00	0.00	0.00	0.00

Figure A.16. 2,4-D normalized applied mass by sample

		Dicloran			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
8/27/15	81.93	18.07	0.00	0.00	0.00
12/11/15	64.40	29.80	5.80		
12/15/15	74.25	23.11	0.97	1.67	0.00
3/10/16	47.88	42.82	9.30	0.00	0.00
		Ricefield			
1/29/16	56.48	41.69	1.83	0.00	0.00
3/8/16	71.56	28.44	0.00	0.00	0.00
3/9/16	75.24	24.76	0.00	0.00	0.00
4/1/16	60.92	35.04	4.04	0.00	0.00
4/7/16	71.42	28.58	0.00	0.00	0.00
		Sea Water			
4/15/15	63.43	29.46	7.11	0.00	0.00
4/22/16	59.92	37.66	2.42	0.00	0.00
4/25/16	73.09	24.57	2.35	0.00	0.00

Figure A.17. Dicloran normalized applied mass by sample

		Flutolanil			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
8/19/2015	94.15	5.85	0.00	0.00	0.00
8/27/2015	93.65	6.35	0.00	0.00	0.00
12/11/2015	57.40	35.43	7.17	0.00	0.00
12/15/2015	80.16	19.84	0.00	0.00	0.00
3/10/2016	57.35	36.04	6.61	0.00	0.00
		Ricefield			
1/29/2016	58.76	41.24	0.00	0.00	0.00
3/8/2016	70.03	26.55	3.41	0.00	0.00
3/9/2016	81.35	18.65	0.00	0.00	0.00
4/1/2016	76.09	23.91	0.00	0.00	0.00
4/7/2016	69.83	30.17	0.00	0.00	0.00
		Sea Water			
4/15/2016	77.33	14.31	8.37	0.00	0.00
4/22/2016	69.76	30.24	0.00	0.00	0.00
4/25/2016	81.37	18.63	0.00	0.00	0.00

Figure A.18. Flutolanil normalized applied mass by sample

		Trifluralin			
		Wetlands			
Date	Water	0.5 cm	1 cm	1.5 cm	2 cm
6/28/2016	51.24	48.76	0.00	0.00	0.00
6/28/2016	75.28	24.72	0.00	0.00	0.00
7/18/2016	72.67	27.33	0.00	0.00	0.00
7/21/2016	68.23	31.77	0.00	0.00	0.00
		Ricefield			
6/26/2016	85.29	14.71	0.00	0.00	0.00
7/27/2016	69.15	30.85	0.00	0.00	0.00
7/29/2016	84.28	15.72	0.00	0.00	0.00
8/3/2016	100.00	0.00	0.00	0.00	0.00
8/4/2016	84.43	15.57	0.00	0.00	0.00
		Sea Water			
8/24/2016	42.69	57.31	0.00	0.00	0.00
8/25/2016	62.06	37.94	0.00	0.00	0.00
8/29/2016	46.35	53.65	0.00	0.00	0.00

Figure A.19. Trifluralin normalized applied mass by sample



604 Highway 15 West
P.O. Box 510
Northwood, ND 58267
(701) 587-6010
FAX (701) 587-6013
email: agvise@polarcomm.com
Homepage: www.agvise.com

AGVISE Soil Characterization Report

Submitted For: BRENDON MARSH
Submitted By: MA6629
BRENDAN MARSH
4005 NICHOLSON DRIVE

BATON ROUGE, LA 70808

Field ID = SERIES I SOIL CHAR OMWB
Co-op/Contr. ID = RICEFIELD
Township = NA
County = NA
Section =
Sample ID = SURFACE
Quarter =

Date Received = 5/18/16
Date Reported = 5/26/16
AGVISE Lab No = 31,069
AGVISE Ref No = 18,826,015

Percent Sand 33
Percent Silt 40
Percent Clay 27
USDA Textural Class (hydrometer method) LOAM

Bulk Density (disturbed) gm/cc 1.07

Cation Exchange Capacity (meq/100 g) 13.7

% Moisture at 1/3 Bar 30.1
% Moisture at 15 Bar 12.8
% Organic Matter (Walkley-Black) 2.0

pH (Water) 6.6
Buffer pH (Adams-Evans) 7.7
% Total Nitrogen (Analyzer) 0.086
Olsen Phosphorus (ppm) 19
Soluble Salts--1:1 (mmhos/cm) 0.33

Base Saturation Data			
Cation	Percent	ppm	
Potassium	1.8	94	
Calcium	57.0	1563	
Magnesium	19.6	323	
Sodium	4.2	132	
Hydrogen	17.5	24	

Agricultural Testing

Figure A.20. Agvise Ricefield Sediment Characterization Report



604 Highway 15 West
P.O. Box 510
Northwood, ND 58267
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FAX (701) 587-6013
email: agvise@polarcomm.com
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AGVISE Soil Characterization Report

Submitted For: BRENDON MARSH
Submitted By: MA6629
BRENDAN MARSH
4005 NICHOLSON DRIVE

BATON ROUGE, LA 70808

Field ID = SERIES I SOIL CHAR OMWB
Co-op/Contr. ID = RICEFIELD 2
Township = NA
County = NA
Section = NA
Sample ID = SURFACE
Quarter =

Date Received = 5/18/16
Date Reported = 5/26/16
AGVISE Lab No = 31,070
AGVISE Ref No = 18,826,016

Percent Sand 27
Percent Silt 46
Percent Clay 27
USDA Textural Class (hydrometer method) LOAM

Bulk Density (disturbed) gm/cc 1.06

Cation Exchange Capacity (meq/100 g) 14.8

% Moisture at 1/3 Bar 30.9
% Moisture at 15 Bar 13.0
% Organic Matter (Walkley-Black) 2.2

pH (Water) 6.2
Buffer pH (Adams-Evans) 7.7
% Total Nitrogen (Analyzer) 0.109
Olsen Phosphorus (ppm) 24
Soluble Salts--1:1 (mmhos/cm) 0.32

Base Saturation Data			
Cation	Percent	ppm	
Potassium	1.9	111	
Calcium	57.3	1698	
Magnesium	19.2	341	
Sodium	3.7	126	
Hydrogen	17.8	26	

Agricultural Testing

Figure A.21. Agvise Ricefield 2 Sediment Characterization Report



604 Highway 15 West
P.O. Box 510
Northwood, ND 58267
(701) 587-6010
FAX (701) 587-6013
email: agvise@polarcomm.com
Homepage: www.agvise.com

AGVISE Soil Characterization Report

Submitted For:
BRENDON MARSH

Submitted By: MA6629
BRENDAN MARSH
4005 NICHOLSON DRIVE

BATON ROUGE, LA 70808

Field ID = SERIES I SOIL CHAR OMWB
Co-op/Contr. ID = WETLANDS
Township = NA
County = NA
Section =

Sample ID = SURFACE
Quarter =

Date Received = 5/18/16
Date Reported = 5/26/16

AGVISE Lab No = 31,067
AGVISE Ref No = 18,826,013

Percent Sand 21
Percent Silt 14
Percent Clay 65
USDA Textural Class (hydrometer method) CLAY

Bulk Density (disturbed) gm/cc 1.05

Cation Exchange Capacity (meq/100 g) 67.3

% Moisture at 1/3 Bar 61.4
% Moisture at 15 Bar 45.8
% Organic Matter (Walkley-Black) 4.2

pH (Water) 6.7
Buffer pH (Adams-Evans) 7.6
% Total Nitrogen (Analyzer) 0.247
Olsen Phosphorus (ppm) 16
Soluble Salts--1:1 (mmhos/cm) 6.15

Base Saturation Data

Cation	Percent	ppm
Potassium	1.4	357
Calcium	50.0	6735
Magnesium	23.3	1886
Sodium	20.3	3142
Hydrogen	5.0	34

Agricultural Testing

Figure A.22. Agvise Wetlands Sediment Characterization Report



604 Highway 15 West
P.O. Box 510
Northwood, ND 58267
(701) 587-6010
FAX (701) 587-6013
email: agvise@polarcomm.com
Homepage: www.agvise.com

AGVISE Soil Characterization Report

Submitted For:
BRENDON MARSH

Submitted By: MA6629
BRENDAN MARSH
4005 NICHOLSON DRIVE

BATON ROUGE, LA 70808

Field ID = SERIES I SOIL CHAR OMWB
Co-op/Contr. ID = WETLANDS 2
Township = NA
County = NA
Section =

Sample ID = SURFACE
Quarter =

Date Received = 5/18/16
Date Reported = 5/26/16

AGVISE Lab No = 31,068
AGVISE Ref No = 18,826,014

Percent Sand 23
Percent Silt 18
Percent Clay 59
USDA Textural Class (hydrometer method) CLAY

Bulk Density (disturbed) gm/cc 1.04

Cation Exchange Capacity (meq/100 g) 68.2

% Moisture at 1/3 Bar 64.8

% Moisture at 15 Bar 47.2

% Organic Matter (Walkley-Black) 5.7

pH (Water) 6.4

Buffer pH (Adams-Evans) 7.5

% Total Nitrogen (Analyzer) 0.298

Olsen Phosphorus (ppm) 15

Soluble Salts--1:1 (mmhos/cm) 6.13

Base Saturation Data			
Cation	Percent	ppm	
Potassium	1.5	408	
Calcium	44.6	6075	
Magnesium	25.4	2074	
Sodium	23.1	3627	
Hydrogen	5.4	37	

Figure A.23. Agvise Wetlands 2 Sediment Characterization Report

VITA

Brendan Michael Marsh, of Slidell, Louisiana, received his bachelor's degree from Louisiana State University. He worked offshore in the oil field as an environmental compliance specialist until he began his graduate studies at LSU in 2014. He began his master's studies at Louisiana State University in the Department of Environmental Sciences. Brendan plans on continuing his research elsewhere after finishing his master's studies.