AN ABSTRACT OF THE THESIS OF

Jeffrey D. Walker for the Master of Science Degree
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Title: Pesticide Flow and Concentration Variation Through the McPherson Valley Wetlands
Abstract Approved:

Pesticides pose a serious threat to wetlands due to their effects on the water, soil, plant life, and the animals that inhabit these areas. The rate that these pesticides degrade or move through the wetland plays an important role in the affect pesticides have in contaminating the wetland and its flora and fauna. After being applied to the area corn fields, the amount of pesticide residue that will contaminate the wetland depends highly on the soil types and the amounts of precipitation that follows the application.

The pesticide monitored during this study was atrazine. Atrazine is the primary herbicide used in Kansas, it is used to control weedy plant species where corn and milo are the primary row crops.

The study was completed at the McPherson Valley Wetlands located four miles west of the city of McPherson in Central Kansas. The wetland covers approximately 595 hectares, depending on the season, and receives runoff from 3200 hectares that lie directly north of the wetland.

Sample sites ranged from where the runoff enters the wetland to a canal where water drains out. The pH of the water was recorded for each sample along with alkalinity, temperature, and dissolved oxygen. High performance liquid chromatography (HPLC) was the procedure used to determine atrazine residue concentrations in the samples.

The objective of this study was to determine if the pesticide concentrations change from site to site as the runoff water flows through the wetland. The changes in the water chemistry along with animal and plant life will be used to help analyze the problem of herbicide contamination.

The McPherson Valley Wetlands acts as a reservoir for runoff that contains large quantities of agricultural herbicides. The hypothesis to be tested was that the wetland rids itself of these contaminants by using the process of dilution due to the runoff activity following the initial application. The extent that the McPherson Valley Wetlands rids itself of the residues was determined from the study.

A Two-Way Analysis of Variance was used to analyze differences in the water samples among sampling locations in the wetlands and among sampling dates. Linear regression was used to determine the rate of degradation of pesticide residue in the wetland.

Very small amounts of herbicide residues were found in the wetland. Concentrations were highest in the samples taken directly following the first runoff event after the application of the herbicide. Samples taken in August, which also were taken following a runoff event, also contained high concentrations of herbicide in comparison to samples taken in other months. The highest concentrations found were 0.33 μg/L and a mean for all the samples was 0.106 μg/L with a standard deviation of 0.088 μg/L. The physicochemical properties of the wetland showed minor affects caused by the herbicide residues.

Pesticide Flow and Concentration Variation Through the McPherson Valley Wetlands

A Thesis Presented
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INTRODUCTION

Pesticides pose a serious threat to wetlands due to their effects on the water, soil, plant life, and the animals that inhabit these areas (Johnson, 1986). Pesticides cause changes in water chemistry that also affect the plants and animals in the wetland. As pesticide residues are consumed and move through the food chain from invertebrates to fish and waterfowl, the concentrations increase at each step (O'Shea et al., 1980). The concentrations of pesticides from the DDT and triazine families contained in the runoff are usually between 0-10 μg/L, but as the producers absorb the contaminated water the concentration can increase to 100 μg/L in the tissues of the organisms (O'Shea et al., 1980). Concentrations as high as 99 mg/L can be found in waterfowl due to their predation on both fish and invertebrates. These high concentrations can cause a decrease in waterfowl populations due to the pesticide's effects on eggshell development and hormone production (Peakall, 1970). The effects on eggshell development and hormone production are linked most often with the use of DDT. If the herbicides degrade or rapidly move through the wetland the concentrations consumed by the producers and consumers are less and lower concentrations are found in their systems(Blum et al., 1993).

The amount of herbicide in the runoff flowing into the wetland from the treated cropland depends on the soil type, precipitation pattern following application, and method of application. A heavy period of precipitation that causes runoff immediately following application may contain very high concentrations of herbicide residues. If a dry period follows the application, a large amount of the herbicide will be absorbed by the crops and will degrade in the soil instead of being transported to the wetland in the runoff (Pionke and Glotfelty, 1989). The water chemistry of the wetland and chemical properties of the pesticide greatly affect the time that the residues persist in the wetland.

A. Herbicides

The herbicides monitored during this study were atrazine and cyanazine. Both of these herbicides belong to the triazine family and their characteristics are similar. The herbicide applied to rowcropped land surrounding the McPherson Valley Wetlands was Extrazine. Extrazine is 67.5% cyanazine and 21.4% atrazine, and the normal rate of application to corn fields is 2 lb/acre (2.24 kg/ha). Both of these herbicides are classified as restricted use herbicides due to their potential as a contaminant to ground and surface water (Extrazine product label, 1994).

Atrazine is the primary herbicide used among the agricultural community in this area. It is used to control weedy broadleaf plant species where corn and milo are the primary row crops. Extrazine is composed of 2-chloro-4-ethylamino-6-isopropylamino-s-triazine (atrazine) and 2-((4-chloro-6-(ethylamino)-s-triazin-2-yl)amino)-2-methylpropionitrile (cyanazine)(Kearney and Kaufman, 1969). The triazine structure is responsible for its persistence in water and soil. The persistence is due to the nitrogen's neutral charge (Feakin et al. 1994). With the charge being neutral the nitrogen molecules are readily adsorbed by the clays. The nitrogen is then later oxidized to nitrite which enters the ground water. However, atrazine is primarily found in surface water and its ability to enter the groundwater is highly debated in the literature. Properties of the triazines that influence their movements in water are their solubility and vapor pressure in soil. Atrazine has a low solubility of 33.0 mg/L and a vapor pressure of 3.0×10^{-7} mm Hg. Cyanazine has a much higher water solubility of 171 mg/L and lower vapor pressure of 1.6×10^{-9} mm Hg. Atrazine has a long half-life ranging from 60-100 days in soil and 100-150 days in water and cyanazine's half life ranges from 14-30 days in soil (Huckins et. al., 1986).

Atrazine is toxic to many plant species, which can be killed at concentrations as low as 10 μg/L, and to invertebrates, which can be killed at concentrations of 20 μg/L (Johnson, 1986). Atrazine and cyanazine are slightly to moderately toxic to humans and other animals. Atrazine is a mild skin irritant and can cause rashes and severe eye irritation. The two herbicides have an LD_{50} of approximately 1,000-2,000 mg/kg on rats and rabbits. Both are slightly toxic to birds with an LD_{50} of 2,000 mg/kg, but cyanazine is moderately toxic to quail with an LD_{50} of 400 mg/kg. Atrazine and cyanazine are also slightly toxic to fish with an LD_{50} of 500 mg/kg or greater, but concentrations can bioaccumulate to 11 times that of the surrounding water (DeNoyelles et al., 1989).

Atrazine and cyanazine are both moderately to highly mobile in soils. With low Koc values in comparison to other herbicides, atrazine and cyanazine both do not adsorb strongly to soil particles. Koc refers to the soil organic carbon content, which represents the ability of the various soils to adsorb the herbicides. Because of their low rate of adsorption, the chemicals readily runoff the fields into surface water. A high Koc value increases the ability of the soils to adsorb the herbicide residue and therefore decreases its runoff from fields. The imporance of Koc varies with the soil types. Atrazine has a moderate potential for ground water contamination due to its rather long half-life of 60-100 days, whereas cyanazine has a half-life of 14-30 days. Due to cyanazine's relatively short soil half-life the EPA does not consider it a major threat in polluting ground water (Sophocleous et al., 1991).

Chemical hydrolysis and biological degradation by microorganisms are the primary means of breaking down atrazine and cyanazine in soils. Hydrolysis is rapid in acidic and basic soils, but can be slow in neutral soils. A high percentage of organic matter also increases the rates of degradation. Rate of degradation in water is under the same restrictions as in soil, with pH and organic matter percentages controlling the rate of breakdown.

The movement and rate of degradation of herbicides is very dependent on the types of soils to which the chemicals are applied. The soil's clay content, percentage of organic matter, pH, temperature, texture, and presence of bacteria play major roles in the degradation of herbicides (Sophocleous et al., 1991). When herbicides are applied to agricultural fields, macropores caused by worms, plant roots, and desiccation cracks can also play major roles in the runoff potential and degradation of the herbicides (Triplett et al., 1978).

The amount of atrazine that is adsorbed by the soil is dependant on the percent of clay, organic matter, and pH of the soil. High percentages of clay and organic matter allow higher concentrations of herbicide to be adsorbed by the soil (Cheng et al., 1990). The amount of herbicide that is adsorbed increases as the pH of the soil decreases below 6.0. Hydrolysis of atrazine to hydroxyatrazine is controlled by the pH and the percentage of organic matter in the soil. Hydrolysis is catalyzed by adsorption of herbicide onto a soil particle and by an increased concentration of H^+ ions in the soil (Sophocleous et al., 1991). For each unit of increase in pH, atrazine can persist 9-29 days longer in the soil, depending on the soil type (Raju et al., 1993). However, pH readings around 7 favor microbial degradation of herbicides. High amounts of available water in the soil decrease the amount of herbicide that can be adsorbed.

B. McPherson Valley Wetland Soils

The McPherson Valley Wetlands is surrounded by primarily clay soils with variations in percentage of silts and loams. The wetland is bordered by Goessel silty clay to the north. Ladysmith silty clay loams to the east and west, Crete silt loam to the south, and Ness silty clay around the edges of the wetland (Figure 1).

The Goessel silty clay soils that lie on the northern edge of the wetland contain clay contents of 40-55%, a pH range of 6.1-7.3, and contain 1-4% organic matter. These soils also have moderate water availability, slow runoff potential, and moderate rates of permeability (Soil

Conservation Service, 1983).

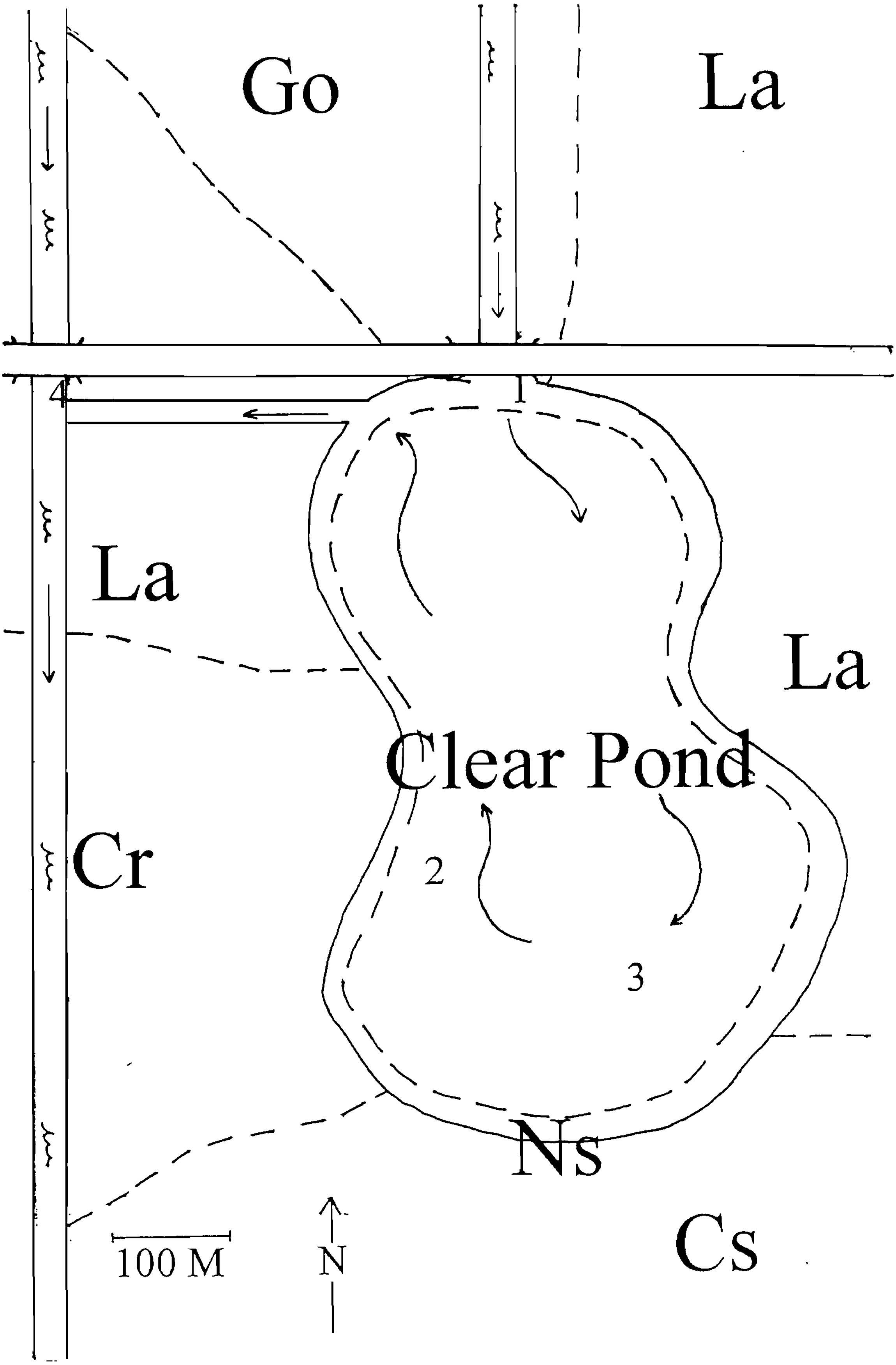
The Ladysmith silty clay loam soil that borders the wetland to the east and west has a slope of 0-1% which slows the rate of runoff and allows the herbicide to be adsorbed by the soil. These soils also contain clay contents of 28-35%, a pH range of 5.6-7.6, an organic matter content of 2-4%, and have very slow permeability and high available water content (Soil Conservation Service, 1983).

The Crete silt loams that border the wetlands to the south have slopes of 0-1% to the southwest, and slopes of 1-3% to the southeast. The Crete silt loams have clay contents of 20-30%, pH's ranging from 5.6-6.1, and organic matter percents of 2-4%. The Crete silt loam with a slope of 1-3% has moderate runoff, whereas the soil with a 0-1% slope has slow rates of runoff. The Crete soils are moderately permeable and contain large amounts of available water (Soil Conservation Service, 1983).

The Ness silty clays that surround the wetland are the primary cause of the wetland's existence. These soils have very poor permeability and all runoff is ponded. The Ness soils contain 40-60% clay, a pH range of 6.1-7.4, and 1-3% organic matter (Soil Conservation Service, 1983).

The herbicide residues in the wetland will decrease by one of two processes. The residues may degrade due to biological processes in the wetland or be reduced by dilution as the water flows through the wetland. Biological degradation of the pesticide by the wetland will cause a rapid decline in concentration as the residues flow from the point of contamination from the field runoff to the individual sites that will be tested. If dilution of the pesticide residues occurs, there will be a gradual decline in pesticide concentrations as the residues flow from where the runoff enters the wetland to the last sample site. The hypothesis of this study is that the wetland rids itself of these contaminants by using the process of dilution due to runoff activity following the initial application.

Figure 1. Map of the McPherson Valley Wetlands, illustrating the boundaries of the various soil types surrounding the wetland. (Sites 1-4 and water flow are shown) Goessel silty clay (Go), Ladysmith silty clay (La), Crete silt loam 0-1% slope (Cr), Crete silt loam 1-3% slope (Cs), Ness silty clay (Ns)


Go
La
La
La
Clear Pond
Cr
Ns
Cs
1
2
3
4
100 M
N

MATERIALS AND METHODS

A. McPherson Valley Wetlands

The study was completed at the McPherson Valley Wetlands located 10.5 km west of McPherson, KS. The McPherson Valley Wetlands once covered more than 201 square kilometers in 52 separate wetlands. At the present time it covers 595 hectares. This decrease in land area was caused by the construction of the Blaze Fork Drainage Ditch around the turn of the century. Big Basin, which once covered 808 hectares, now fluctuates in area each season with varying volumes of water determined by rainfall amounts.

The pesticide applied to the corn fields north of the wetland during this study was Extrazine, which is comprised primarily of cyanazine. Drainage from this field enters the wetlands at its southwest corner. Entering this point of the wetland will come runoff from approximately 3200 hectares (Figure 1).

Samples were taken from Clear Pond and its drainage outlet. In the Spring of 1995, Clear Pond contained approximately 30 cm of water and supported a variety of bird species. The first sample area was on the north edge of Clear Pond near the McPherson Valley headquarters. Directly north of this point are row-cropped fields that contained corn. After application of the pesticides to the crops the runoff from the fields flowed in a southerly direction toward the north edge of Clear Pond. The second sample was taken from the west edge of Clear Pond. This area is about half way between the north edge of Clear Pond and its southern boundary. Sampling from this area enabled me to determine if pesticide concentrations were decreasing through the wetland. The third sample was taken from the south end of Clear Pond. This sample was taken from about a half of a kilometer south of the north edge of Clear Pond. From this sample, I could detect a difference in pesticide concentration from the other two samples due to the greater distance the residues had to flow from the point at which it entered the wetland. A fourth sample was taken from a drainage ditch on the west side of the wetlands. This ditch contains a continual flow of water from north to south. Water samples were taken from this area due to its available water supply during a drought. In case a drought was to occur, samples would have been taken from the length of this waterway. North of the ditch there are also row-cropped fields that could have contributed pesticide residues in the runoff water (Figure 1). The fifth sample was taken two and a half kilometers south of Clear Pond. This sample was used to determine herbicide concentrations after flowing through the wetland.

The control samples were taken on 31 March 1995 from each of the five sites. These samples were taken one week previous to the application of herbicide. The first sample taken post-application was collected after the first precipitation fell on the application area. Water samples were then collected each month until definite changes in the water chemistry ceased. The water samples were placed in 1-liter polyethylene containers and frozen after completion of the testing.

B. Water Chemistry

In studying the effects of the pesticide concentrations to the wetland, data on water chemistry were collected. The pH was recorded at each site with a hand-held pH meter and dissolved oxygen was determined by using the Winkler method. Alkalinity was tested by the method of Schroeder (1992).

The temperature of the water was recorded with a thermometer and the weather conditions were recorded. The alkalinity test was performed in the laboratory within three hours following extraction.

The discharge of runoff in m^3/s was calculated to determine the volume of runoff that was entering the wetland. This was completed after a period of precipitation by floating an object one meter in the runoff flow and recording the time. With this measurement along with the water depth and width of the flow the volume was calculated (Haith, 1987).

C. Herbicide Analysis

The atrazine in the samples was first extracted from the sample. In a separatory funnel, 500 ml of water sample was added to 100 ml methylene chloride. The solution was then shaken for approximately two minutes to insure complete mixing of the sample and the methylene chloride. The methylene chloride dissolves the less polar chemical compounds in the sample and the methylene chloride and atrazine were then extracted from the funnel. The atrazine from the wetland water samples remained in the portion of methylene chloride, which was then placed in a Danish-Kuderna evaporator. The evaporator was placed in a hot water bath set at approximately 50°C. This temperature was the boiling point for methylene chloride. Following the evaporation of the sample, 5 ml of methanol was poured into the receiver to dissolve the remaining atrazine sample. The sample was then analyzed by high performance liquid chromatography.

A reversed phase C-18 column that was 25 cm long with a 0.46 mm diameter and spherical particles 5 µm in diameter was used. In the reversed-phase method, the most polar component elutes first, which was methanol in this analysis (Steinheimer, 1993). The mobile phase was a 75% $^{v}/_{v}$ methanol in water solution. The flow rate was set at 1.0 ml/min. The best ultraviolet wavelength was found to be 225 nm for the detection of atrazine. This was determined by measuring absorbance of the atrazine samples using a spectrophotometer. According to the spectrophotometer readings, the highest absorbance is around 220-230 nm (Cresser and Marr, 1983).

Optimization tests were run on the atrazine extracts using the HPLC to determine the best mobile phase. An increased amount of methanol in the mobile phase would decrease the retention times (Cresser and Marr, 1983). The mobile phase of methanol and water was adjusted for the best peak performance in analyzing the atrazine extracts. The ranges were at 0.08 and 0.16 which were about twice the expected height of the largest peaks. The retention times for the atrazine samples ranged from 4.22 minutes to 5.00 minutes.

Before each set of samples were analyzed, a known concentration of atrazine was injected into the HPLC to determine the retention time and peak heights of that concentration. The peaks were recorded in centimeters. The concentration of atrazine in the samples was computed by using the equation $C_o = H_1 \times C_s \times R_1 \times V_1 \; / \; H_s \times R_s \times V_o$, where C_o and C_s are the concentrations of the atrazine unknown and the standard in μg/L, H_1 and H_s are peak heights of the unknown and the standard, R_1 and R_s are the ranges of the unknown and the standard, V_1 is the volume of methanol added to the sample after evaporation, and V_o is the volume of methylene chloride added to the wetland water sample. This analysis was completed by the method of Schroeder (1992).

HPLC chromatograms were used to illustrate the concentrations of herbicide in the wetland water samples. Chromatograms were produced at the ranges of (0.08), (0.16) and (0.32), mobile phase (75% methanol : 25% water), with a U.V. detection of(225 nm).

Dissolved oxygen, alkalinity, pH, plant life, and invertebrate life were compared throughout the study, to follow the changes in the wetland. The samples taken from each of the five sites were compared to the control as well as the previous samples taken from that particular site.

The statistical analysis that was completed to test the variability among the water samples was a Two-Way Analysis of Variance. This analysis tested the difference in herbicide concentration among sampling times and among sites (Zar, 1984). A linear regression using the Julian date for each sampling date and concentrations for each site was done. The slope of the regression line indicates the rate of degradation of pesticides in the wetland (Zar, 1984). The concentration of pesticide residue at a certain time period of the study was compared to its distance from the initial source of the pesticide runoff. This test determined the rate of biological degradation or dilution of the pesticide residues in the wetland.

RESULTS

The pH of the wetland water remained primarily neutral with a range of 5.85 to 8.95. The pH was 7.6 when the control sample was taken prior to the herbicide application. Following the first occurance of precipitation the pH became slightly acidic. The pH then rose to slightly basic and remained there for the entire sampling period (Figure 2).

The dissolved oxygen in the wetland declined dramatically after the control samples were taken. This could have been caused by the herbicide's photosynthesis inhibiting effects on the wetland plant life. The dissolved oxygen remained low for the entire Summer and then the oxygen concentrations increased in the last two months of the sampling period (Figure 2). The temperature of the wetland acted typically, increasing to high temperatures in the middle Summer and decreasing rapidly going into the Fall season (Figure 2).

The volume of runoff entering the wetland at its northern edge was 0.996 m^3/s following the first precipitation after the herbicide application. The runoff was 0.475 m^3/s on the sampling date of 15 August 1995. These were the only sampling dates where precipitation had occurred within three days of the sampling.

The peaks from the HPLC chromatograms were relatively small. The tallest peaks ranged from 1.0 cm to 1.9 cm at the (0.08) range. This represents the relatively small concentrations of herbicide that are in the wetland. A majority of the peaks ranged from 0.10 cm to 0.20 cm in height at the (0.16) range. These represented concentrations from 0.05 μg/L to 0.12 μg/L (Figures 3 and 4).

Larger concentrations of herbicide were seen in the wetland water samples from the May and August sampling periods. These concentrations of herbicide ranged from 0.02 to 0.33 μg/L. These samples were taken immediately following a heavy period of precipitation (Table 1). Regression analysis showed that the concentrations were decreasing slowly throughout the sampling period. (Figure 5).

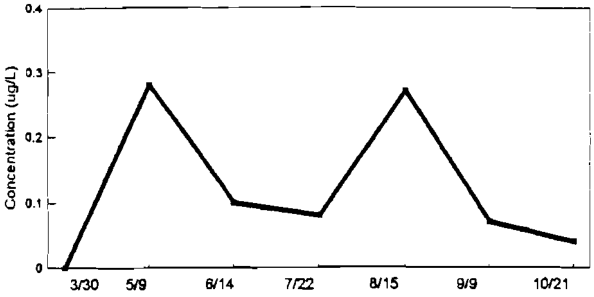
A Two-Way Analysis of Variance showed no significant differences among sampling dates ($\underline{F}$ = 1.036, d.f. = 29, $\underline{P}$ = 0.424) and no significant differences among sampling sites ($\underline{F}$ = 0.348, d.f. = 29, $\underline{P}$ = 0.842). A linear regression analysis was completed to determine if there were any differences between herbicide concentrations when compared to the days of the entire sampling period and also to the amounts of precipitation that occurred previously to the sampling dates.

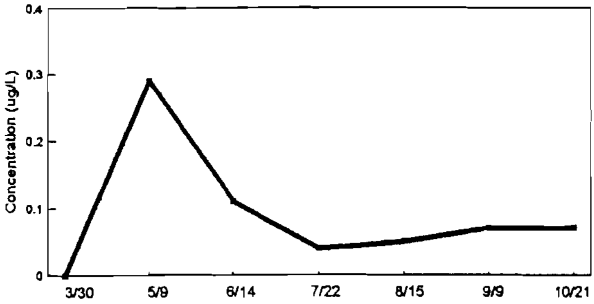
In the linear regression analysis using the herbicide concentrations as the dependant variable and days of the sampling period as the independent variable for each site, no sites were significant. When using the herbicide concentrations and amounts of rainfall falling previous to sampling, sites 1 and 2 proved significant. This indicates that the rainfall that occurred directly before sampling had significant effects on the amounts of herbicide residue that was entering the wetland in the runoff.

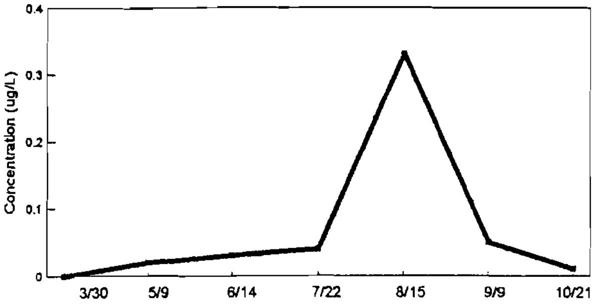
A linear regression comparison was also completed, again using concentrations, days, and rainfall. In this analysis the F-ratio for a certain site and number of days or rainfall amount, which were calculated in Table 2., were calculated using a linear regression comparison. This test was completed to determine if the slopes from the regression analysis for concentrations of herbicide with days of the sampling period and precipitation were significantly different. For this test, sites (2,3), (1,5), and (3,5) when used with days of the sampling period, were found to be significantly different. This indicates the concentrations of herbicide were changing significantly as the water flowed through the wetland. When using rainfall and the sampling sites, only sites 1,2 proved to be equal. The reason for these sites being equal is that they are the initial sites contaminated by the runoff following a precipitation event. At the time of sampling the runoff had not yet reached the last three sampling sites. Therefore they had not been contaminated. The null hypothesis, that the sites were equal, was rejected for each comparison calculated for the sampling dates (Table 3).

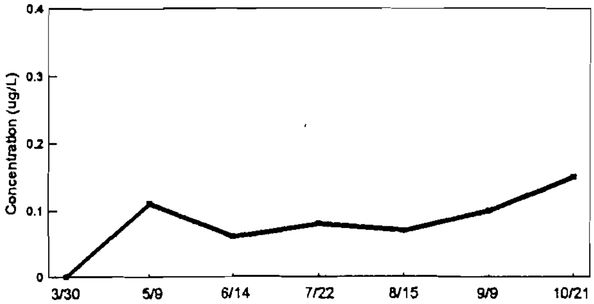
Figure 2. (a)Temporal changes in rainfall for each month(open diamond), dissolved oxygen (closed square), and temperature (open square), (b) pH (closed square) and alkalinity (closed diamond) in the McPherson Valley Wetlands, from March 1995 through October 1995.

Figure 3. Temporal variations in herbicide residues at each site (1-5) in the McPherson Valley Wetlands from March 1995 through October 1995.


0.4
0.3
0.2
0.1
0
Concentration (ug/L)
3/30
5/9
6/14
7/22
8/15
9/9
10/21


0.4
0.3
0.2
0.1
0
Concentration (ug/L)
3/30
5/9
6/14
7/22
8/15
9/9
10/21


0.4
0.3
0.2
0.1
0
Concentration (ug/L)
3/30
5/9
6/14
7/22
8/15
9/9
10/21


0.4
0.3
0.2
0.1
0
Concentration (ug/L)
3/30
5/9
6/14
7/22
8/15
9/9
10/21

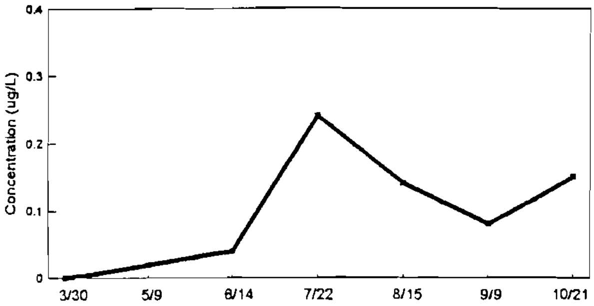

0.4
0.3
0.2
0.1
0
Concentration (ug/L)
3/30
5/9
6/14
7/22
8/15
9/9
10/21

Figure 4. Chromatograms of herbicide concentrations on 9 May 1995 at sites 1,4, and 5 at the McPherson Valley Wetlands.

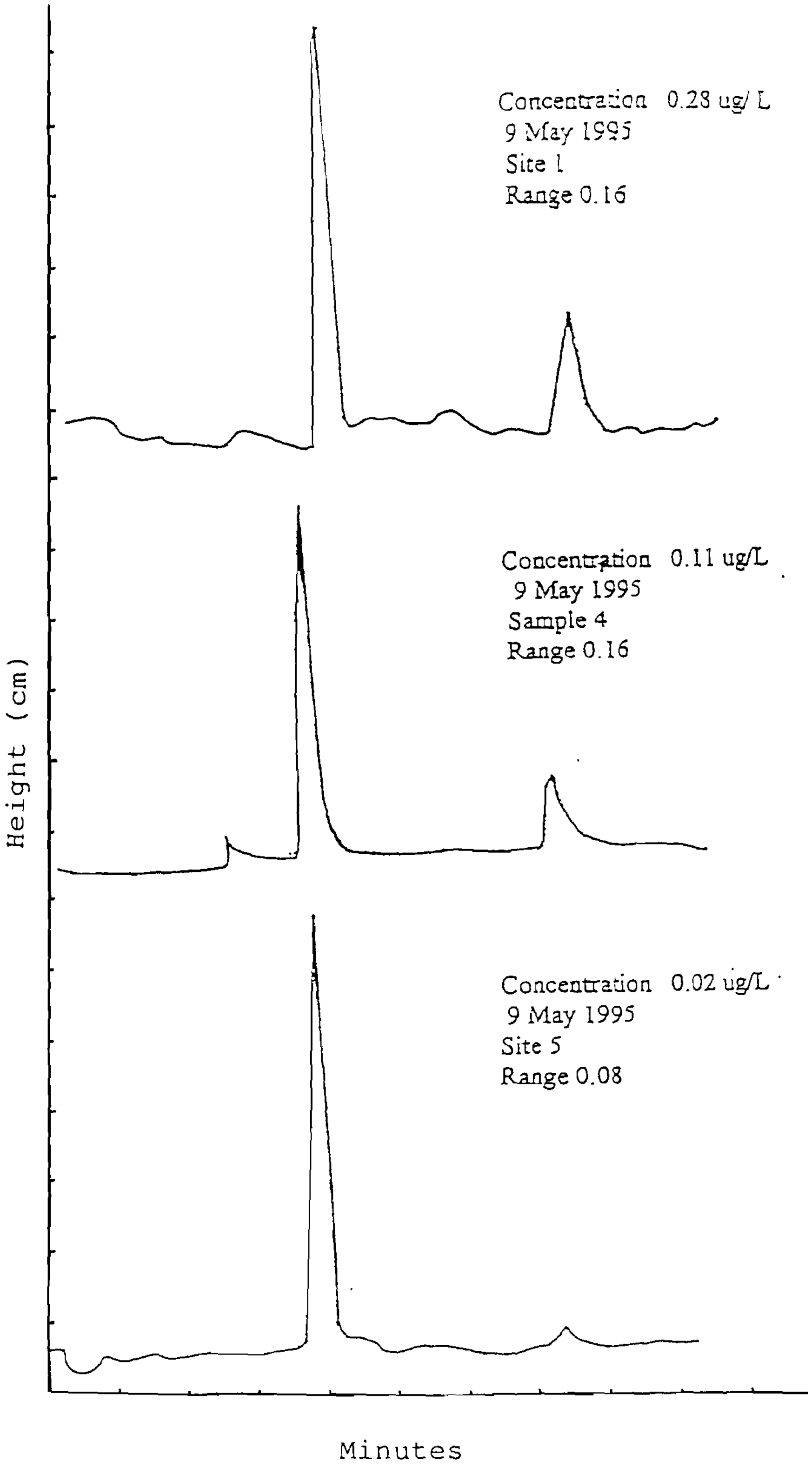

Concentration 0.28 ug/ L
9 May 1995
Site 1
Range 0.16
Concentration 0.11 ug/L
9 May 1995
Sample 4
Range 0.16
Concentration 0.02 ug/L
9 May 1995
Site 5
Range 0.08
Height (cm)
Minutes

Table 1. Concentrations of herbicide (μg/L) found at each site during the sampling period from 9 May 1995 through 21 October 1995 at the McPherson Valley Wetlands.

	Sampling Dates					
	9 May	14 June	22 July	15 Aug	9 Sept	21 Oct
Site						
1	0.28	0.10	0.08	0.27	0.07	0.04
2	0.29	0.11	0.04	0.05	0.07	0.07
3	0.02	0.03	0.04	0.33	0.05	0.01
4	0.11	0.06	0.08	0.07	0.10	0.15
5	0.02	0.04	0.24	0.14	0.08	0.15

Mean	0.106 ug/L
Standard Dev.	0.088 ug/L

Figure 5. Regression of herbicide concentrations against sampling time found in the McPherson Valley Wetlands.

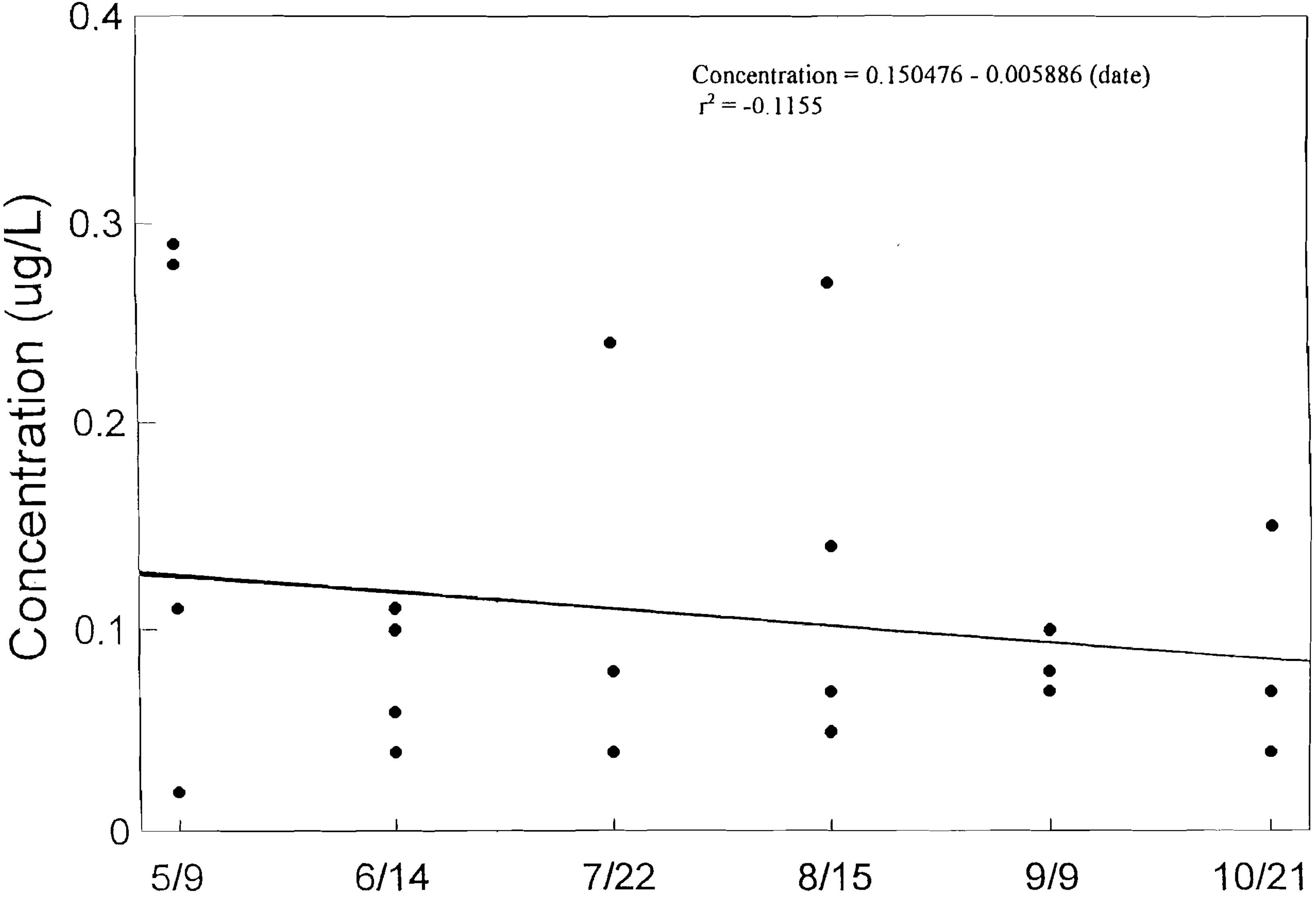

Concentration = 0.150476 - 0.005886 (date)
r^2 = -0.1155
Concentration (ug/L)
0.4
0.3
0.2
0.1
0
5/9
6/14
7/22
8/15
9/9
10/21

Table 2. Linear regression analysis of concentration vs. sampling date for each site and of concentration vs. rainfall in the 24 hours previous to sampling. Critical F (1,4) 0.05 = 7.71

Site	Days		Rainfall	
	F	Slope	F	Slope
1	1.988	-0.00103	11.878	0.09426
2	4.308	-0.00113	12.558	0.08363
3	0.061	0.00025	0.055	0.01477
4	1.334	0.00027	0.034	0.00307
5	1.326	0.00068	1.288	-0.04124

Table 3. Calculated *t* value for the comparison of slopes of the regression lines at each site for concentration vs. sampling date and concentration vs. rainfall in the 24 hours previous to sampling. Critical *t* > 2.776

Sites	Days	Rainfall
1,2	0.000661	1.976
2,3	5.150	9.370
3,4	2.498	3.986
4,5	1.002	4.345
1,5	12.685	48.731
3,5	6.590	10.112

DISCUSSION

The physicochemical properties that were measured, dissolved oxygen, pH, water temperature, and alkalinity showed very minor effects of herbicide contamination. The dissolved oxygen concentrations ranged from 6.3 mg/L to 12.8 mg/L. The decrease that occurred from May to August could have been caused by the increase in water temperature that occurred over the summer months. The concentrations of dissolved oxygen increased in September and October, cooler water holds higher concentrations of dissolved oxygen.

The pH and alkalinity of the wetland water remained relatively stable throughout the sampling period. The pH was neutral to slightly basic and ranged from 6.98 to 8.25. There was a slight decrease in pH directly following the herbicide application. This could have occurred due to a decrease in photosynthesis caused by the herbicides. However, the concentrations of herbicide were minimal, so the change in pH is probably due to other causes.

The alkalinity of the water ranged from 5.24 to 7.55 meq/L $CaCO_3$. A slight decrease was also seen in the alkalinity directly following herbicide application. However, this minute change in alkalinity is not biologically meaningful.

The concentrations of herbicide that were found using HPLC were less than what was expected to be found in the McPherson Valley Wetlands. The concentrations ranged from 0.02 to 0.33 μg/L. The primary reason for the small amounts of herbicide residues that were found in the wetland is due to the soils that surround the wetland, and also the type of herbicide that was applied.

The herbicide that was applied in the proximity of the wetlands has a relatively short half-life of 14-60 days. Even though atrazine and cyanazine are moderately to highly mobile in runoff, runoff did not enter the wetland for thirty-two days following the application. It was also twenty-one days before significant precipitation fell on the area, which was not enough to produce runoff. Due to this delay in precipitation following the herbicide application, enough time passed for the soils to adsorb the herbicide residues.

The soils that lie directly north of the wetland are relatively high in clay content, available water, and also have 0-1% slopes which are able to adsorb precipitation readily, and runoff is held to a minimum. These factors allow the soils to retain the residues where bacteria and chemical degradation are able to breakdown the herbicides into their daughter products. The amounts of organic matter in the soils are also involved in the breakdown of herbicide residues. With the percentage of organic matter in these soils ranging from 1% to 4%, and the pH staying near neutral in the various soils, biological activity would add to the increased rate of degradation (Cheng, 1990).

The concentrations of the herbicide residues in the McPherson Valley Wetlands generally were correlated with the rainfall events that occurred. Rainfall occurred one day previous to the first water sampling, which resulted in higher concentrations at the first two sites, nearest to the point at which runoff entered the wetland. Also in the month of August rain fell the day before and on the sampling date. The August water samples also contained higher amounts of herbicide residue. In other months precipitation did not occur near the sampling dates and lower concentrations were found.

With the higher concentrations of herbicide occurring directly after a precipitation event, the herbicides are not totally degrading in the soil. However, the soils are adsorbing the residues and each runoff event is washing small amounts of herbicide into the wetland. This is due to the high clay content in surrounding soils. Herbicide residues can remain in the soil for as long as eleven months, and has been found to persist in some soils for as long as four years, even though the half-lives range from 14 to 130 days (Pionke, et al. 1988).

Sampling of the wetland waters ended in October due to the small amounts of herbicide that were being found. Residues may still remain in the surrounding soils, but at very small concentrations. Biological degradation and dilution were the primary degradation processes. Biological degradation is much slower than hydrolysis. The breakdown of herbicide residues was occurring very slowly and as seen in the results, residue was still present late in the sampling period. Dilution was also important in producing very small concentrations in the wetland produced by the runoff.

The small amounts of herbicide residues that were found in the McPherson Valley Wetlands were caused primarily by the soil types surrounding the wetland, herbicide chemistry, and slope of the terrain around the wetland. The McPherson Valley Wetlands would be an excellent area for further research on the effects of small amounts of pesticide residue on a wetland environment.

Research completed by the Kansas Department of Health and Environment also concluded that concentrations between 0.10 μg/L and 1.2 μg/L with a mean of 0.49 μg/L are common in Central and Western Kansas bodies of water (Carney et al. 1991). The small slopes, that are found in Western Kansas agricultural regions and the soil types contribute to the low values of herbicide found in the surface water.

The amounts of herbicide residue found in Eastern Kansas differ greatly from Western Kansas. The reservoirs and rivers in the eastern part of the state contain atrazine concentrations as high as 2.4 to 12.8 μg/L with a mean of 3.12 μg/L (Carney et al., 1991). The rocky terrain and steep slopes that are found in many agricultural areas in this region of Kansas have very large amounts of runoff, containing large amounts of herbicide that enter the streams and rivers that feed the reservoirs.

In order to decrease the amounts of pesticide residue in the waters of Northeast Kansas, edgerows have been used along with other practices. If these same practices were initiated in Western Kansas the concentrations found in the surface water could possibly be eliminated.

The triazine herbicides do not pose a serious threat to wetlands and other bodies of water in Western Kansas to this date, but as residues build up from year to year concentrations of herbicide residues could increase. Over the last ten years soil residues have increased slightly, but has yet to become a problem for the quality of drinking water or to the plants and animals that exist in these bodies of water (Carney et al., 1991). With an increase in usage of herbicides like cyanazine that contain a rather short half-life, a build up of residue can be prevented before the concentrations become so extreme as to damage the plants and wildlife in these wetland communities.

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