MITIGATION OF ATRAZINE IN DRAINAGE DITCHES AND CONSTRUCTED WETLANDS FOR AGRICULTURAL NON-POINT SOURCE RUNOFF

R. F. Cullum¹, M. T. Moore¹, S. S. Knight¹, and P. Rodrique²
Agricultural Engineer, Ecologist, Ecologist, Hydrologist

ABSTRACT
Atrazine was amended into an agricultural drainage ditch and constructed wetlands for the purpose of monitoring transport and fate of the pesticide. Aqueous half lives of 6 and 16 to 48 days in drainage ditch and constructed wetlands, respectively, were found. Flow paths of 50 m and 103 to 281 m were required to mitigate atrazine in the drainage ditch and constructed wetlands, respectively. This information provided design parameters for ditches and constructed wetlands to mitigate the herbicide in agricultural runoff.

KEYWORDS. Atrazine, drainage ditch, constructed wetlands.

INTRODUCTION
Atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) is one of the most intensively used herbicides in North America, with over 24 million kg applied to the United States corn (Zea mays L.) crop alone (Solomon et al, 1996; USDA, 1999). Public concern over the presence of this and other pesticides in surface and ground water has resulted in intensive scientific efforts to find economical, yet environmentally-sound solutions to the problem. This research suggests utilizing current agricultural landscape features (e.g. drainage ditches and wetlands) for mitigation of pesticides associated with storm water runoff.

Drainage ditches and wetlands are integral components of the agricultural production landscape, particularly in the Mississippi Delta region of the United States. Most agricultural fields are surrounded by a network of ditches, whose purpose is to promote field drainage and reduce flooding on production acreage. Water from these ditches normally drains into wetland areas prior to entering lakes and streams. In the past, the value and function of such marginal land has been generally ignored; however, due to their crucial role in transfer/transformation of contaminants (nutrients, sediments, pesticides, etc.), more intensive research is needed to examine the intricacies of ditches and wetlands for mitigation purposes.

Drainage ditches and wetland areas are the forgotten links between agricultural fields and aquatic receiving systems. Little information concerning natural ditch classification, ecology, or potential mitigation capabilities is available. In the United States in order to increase food and fiber production in the 1950s, ‘edge-of-field’ wetlands were drained to boost growing agricultural production needs (Reddy and Gale, 1994). With this increase in agricultural land usage has come a concomitant increase in pesticide usage. Wetland draining along with increased pesticide usage resulted in the lost of the wetland’s original function of water quality enhancement or mitigation for pesticide-associated cropland runoff. These unique ecosystems provide a myriad of potential

¹ USDA-ARS National Sedimentation Laboratory, Oxford, MS 38655 email: bcullum@ars.usda.gov
² USDA-NRCS Wetland Institute, National Sedimentation Laboratory, Oxford, MS 38655
services other than water drainage, including sediment trapping and nutrient and pesticide mitigation.

Less well documented is the use of constructed wetlands for the treatment of agricultural non-point source discharges. Work on experimental cells has documented possible benefits while there is still little quantification of benefits on the landscape scale.

Water resources damage can be limited by using best management practices and installing constructed wetlands to control agricultural non-point runoff. Size and design of these constructed wetlands is more difficult to determine due to the wide variety of conditions found from farm to farm. Contributing drainage area, soil type, slope, rainfall, soil and crop amendments all must be considered. In planning constructed wetlands for pesticide mitigation, the goal is to mathematically model the fate of pesticides in herbaceous wetlands and determine wetland size and design requirements using various inputs.

This research focuses on pesticide mitigation of drainage ditches and constructed wetlands to act as ‘buffers’ between agricultural fields and subsequent receiving water bodies. Examination of the fate of atrazine associated with simulated cropland runoff in ditches and constructed wetland mesocosms was addressed by: (1) determining effectiveness of ditches and constructed wetlands to decrease concentrations of the pesticides from inflow to outflow; (2) determining the mass partitioning (plants, sediment, water) of pesticide in these two structures; and (3) determining appropriate drainage ditch and constructed wetland design parameters for mitigation of pesticide-associated agricultural runoff. This paper further will provide some basic information on the planning of a constructed wetland system for pesticide reduction in agricultural non-point source discharges.

**PROCEDURES**

A 50-m portion of an agricultural drainage ditch located within the Mississippi Delta Management Systems Evaluation Area (MDMSEA), near Indianola, MS, USA, was used in evaluating pesticide mitigation. The ditch was approximately 4 m wide (top width), 1.3 m deep, and had a bottom slope of 0.004. Ditch water width was approximately 1.5 m. Discharge during the simulated runoff event was 3680 L h⁻¹; velocity was less than 3 cm s⁻¹. Sampling sites within the ditch were established at the runoff point of contact, 10 m above point of contact, and 10, 20, 40, and 50 m below point of contact. Two weeks prior to simulated runoff event, plant densities were recorded at each sampling site along with plant density and biomass estimates (Moore et al., 2001). A simulated storm runoff event was conducted on the designated area of the drainage ditch in July 1998. A mixture of atrazine (triazine herbicide sold as Aatrex®), and water was amended directly into the ditch. Pesticide concentration (68.9 mg L⁻¹ atrazine) was based on recommended application rates and worst-case storm runoff (5% pesticide runoff) predictions (Wauchope, 1978). This simulation was of a 0.64 cm precipitation event from a 2.03 ha contributing area. A 2.0 m length of 7.6 cm diameter PVC pipe (with 16, 1.5 cm holes) was used for simulating runoff from a diffuse area. Two, 3600 L water tanks (filled with groundwater) were connected to the end of the diffuser and used as water sources for the simulated rainfall. Atrazine was mixed with water in a 110 L container, then delivered to the top of the PVC diffuser through Tygon® tubing via an Atwood® V450 submersible pump at a rate of 0.019 L s⁻¹ for 80 min. A 5 cm hose delivered water from the 3600 L tanks directly to the PVC diffuser at a rate of 1 L s⁻¹. Samples were collected from water tanks and analyzed for background concentrations of atrazine.

Grab samples of water were collected in 1 L amber glass bottles at -7 day, 0 h, 1 h, 1.5 h, 2 h, 2.5 h, 3 h, 24 h, 7 day, 14 day, and 28 day post-application from each site. After samples were collected, they were stored on ice and returned to the laboratory for extraction (within 24 h). Plant samples (portion of plant exposed to water column) and sediment were collected at -7 day, 0 h, 3 h, 24 h, 7 day, 14 day, and 28 day post-application from each site, wrapped in solvent washed foil, stored on ice, and returned to the laboratory to be dried. Sediment samples (820 ± 110 g kg⁻¹ silt) were collected from the top 3 cm using sterilized scoops. 2.3. Extraction and
analysis of water; sediment, and plant samples. Pesticide extraction and analysis of water, sediment, and plant samples followed procedures in Moore et al. (2001).

Constructing Wetland

Constructed wetland cells (59-73 x 14 x 0.3 m) at the University of Mississippi Field Station were specifically designed to evaluate fate of pesticides in wetlands (Rodgers and Dunn, 1992). Eight of those constructed wetland cells were used for this research. Five wetland cells were chosen as experimental cells (one cell served as an unamended control). The three remaining wetland cells were used as water sources for the simulated storm event. Each experimental wetland cell was randomly assigned an atrazine concentration (representing potential worst-case atrazine-runoff scenarios) (Wauchope, 1978). The amount of atrazine applied as simulated runoff was based on assumptions of an immediate (post- application) 2.54 cm rainfall on 4, 40, and 400 hectare agricultural fields. Using the assumptions of percent pesticide runoff (Wauchope, 1978), an estimate of actual water runoff from storm events, and various field sizes, the same mathematical concentration was derived for each of the three field sizes. This was possible since target pesticide applications were based on concentration, not mass, of pesticide. Calculated wetland cell volumes were used to determine appropriate atrazine masses to apply to systems, as well as time required for their hydraulic turnovers. Targeted concentrations following simulated rainfall dilution were 73 and 147 µg L⁻¹ atrazine for experimental wetland cells. Each atrazine concentration was repeated in another experimental wetland cell, giving a total of four experimental cells in addition to an unamended control. Aqueous atrazine applications were introduced into the inflow of each wetland. Following each wetland’s atrazine application, a one-time simulated rainfall with an intensity of 12.6 L s⁻¹ was initiated. The simulated rainfall duration provided three volume additions within each wetland cell. To simulate this event, a diffuser was constructed by drilling holes every 5 cm in a 6.1-m length of 7.6 cm diameter PVC pipe and placed above the inflow of the wetland. The diffuser was then connected to a 7.6- cm diameter hose which ran from a gas-powered 8-HP pump, located at one of the three water source wetland cells.

Individual wetland mesocosms, including control, were divided into four equal longitudinal transects (designated as inflow, #2, #3, and outflow). Plant, sediment, and water samples were collected along each transect (in each wetland) one week prior to atrazine application, as well as once a week for 5 weeks following application, and analyzed for the presence of atrazine. Collected plant samples (approximately 10 g dry wt.) consisted of that portion of the plant exposed in the water column (i.e. between sediment surface and top of the water column). Sediment samples (approximately 10 g dry wt.) were collected from the top 6 cm of wetland sediment with stainless steel scoops (100 ml volume). Plant and sediment samples were individually wrapped in aluminum foil and stored on ice (<2 h) until transported to a freezer (0°C) for storage pending analysis. Acid and acetone-rinsed 100-ml amber glass bottles were used to collect aqueous samples. Following collection, samples were placed on ice (<2 h) until transported to a walk-in cooler (4°C) pending analysis.

Ethyl acetate extracts of plant, sediment, and water samples were analyzed for atrazine at the USDA-ARS National Sedimentation Laboratory using gas chromatographic procedures similar to those reported by Smith et al. (1995). Gas chromatographs used were ‘Tracor model 540, with Dynatech Precision GC-411V autosamplers. A PE Nelson 2700 chromatography data system, consisting of three model 970 interfaces, Turbochrom™ 4.11 software and a microcomputer, was used for automated quantification and reporting of pesticide peak data including gas chromatograms. A multi-level calibration procedure was used with standards and samples injected in triplicate. Updated calibration curves were constructed after every tenth sample. The main analytical column was a 15 m x 0.53 mm i.d. J&W Scientific DB 210 (1.0 µm film thickness) Megabore column. The carrier gas was ultra-high purity helium at 12.3 cc/min, whereas both the column makeup gas and detector purge gas were ultra-high purity nitrogen at 60 and 10 cc/min, respectively. Column oven, inlet, and electron-capture detector temperatures were 140, 240, and 350°C, respectively. Under these conditions, atrazine had a retention time of
1.68 min. The lower limit of quantitative detection for atrazine was 0.05 µg/l. Mean extraction efficiencies, based on fortified samples, were > 90% from plant, sediment, and water samples. Atrazine residues were confirmed with a second analytical column of intermediate polarity (DB 17) and/or with a nitrogen—phosphorus detector.

**Pesticide fate modeling**

Initial estimates of initial atrazine fate were determined using physical, chemical, and biological attributes of the pesticide. Factors which affect fate, including transfer and transformation processes, were assimilated into individual partition coefficients for water, sediment, and plants. These partition coefficients were then summed to provide an ‘overall’ partition coefficient for each wetland and ditch. By substituting the new partition coefficient into the following equation, the amount of time necessary to retain atrazine (PRT, pesticide retention time) was determined in order to reach a final target concentration:

\[ C_t = C_i e^{kt}, \]  

(1)

where \( C_t \) = final target concentration (µg/l) of atrazine at time \( t \); \( C_i \) = initial (day 0) measured concentration of atrazine (µg/l); \( k \) = removal of atrazine (days\(^{-1}\)); and \( t \) = time (days). Once results from this equation were generated, specific half-lives were determined by substituting \( k \) into the following equation:

\[ t_{1/2} = \frac{0.693}{k} \]  

(2)

where \( t_{1/2} \) = half-life (days).

Use of these equations for treatment of pesticides in constructed wetlands was first suggested by Rodgers and Dunn (1992). This same basic equation assuming first order was used to calculate final design requirements for constructed wetland buffers. By substituting distance required to sequester one-half of the intended pesticide, a partition coefficient is derived for the actual wetland width. Constructed wetland width is derived from the following equation:

\[ \text{Percent pesticide remaining} = 100\% e^{-Kd} \]  

(3)

where \( K \) = partition coefficient (m\(^{-1}\)); and \( d \) = distance (flow length or width) of constructed wetland buffer (m).

To perform regression analyses on collected data, the maximum concentration of each pesticide at each sampled location was plotted against the distance from the injection point (0 m). Water, sediment, and plant analyses were conducted independently. Formulas developed from regression analyses were used to predict pesticide concentrations at various distances within the ditch and constructed wetlands. Half-lives of atrazine in water, sediment, and plants were determined by regression analysis on collected data from plotting maximum observed concentrations versus time.

**RESULTS**

**Evaluated Pesticide Half-lives**

For the proper evaluation of a constructed wetland or ditch for the removal of pesticide, the critical data from this study is the observed half-life in water of the respective pesticide. The half-life is used to determine a partitioning coefficient for treatment of the pesticide in the water column.

Within the ditch and one hour following initiation of simulated storm runoff, 61% of the total measured atrazine was associated with plant material. Only 2% of the total measured atrazine was associated with sediment, leaving 37% associated with the water column. 24 h following initiation of simulated storm runoff, 59% of the total measured atrazine was associated with plant material, while 29 and 12% were associated with sediment and water, respectively. Examining various cross-sections of the ditch over the study’s duration (28 days), 42 to 77% of the total measured atrazine was associated with plant material. Observed half-lives for atrazine in water,
sediment, and plants were 5.4, 19.7, and 6 days, respectively, for the entire ditch. According to regression analyses and previous storm event assumptions, aqueous atrazine concentrations could be mitigated to a no effects concentration (<20 µg L⁻¹) in a 50 m length of agricultural drainage ditch (Moore et al., 2001).

To effectively migrate the atrazine in the ditch with a 3 m width and a 50 m flow path would require a surface area of 150 square meters. In theory, a 50 m wide ditch with a 3 m flow path would similarly mitigate the atrazine.

In the constructed wetland prior to initiation of atrazine application, no detectable concentrations of atrazine were measured in plant, sediment, or water samples, including the control wetland. Atrazine (expressed as total measured percent mass) in wetland inflow samples (aqueous, sediment, plant) at day 0 ranged from 0 to 31 %, with individual wetland inflows ranging in length from 15 to 18 m. Between 17 and 42% of the total measured atrazine was within the first half of the wetlands (30 to 36 m) on day 0. Atrazine was below lower limits of analytical detection (0.05 µg/kg) in all sediment and plant samples collected for the duration of this study. Therefore, all reported concentrations are from aqueous samples only.

Approximately 35 days following initial atrazine application, percent ‘removal’ (transfer/ transformation) of atrazine was determined for aqueous samples. In wetlands with targeted concentration of 147 µg L⁻¹, 70% of atrazine was transferred or transformed from the water column. Of the percentage of atrazine mass detected in the wetlands, 66 to 82% was located in the first three transects or 75% of the wetland. The wetlands with targeted concentration of 147 µg L⁻¹ transferred or transformed only 34 to 37% of atrazine. Percent measured atrazine in inflows of each wetland was below 35%. Observed half-lives in aqueous portions of wetlands with targeted atrazine concentrations of 73 µg L⁻¹ and 147 µg L⁻¹ were 18 and 47 days, respectively (Moore et al., 2000).

The threshold concentration of atrazine exiting the wetland was determined to be 20 µg L⁻¹. This estimate was based on a study by Huber (1993) in which 20 µg L⁻¹ was the no observed effects concentration for aquatic ecosystems. Using this concentration as C, in the pesticide fate model, initial estimates of pesticide retention time were 59 days for wetlands amended with initial target concentration of 73 µg L⁻¹ and 91 days for wetlands amended with initial target concentration of 147 µg L⁻¹. Refinement of initial partition coefficients using field-derived data concluded that observed pesticide retention time were 30 and 39 days for wetlands with initial target concentration of 73 µg L⁻¹, and 143 and 133 days for wetlands with initial target concentration of 147 µg L⁻¹. Using Eq. (3) to further derive wetland design, it was determined that for initial atrazine concentrations of 73 µg L⁻¹, wetland travel distance needed for effective mitigation of atrazine under these conditions ranged from 101 to 164 m. For those wetlands with initial atrazine concentrations of 147 µg L⁻¹, effective pesticide travel distances in constructed wetlands ranged from 103 to 281 m.

These wetland travel distances are greater than that proposed by the ditch distances to mitigate atrazine. Further wetland studies are ongoing that should support the lower flow paths required to assimilate atrazine in constructed wetlands than in the ditch.

**DISCUSSION**

**Pesticide Reduction in Constructed Wetlands**

When an attempt is made to use constructed wetlands to treat non-point source pesticide discharges, the pesticide retention time (PRT) is more important than the hydraulic retention time (HRT), therefore HRT=PRT. Characteristics of pesticides that would be candidates for treatment with constructed wetlands include: low water solubility, adequate biotransformation capacities, decreased half-life, and little or no phytotoxicity.
Constructed wetlands would serve as sufficient protective buffers of agricultural runoff containing pesticides; however retention capacities differ with varying pesticide environmental chemistries and concentrations.

The design of a constructed wetland for pesticide reduction from agricultural non-point discharge can be based upon the equations above. For example, if the conservation plans call for reducing atrazine runoff by 50%, with a half-life in water of 24 days, the constructed wetland flow length is computed by first determining the partition coefficient using equation 2:

\[
T_{1/2} = \frac{0.693}{K} \\
24 = \frac{0.693}{K} \\
K = 0.029
\]

Using the assumption that the first order partition coefficient with respect to time is the same for distance, then the constructed wetland flow length is derived from equation 3:

\[
\text{Percent pesticide remaining} = 100\% e^{-Kd} \\
50\% = 100\% e^{-0.029d} \\
d = 24 \text{ m}
\]

Although the flow path is determined to be 24 m, to achieve the necessary half-life time (24 days), it will be necessary to capture and detain the runoff in the constructed wetland before release. This will require establishing a particular design event which will be fully treated but above which only partial treatment will occur. This is a practical approach to non-point source discharge treatment: treat ‘normal’ events, partially treat “extreme” events. This may differ from a Nutrient and Sediment Control (NSC) system, where extreme events may carry the most sediment and nutrients. A decision must be made on what discharge component (pesticide, sediment, nutrient) is being planned for principal treatment. Then treatment of other components can be maximized as much as possible.

**Example Problem**

A constructed wetland is being planned for a 40 hectare (98.8 acres) cornfield. The goal is to reduce the pesticides in the discharge by 50%. Since atrazine has a half-life in the water column (24 days) greater than metolachlor (10 days), atrazine will be used as the limiting design parameter. For the location selected, the 2 yr-24 hr storm event is 8.9 cm (3.5 inches). For corn on a hydrologic soil group B, contoured and terraced with crop residue, the Runoff Curve Number is 70. The runoff for this event is 2.6 cm (1.01 inches), which becomes the design runoff. Runoff greater than 2.6 cm (1.01 inches) may by-pass the constructed wetland if it would impractically increase the size and cost of the constructed wetland.

From above, the design flow-path was determined to be at least 24 m to reduce the atrazine by 50%, so long as the detention time was 24 days. Smaller events are anticipated within the 24-day period; however, some detention capacity should have been restored. The runoff of 2.6 cm (1.01 inches) from 40 ha (98.8 acres) requires 10,400 m³ (13,624 yds³) of detention storage. The outlet would be designed to remove the detention storage over the half-life period.

If the designer starts with a NSC system design, to meet pesticide reduction goals, the appropriate detention could be incorporated by either adding to the NSC capacities, or adding additional detention storage. Table 1 shows the incorporation of pesticide reduction into the NSC design guidance. Local conditions will necessitate changes in the design procedure.
Table 1

<table>
<thead>
<tr>
<th>Practice Components</th>
<th>Cont. Sed.</th>
<th>Grassed Buffer</th>
<th>Vegetated</th>
<th>Deep</th>
<th>Vegetated</th>
<th>Apparent</th>
<th>Pesticide Detention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Drain. Basin Area</td>
<td>(ac)</td>
<td>(sq ft)</td>
<td>(sq ft)</td>
<td>(sq ft)</td>
<td>(sq ft)</td>
<td>(cu. yds)</td>
<td>(cu. yds)</td>
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<tr>
<td>&lt;25</td>
<td>1,000</td>
<td>10,000</td>
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<td>10,000</td>
<td>3,750</td>
<td>2,600</td>
<td>3,400</td>
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<tr>
<td>50</td>
<td>1,250</td>
<td>12,500</td>
<td>12,600</td>
<td>16,000</td>
<td>5,000</td>
<td>4,000</td>
<td>6,800</td>
</tr>
<tr>
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<td>15,000</td>
<td>15,000</td>
<td>22,000</td>
<td>6,250</td>
<td>5,400</td>
<td>10,200</td>
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<tr>
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<td>2,000</td>
<td>17,500</td>
<td>11,500</td>
<td>28,000</td>
<td>7,500</td>
<td>6,800</td>
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<tr>
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<td>22,500</td>
<td>22,500</td>
<td>40,000</td>
<td>10,000</td>
<td>9,700</td>
<td>20,400</td>
</tr>
<tr>
<td>&gt;150 acres - increase size of components proportional to contributing area.</td>
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By including pesticide reduction into a NSC design, the deep pond surface area required will be from 1.3 (25 acres) to 2.1 (150 acres) larger in this example. Accepting treatment of a smaller design storm could reduce these values. For instance, reducing the design storm rainfall to 6.4 cm (2.5 inches), would reduce the runoff to 1.2 cm (0.46 inches), decreasing the detention capacity by one-half (in that case, NSC existing detention would appear adequate). A review of a long-term rainfall record (this record includes extreme tropical events) in Mississippi found that 86% of all precipitation occurred in events of less than 6.4 cm (2.5 inches). Therefore, treatment design based upon lower precipitation (and therefore runoff) events appears reasonable.

Whereas normally hydrologic designs (e.g. dams) are based on worst-case scenarios for safety reasons, treatment wetlands can be based upon treating the majority of normal events, with provisions (by-pass) made to prevent structural damage or failure due to extreme, partial-treatment events.

CONCLUSIONS

The use of constructed wetlands and drainage ditches to treat pesticides contained in agricultural non-point discharges must be cautiously assessed. The pesticides involved, effectiveness in removing the pesticides, treatment level required, the cost of the constructed wetland and drainage ditches, the surface area required, and other applicable Best Management Practices (BMP) must be evaluated carefully to ensure that the correct and best methodology to reduce pesticide delivery to receiving water bodies is selected and applied. Pesticides that sorb readily to plants and soil (chlorpyrifos) will be treated more easily in a constructed wetland and drainage ditch than a more water-soluble pesticide (atrazine), although initial concentrations in runoff may offset this increased solubility.

Characteristics which make pesticides candidates for use with constructed wetlands and drainage ditches for mitigation purposes include low water solubility, adequate biotransformation capacities, decreased half-lives, and little or no phytotoxicity, although this does not automatically exclude all herbicides from consideration.

Constructed wetlands and drainage ditches are not panaceas for environmental problems. In the case of mitigation of pesticide-associated runoff, these systems are useful and effective, but it is highly dependent upon what pesticide the planner is attempting to mitigate. Careful
consideration must be involved in the planning phases in order to determine whether or not constructed wetlands and drainage ditches would be the most beneficial (or sole) BMP to use for risk aversion. This study offers field data for atrazine, as well as conservative models and design characteristics for determining the utility of implementing constructed wetlands for pesticide mitigation.

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REFERENCES


