Mitigation of metolachlor-associated agricultural runoff using constructed wetlands in Mississippi, USA

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Abstract

A loss of marginal wetland acreage adjoining agricultural fields has created a potential problem with water quality enhancement of agricultural runoff via wetlands. Current research is investigating the utility of constructed wetlands for pesticide mitigation purposes, thereby restoring water quality enhancement capability to the area. Constructed wetland mesocosms (59–73 m x 14 m), located at the University of Mississippi Field Station (Lafayette County, MS), were amended with metolachlor to simulate a cropland runoff event. Target concentrations for wetlands were 73 and 147 µg/l metolachlor in addition to an unamended control (0 µg/l). Water, sediment, and plant samples were collected weekly for 35 days following metolachlor amendment. Samples were collected from sites, longitudinally distributed within each wetland, and analyzed for metolachlor using gas chromatography. Between 7 and 25% of measured metolachlor mass was in the first 30–36 m (from inflow) of wetlands immediately following application and simulated rainfall. Approximately 10% of measured metolachlor mass was in plant samples. Suggested wetland travel distances for effective mitigation of metolachlor runoff ranged from 100 to 400 m. According to the results from this research, aquatic receiving system impacts due to metolachlor runoff could be mitigated by using constructed wetlands as buffers. Landowners and government agencies can integrate this information into a water management plan, allowing for better control of both quantity and quality of runoff water from individual agricultural fields.

1. Introduction

The agricultural production landscape in North America, particularly the Mississippi Delta, once had abundant wetland acreage. Due to increased food and other resource demands, many wetlands associated with agricultural fields were drained for immediate use in crop production (Ort et al., 1994; Reddy and Gale, 1994). While increased acreage generally benefited agricultural production, an unforeseen consequence of decreased wetland acreage was decreased water quality enhancement.

Water quality and agriculture are closely linked because of potential non-point source pollution of lakes, rivers, streams, etc. by agricultural runoff (Cooper, 1993; Maul and Cooper, 2000). Contaminants such as sediments, bacteria (e.g., dairy waste),...
Table 1
Physical, chemical, and fate characteristics of the herbicide metolachlor

<table>
<thead>
<tr>
<th>Structure</th>
<th>Molecular weight (g/mol) (^a)</th>
<th>283.79</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Specific gravity (g/mol) (^a)</td>
<td>1.085</td>
</tr>
<tr>
<td></td>
<td>Vapor pressure (mm Hg) (^b)</td>
<td>(1.0 \times 10^{-5})</td>
</tr>
<tr>
<td></td>
<td>Water solubility (mg/l) (^b)</td>
<td>530</td>
</tr>
<tr>
<td></td>
<td>(\log K_{ow}) (^c)</td>
<td>3.28</td>
</tr>
<tr>
<td>Aqueous photolysis, (T_{1/2}) (day) (^c)</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Soil photolysis, (T_{1/2}) (day) (^c)</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Water persistence, (T_{1/2}) (day) (^c)</td>
<td>47</td>
<td></td>
</tr>
<tr>
<td>Soil persistence, (T_{1/2}) (day) (^b)</td>
<td>70</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis, (T_{1/2}) (day) (^a)</td>
<td>&gt;200</td>
<td></td>
</tr>
<tr>
<td>Plant persistence, (T_{1/2}) (^d)</td>
<td>120</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) USEPA (1980).
\(^b\) EXTOXNET (1996).
\(^c\) USDA (1995).
\(^d\) Personal communication with Novartis source, 1998.

nutrients (e.g., nitrate and phosphorus), and pesticides may be transported from agricultural fields during storm events (Cooper, 1990). Metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl)acetamide] is an extensively used herbicide that controls broadleaf weeds and grasses mainly in soybeans (Glycine max), but in corn (Zea mays) as well (Seybold and Mersie, 1996; Barnes et al., 1992; LeBaron et al., 1975) (Table 1). It was estimated that some 56 t of metolachlor were transported in the Mississippi River to the Gulf of Mexico in 1991 (Ro and Chung, 1994). As Cooper (1993) stated, pesticides have played key role against food shortages and vector-borne diseases, and humankind would be vastly different without their usage. However, there remains the possibility of non-target effects of pesticide-associated agricultural runoff, and scientists are currently studying methods to minimize these risks.

One possible solution for minimization of agricultural runoff impacts upon receiving streams and other water bodies involves development of constructed wetlands to replace lost edge-of-field wetlands and serve as buffers for runoff. The utility of constructed wetlands for mitigating several different kinds of contaminants has been extensively studied. Their efficiency in removing organics, nutrients, and metals has been previously reported (Wolverton and McDonald, 1981; Nichols, 1983; Gersberg et al., 1984a,b; Wieder and Lang, 1984; Wolverton et al., 1984; Cooper et al., 1994; Hawkins et al., 1997). Few studies, however, have focused on the potential of constructed wetlands to serve as buffers for mitigation of pesticide runoff (Wolverton and Harrison, 1973; Gilliam, 1994).

This research focused on examination of the fate of metolachlor (associated with simulated cropland runoff) in constructed wetlands, as well as an evaluation of the potential buffering capacity of these wetlands. The objectives addressed by this research included: (1) determining effectiveness of constructed wetlands at decreasing concentrations of metolachlor from inflow to outflow, (2) determining mass partitioning (plants, sediment, and water) of metolachlor in constructed wetlands, and (3) determining appropriate wetland design parameters for effective mitigation of metolachlor-associated agricultural runoff.

2. Materials and methods

2.1. Study site

The 300 ha University of Mississippi Field Station (UMFS) is located approximately 18 km east of Oxford in Lafayette County, MS. Wetlands used for pesticide research were constructed with a liner of 10 cm compressed bentonite clay beneath the hydrosoil to prevent potential groundwater contamination. Wetland hydrosoils were predominantly sand with approximately 16% silt (Table 2).
2.2. Design of wetland cells

Eight constructed wetland cells at the UMFS, specifically designed to evaluate fate of pesticides in wetlands were used for this research (Rodgers and Dunn, 1992). Five wetland cells were chosen as test cells, with one cell serving as an unamended control. Three remaining wetland cells served as water sources for the simulated rainfall. Each experimental wetland cell was randomly assigned a metolachlor concentration representing potential worst-case metolachlor-runoff scenarios (Wauchope, 1978). Amount of metolachlor applied (as simulated runoff) was based on simulations of an immediate 2.54 cm rainfall on 4, 40, and 400 ha agricultural fields. Calculated wetland cell volumes were used to determine appropriate metolachlor masses to apply to systems, as well as time required for their hydraulic turnovers. Wetland mesocosm #2 was amended with 38.24 g of metolachlor, while mesocosms #3, #5, and #6 were amended with 55.37, 31.96, and 44.66 g of metolachlor, respectively. Targeted concentrations following simulated rainfall dilution were 73 and 147 m g/l metolachlor for wetland mesocosms. Each concentration was repeated in a second mesocosm, giving a total of four experimental cells in addition to an unamended control. Because of slight differences in wetland lengths and widths, masses of metolachlor necessary to be amended into mesocosms differed between systems with the same target concentration. Daily rainfall was recorded at the nearest weather station (USDA-ARS National Sedimentation Laboratory, Oxford, MS). Following each mesocosm’s metolachlor application, a one-time simulated rainfall with an intensity of 12.6 l/s was initiated. The “rainfall” duration provided three volume additions within each wetland mesocosm. This event was simulated by using a diffuser which was constructed by drilling holes every 5 cm in a 6.1 m length of 7.6 cm diameter PVC pipe. 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 mesocosms.

2.3. Sample collection

Each experimental wetland (including control) was divided into four equal longitudinal transects (designated as inflow, #2, #3, and outflow). Aqueous, sediment, and plant (primarily Juncus sp.) samples were collected across these transects (in each wetland) 1 week prior to metolachlor application, as well as every 7 days, for approximately 35 days following metolachlor application. Aqueous samples were collected in acid/acetone-rinsed 100 ml amber glass bottles. Sediment samples were collected from the top 6 cm of wetland sediment using a stainless steel scoop (100 ml volume). Samples were wrapped in aluminum foil and stored on ice until they could be placed in a freezer (−4°C) for storage pending analysis. Plant samples collected consisted of only that portion of the plant exposed in the water column (i.e. above the sediment, but not exposed to atmosphere). Samples were likewise wrapped in aluminum foil and stored on ice until being placed in a freezer pending analysis.

2.4. Metolachlor analysis

Ethyl acetate extracts of water, sediment, and plant samples were analyzed for metolachlor 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, equipped 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. Standards and samples were injected in triplicate while using a multi-level calibration procedure. Calibration curves were updated every 10th sample. A 15 m x 0.53 mm i.d. J and W Scientific DB 210 (1.0 μm film thickness) Megabore™ column was the central analytical column used for this analysis. The carrier gas was ultra-high purity helium at 12.3 cm³/min. Column makeup gas and detector purge gas were ultra-high purity nitrogen at 60 and 10 cm³/min, respectively. Column oven, inlet, and electron-capture detector temperatures were 140, 240, and 350°C, respectively. Under these conditions, metolachlor had a retention time of 4.82 min. Lower limit of quantitative detection for metolachlor was 0.05 μg/l. Based on fortified samples, mean sample extraction efficiencies were 94.6±1.4% for water, 90.1±1.4% for sediment, and 92.9±2.1% for plant material. Metolachlor residues were confirmed with
a second analytical column of intermediate polarity (DB 17) and/or with a nitrogen–phosphorus detector.

2.5. Pesticide fate modeling

Initial estimates of pesticide fate were determined after examination of physical, chemical, and biological data. Factors affecting fate (i.e. transfer and transformation processes) were assimilated into partition coefficients for each environmental compartment (water, sediment, and plants). These individual partition coefficients were then incorporated into an overall partition coefficient for the entire wetland. Using the following equation, it was possible to determine the amount of time necessary to retain pesticides in order to reach a final target concentration:

\[ C_t = C_i e^{-Kt} \]  

where \( C_t \) is the concentration (final target concentration) (µg/l) at time \( t \), \( C_i \) the initial (day 0) target concentration (µg/l), \( K \) the overall partition coefficient (per day), and \( t \) the time (day).

Final target concentrations are variable within this model. For the scope of this research, the final target concentration was one in which there were no observed effects on the most sensitive (non-algal) species tested (44 µg/l metolachlor). This information was derived from a summary of toxicity test results with metolachlor from USEPA's Pesticide Ecotoxicity Database. Substitution of known variables into the model allowed for prediction of the time required to retain pesticides (e.g. metolachlor) within a wetland (pesticide retention time (PRT)). It is worthy to note that initially, PRT and hydraulic retention time (HRT) cannot be assumed as equal. Only after field validation can such an assumption be used in design and model applications.

Observed half-lives in aqueous, sediment, and plant compartments of each wetland were determined by performing an exponential regression on measured metolachlor concentrations across each entire wetland. The general equation used to determine observed half-lives was the same as above. By substituting \( K \) into the following equation, observed half-lives were determined:

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

where \( T_{1/2} \) is the half-life (day).

This same basic equation 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:

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

where \( K \) is the partition coefficient, and \( d \) the distance (width) of constructed wetland buffer (m).

3. Results

3.1. Background and initial samples

In samples of water, sediment, and plant tissues collected 1 week prior to metolachlor application, no detectable concentrations of metolachlor were measured. Additionally, no detectable concentrations of metolachlor were measured in the control wetland throughout the 35 days duration of this research. Rainfall did not appear to influence metolachlor concentrations. Aqueous, sediment, and plant tissue samples collected immediately following the simulated runoff event (day 0) provided a baseline indication of retained metolachlor in wetlands from which to analyze the pesticide’s fate for 35 days. No detectable concentrations of metolachlor were observed in any sediment sample collected following the application. Between 7 and 25% of the total measured metolachlor mass was located within the first 30–36 m of the wetlands on day 0, indicating increased movement of metolachlor into the latter two transects of the constructed wetlands (Table 3).

3.2. Metolachlor transfer and transformation

Percent transfer/transformation was determined for both aqueous and plant phases of each wetland following 35 days. In wetlands with targeted concentrations of 73 µg/l, 91±4% of the aqueous metolachlor was transferred/transformed, while 16±15% of the plant-associated metolachlor was transferred/transformed. In wetlands targeted with metolachlor concentrations of 147 µg/l, 87±0.5% of the aqueous metolachlor was transferred/transformed. Additionally, 67±12%, respectively, of the plant-associated metolachlor was...
transferred/transformed. Following 35 days, 64–85% of measured metolachlor was present within the first three transects of the constructed wetlands. The greatest mean mass percentage of metolachlor detected in the inflows was 32% (wetland #3) (Table 4). By combining total measured metolachlor concentrations in water and plants from each wetland, overall metolachlor transfer/transformation efficiencies ranged from 48% (wetland #2) to 83% (wetland #3) (Fig. 1). Observed half-lives in aqueous portions of wetlands ranged from 8 days (wetland #6 with targeted concentration of 147 μg/l) to 13 days (wetland #5 with targeted concentration of 73 μg/l). No observed relationship was evident between aqueous half-lives and targeted concentrations. Observed half-lives were determined for metolachlor and plant material as well. Half-lives in plants ranged from 17 days (wetland #2 with targeted concentration of 73 μg/l) to 61 days (wetland #6 with targeted concentration of 147 μg/l) (Table 5).

3.3. Plant sorption

Sorption of metolachlor to plant material was determined in this study by derivation of plant sorption coefficients ($K_p$) throughout the 35 days duration of this research (Table 6). Sorption coefficients in all wetlands generally increased throughout the duration of this research, with all wetlands reaching their greatest sorption coefficients on day 35, with the exception of

### Table 3
Percentage of total metolachlor in individual transects within constructed wetlands at day 0 in Lafayette County, MS

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Targeted concentration (μg/l)</th>
<th>Inflow</th>
<th>Percent total mass</th>
<th>Outflow</th>
<th>Transect length (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Transect 2</td>
<td>Transect 3</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>73</td>
<td>2</td>
<td>5</td>
<td>55</td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>147</td>
<td>5</td>
<td>20</td>
<td>29</td>
<td>46</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>10</td>
<td>2</td>
<td>1</td>
<td>86</td>
</tr>
<tr>
<td>6</td>
<td>147</td>
<td>3</td>
<td>4</td>
<td>83</td>
<td>10</td>
</tr>
</tbody>
</table>

*a The wetland number corresponds to the actual physical designation of the wetland at the UMFS (e.g., Wetland 2).

### Table 4
Transport of metolachlor within wetland mesocosms 35 days post-application in Lafayette County, MS

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Targeted concentration (μg/l)</th>
<th>Measured mean percent metolachlor (±S.D.)</th>
<th>Inflow</th>
<th>Transect 2</th>
<th>Transect 3</th>
<th>Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>73</td>
<td>12 (8)</td>
<td>19 (8)</td>
<td>33 (11)</td>
<td>35 (5)</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>147</td>
<td>32 (18)</td>
<td>37 (13)</td>
<td>16 (7)</td>
<td>14 (16)</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>30 (16)</td>
<td>28 (15)</td>
<td>17 (10)</td>
<td>30 (28)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>147</td>
<td>16 (7)</td>
<td>17 (8)</td>
<td>38 (23)</td>
<td>30 (11)</td>
<td></td>
</tr>
</tbody>
</table>

*a The wetland number corresponds to the actual physical designation of the wetland at the UMFS (e.g., Wetland 2).

### Table 5
Observed metolachlor half-lives in water and plants in wetland mesocosms in Lafayette County, MS

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Targeted concentration (μg/l)</th>
<th>Half-life (day)</th>
<th>Overall transfer/transform (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Water</td>
<td>Plants</td>
</tr>
<tr>
<td>2</td>
<td>73</td>
<td>9</td>
<td>60</td>
</tr>
<tr>
<td>3</td>
<td>147</td>
<td>10</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>13</td>
<td>61</td>
</tr>
<tr>
<td>6</td>
<td>147</td>
<td>8</td>
<td>60</td>
</tr>
</tbody>
</table>

*a The wetland number corresponds to the actual physical designation of the wetland at the UMFS (e.g., Wetland 2).
wetland #3 (maximum at day 28). Mean plant sorption coefficients for entire wetlands ranged from 17 (wetland #3) to 51 (wetland #5). No visual signs of herbicide stress (e.g., stunted growth, chlorosis, necrosis) upon plant material were observed during this study.

3.4. Suggested travel distances

Based on design equations, for wetlands receiving initial metolachlor concentrations of 73 μg/l, adequate travel distance for constructed wetland buffers would

Table 6
Sorption coefficients for plant (Kp) partitioning in constructed wetlands in Lafayette County, MS

<table>
<thead>
<tr>
<th>Day</th>
<th>Wetland #2</th>
<th>Wetland #3</th>
<th>Wetland #5</th>
<th>Wetland #6</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>3.85</td>
<td>0</td>
<td>17.28</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>8.55</td>
<td>8.55</td>
<td>21.72</td>
<td>4.32</td>
</tr>
<tr>
<td>14</td>
<td>4.60</td>
<td>18.56</td>
<td>29.92</td>
<td>21.44</td>
</tr>
<tr>
<td>21</td>
<td>21.61</td>
<td>20.28</td>
<td>72.22</td>
<td>58.41</td>
</tr>
<tr>
<td>28</td>
<td>0</td>
<td>41.20</td>
<td>51.34</td>
<td>32.47</td>
</tr>
<tr>
<td>35</td>
<td>133.32</td>
<td>15.28</td>
<td>113.22</td>
<td>71.16</td>
</tr>
</tbody>
</table>
range from 102 to 170 m. On the other hand, for those constructed wetlands receiving initial concentrations of 147 µg/l metolachlor, wetland travel distances necessary for effective mitigation would range from 100 to 400 m.

4. Discussion

4.1. Metolachlor fate

Observed aqueous half-lives varied little between the four experimental wetland mesocosms (8–13 days). Ng et al. (1995) reported the half-life of metolachlor in water to vary between 19 and 52 days. With the exception of wetland #3, observed plant half-lives were basically the same (60 or 61 days). Unlike the other wetland mesocosms, the \( K_p \) for wetland #3 did not reach its maximum until day 28; however, between days 28 and 35, there was approximately 75% transfer/transformation which most likely accounted for the relatively short half-life (compared to the other mesocosms). Perhaps another reason for the behavior of metolachlor in wetland #3 versus wetland #6 (same target concentrations of 147 µg/l) stems from the amount of metolachlor (as active ingredient) amended into the two wetlands. Wetland #3 received approximately 10 g more metolachlor (as active ingredient) than did wetland #6. This difference in mass of active ingredient applied was necessary in order to obtain identical target concentrations. Because wetland volumes differed, so did metolachlor active ingredient applications. Additionally, there was an almost 25% increase in transfer/transformation efficiency in constructed wetlands with targeted concentrations of 147 µg/l as opposed to those wetlands with targeted concentration of 73 µg/l.

Most of the research concerning metolachlor has been limited to studies examining dissipation, loss, leaching, and other properties (Masse et al., 1998; Seybold and Mersie, 1996; Gaynor et al., 1995; Ng et al., 1995; Barnes et al., 1992). Few, if any, studies have directly examined metolachlor’s fate in constructed wetlands or similar exposure methods. Surprisingly, when compared to other herbicides such as atrazine, little overall research has been performed on metolachlor. It is believed that metolachlor and other acetanilide herbicides affect target plant species by interfering with different physiological processes such as lipids, protein, and flavonoid biosynthesis; however, research is still inconclusive at this point (Fairchild et al., 1998; Weed Science Society of America, 1994). Fairchild et al. (1998) further commented on the lack of published metolachlor-plant toxicity data. It is anticipated that results from the current research will aid in the construction of a better database for fate of metolachlor in aquatic and plant environments.

4.2. Wetlands as BMPs

Best management practices (BMPs), such as the currently-proposed constructed wetland buffers, serve as risk aversion strategies for agricultural producers. Implementation of such BMPs, while primarily voluntary, aid in decreasing potential risk to downstream aquatic receiving systems due to sediment, nutrient, or pesticide runoff. Use of constructed wetlands as mitigation tools, while specifically effective, is not to be mistaken as a “cure-all” for any environmental problem. When dealing specifically with herbicides, such as metolachlor, many factors must be considered during the design process. Intended threshold concentration of the wetland, size necessary for effective mitigation, and potential impacts to the wetland itself (from metolachlor-associated runoff) are important considerations. Based on current results, constructed wetland buffers could be implemented as BMPs on sufficient size agricultural fields (>4 ha). Scientists must still be cautious since metolachlor, as other herbicides, have the potential to damage an essential macrofeature of constructed wetlands — macrophytes. With careful guidance and planning, constructed wetlands have the potential to serve in a variety of useful capacities in agricultural systems.

5. Conclusions

The fundamental premise of this research lies in the potential to replace or construct wetlands at the land–water interface of agricultural fields in order to mitigate potential risks to downstream aquatic receiving systems from pesticide runoff. In order for this to be a viable option, pesticides must be retained, in some form, within the proposed wetland (Rodgers and
Dunn, 1992). Most likely, this is achieved through the process of sorption to either plant or sediment material. Current results suggest that wetland buffer travel distances of 100–400 m (for fields 4, 40, and 400 ha in size) would be sufficient to mitigate metolachlor from potential contamination of downstream aquatic receiving systems.

References


USDA (US Department of Agriculture), 1995. Pesticide Properties Database Website. USDA.


