Constructed wetlands for mitigation of atrazine-associated agricultural runoff

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Received 4 June 1999; accepted 18 December 1999

“Capsule”: Buffer travel distances of 100–280 m were shown to be necessary to effectively manage atrazine runoff.

Abstract

Atrazine was amended into constructed wetlands (59–73×14×0.3 m) for the purpose of monitoring transport and fate of the pesticide to obtain information necessary to provide future design parameters for constructed wetlands mitigation of agricultural runoff. Following pesticide amendment, a simulated storm and runoff event equal to three volume additions was imposed on each wetland. Targeted atrazine concentrations were 0 μg/l (unamended control), 73 μg/l, and 147 μg/l. Water, sediment, and plant samples were collected weekly for 35 days from transects longitudinally distributed throughout each wetland and were analyzed for atrazine using gas chromatography. Between 17 and 42% of measured atrazine mass was within the first 30–36 m of wetlands. Atrazine was below detection limits (0.05 μg/kg) in all sediment and plant samples collected throughout the duration of this study. Aqueous half lives ranged from 16 to 48 days. According to these data, conservative buffer travel distances of 100–280 m would be necessary for effective runoff mitigation. Published by Elsevier Science Ltd.

Keywords: Atrazine; Fate; Constructed wetlands; Mitigation

1. Introduction

In response to an increased demand for food and fiber production in the 1950s, land that was previously undisturbed habitat has since been used for agricultural purposes (Ort et al., 1994). These habitats included wetlands located at the edge of some agricultural fields. Such ‘edge-of-field’ wetlands were drained in order 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. One potential problem with this scenario of wetland draining and increased pesticide usage is that the former wetland area is no longer capable of water quality enhancement or mitigation for pesticide-associated cropland runoff, a previous potential function of the wetland.

The presence of pesticides in surface, ground, and drinking water have been of particular concern. The triazine herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine), one of the most intensively used pesticides in North America, has frequently been detected in such aqueous samples (Solomon et al., 1996) (Table 1). Concentrations of atrazine in surface and groundwater samples have not always elicited ecological or human health concern; however, due to atrazine’s persistence, there is occasionally the potential for concern, especially immediately following pesticide application and in drainage areas with little or no lateral pesticide transport or flow (lakes, small water bodies, reservoirs, etc.) (Pratt et al., 1988).

Atrazine usage (as kilograms of active ingredient) increased by a factor of eight between 1966 and 1991 (Larson et al., 1997). Extensive biological research concerning effects of atrazine has been performed, including a substantial literature review and ecological risk assessment by Solomon et al. (1996). According to Nowell and Resek (1994), the knowledge base of atrazine’s presence in the Mississippi River basin is greater
Table 1

Physical properties and fate characteristics of atrazine

<table>
<thead>
<tr>
<th>Structure</th>
<th>Molecular weight (g/mol) (a, b, c)</th>
<th>215.70</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific gravity (g/mol) (a)</td>
<td>1.187</td>
<td></td>
</tr>
<tr>
<td>Melting point (°C) (a)</td>
<td>175–177</td>
<td></td>
</tr>
<tr>
<td>Vapour pressure (mm Hg) (a, c)</td>
<td>(3.0 \times 10^{-7})</td>
<td></td>
</tr>
<tr>
<td>Water solubility (mg/l) (a, c)</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>(\log K_{ow}) (a, c)</td>
<td>2.68</td>
<td></td>
</tr>
<tr>
<td>(K_{ow}) (a)</td>
<td>25–155</td>
<td></td>
</tr>
<tr>
<td>Aqueous photolysis (T_{1/2}) (days) (a, d)</td>
<td>335</td>
<td></td>
</tr>
<tr>
<td>Soil photolysis (T_{1/2}) (days) (a, d)</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Hydrolysis (T_{1/2}) (days) (a)</td>
<td>244</td>
<td></td>
</tr>
</tbody>
</table>

\(a\) Ciba-Geigy Corporation (1994).
\(b\) RSC (1987).
\(c\) EXTOXNET (1996).
\(d\) Solomon et al. (1996).
\(e\) Li and Feldbeck (1972).

than for any other pesticide in any other part of the nation. Use of atrazine is widespread in the United States (including the Mississippi Delta) and there are potential ecological and human health concerns in bodies of water with little or no lateral movement. As previously stated, ‘edge-of-field’ wetlands in many Mississippi Delta agricultural fields have been drained for production use, thereby losing their potential function of water quality enhancement and agricultural runoff mitigation. Current research was directed towards evaluating the potential of 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 constructed wetland mesocosms was addressed by: (1) determining effectiveness of constructed wetlands to decrease concentrations of atrazine from inflow to outflow; (2) determining the mass partitioning (plants, sediment, water) of atrazine in constructed wetlands; and (3) determining appropriate constructed wetland design parameters for mitigation of atrazine-associated agricultural runoff.

2. Materials and methods

2.1. Design

Constructed wetland cells 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 (in consecutive series) 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 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 was initiated. The simulated rainfall had an endurance of approximately 1 min. The water from each wetland was sampled at the outflow for analysis. 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) 1 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.

### 2.3. Atrazine 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 Tracer model 540, with Dynatech Precision GC-411V autosamplers. A PE Nelson 2700 chromatography system, consisting of three model 970 interfaces, 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 10th sample. The main analytical column was a 15 m×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.

### 2.4. 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. By substituting the new partition coefficient into the following equation, it was possible to determine the amount of time necessary to retain atrazine (PRT, pesticide retention time) in order to reach a final target concentration:

\[ C_t = C_i e^{-K_t t} \]

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

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

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 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:

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

where \( K \) = partition coefficient; and \( d \) = distance (width) of constructed wetland buffer (m).

Observed half-lives in each wetland’s environmental compartments (plant, sediment, water) were determined by performing a regression on measured concentrations across each wetland. The preceding general Eq. (2) was also used to determine observed half-lives. Refinement of the initial estimated PRT was performed after all field data were collected. The new observed PRT was based on amendments to partition coefficients based on data collected from the intensive field study.

### 3. Results

Prior to initiation of atrazine application, no detectable concentrations of atrazine were measured in constructed wetland 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 (Table 2). Between 17 and 42% of the total measured atrazine was within the first half of the wetlands (30–36 m) on day 0 (Fig. 1). 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 73 μg/l (#2 and #5), 70 and 66% of atrazine, respectively, was transferred or transformed from the water column (Fig. 2). Of the percentage of atrazine mass detected in the
wetlands, 66–82% was located in the first three transects (75%) of the wetland (Table 3). Wetlands #3 and #6 (targeted concentration of 147 µg/l) transferred or transformed only 34 and 37% of atrazine, respectively (Fig. 2). 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 were 16 and 21 days. Wetlands #3 and #6 (targeted atrazine concentration of 147 µg/l) had aqueous half-lives of 48 and 46 days, respectively.

The threshold concentration of atrazine exiting the wetland was determined to be 20 µg/l. This estimate was based on a study by Huber (1993) in which 20 µg/l was the no observed effects concentration for aquatic ecosystems. Using this concentration as $C_i$ in the pesticide fate model, initial estimates of PRT were 59 days for wetlands amended with initial target concentration of 73 µg/l and 91 days for wetlands amended with initial target concentration of 147 µg/l. Refinement of initial partition coefficients using field-derived data concluded that observed PRTs for wetlands were 30 and 39 days for wetlands with initial target concentration of 73 µg/l, and 143 and 133 days for wetlands with initial target concentration of 147 µg/l. Using Eq. (3) to further derive wetland design, it was determined that for initial atrazine concentrations of 73 µg/l, 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, effective pesticide travel distances in constructed wetlands ranged from 103 to 281 m.

4. Discussion

Migration of pesticides from agricultural fields into aquatic receiving systems (rivers, lakes, reservoirs, etc.) has received increased attention due to potential stress that may be inflicted upon such aquatic ecosystems. The mobility of certain pesticides (e.g. atrazine) has also resulted in evaluation of potential groundwater contamination (Klaine et al., 1988). Atrazine residues detected in groundwater wells sometimes exceeded the 3 µg/l maximum contaminant level for human consumption (US Environmental Protection Agency, 1991).

Several studies have reported values for atrazine lost during storm runoff events ranging from 0 to 2500 µg/l (Hall, 1974; Triplett et al., 1978; Jones et al., 1982; Klaine et al., 1988; Schottler et al., 1994; Solomon et al., 1996). A special review was initiated in 1994 by the US EPA because of atrazine residue concerns in different environmental compartments. Solomon et al. (1996) reported that concentrations in most rivers and streams.

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rarely exceed 20 µg/l, except for some pulse exposures in small-order streams.

Use of mentioned runoff models implies that atrazine fate may be described by simple exponential decay, which may be simpler than what actually occurs. Several studies have shown usefulness and predictability using similar modeling efforts in wastewater–wetland processing (Kadlec, 1989; Steiner and Freeman, 1989). Exponential modeling has also been useful for predictive fate of pesticides in wetlands (Reinert and Rodgers, 1984; Cassidy and Rodgers, 1988; Reinert et al., 1988). For this study, targeted concentrations were based on runoff models and manufacturer’s application rates. This allowed simulation of worst-case scenarios (rainfall immediately following pesticide application). According to previous studies between 0.1 and 3% of applied agricultural atrazine is lost to adjacent freshwater stream environments (Muir et al., 1978; Hormann et al., 1979). These percentages fall within the range of estimated atrazine runoff used for the current study’s target concentrations. Additionally, the current proposed model is conservative in the way that it integrates the rate coefficient, summarizing several transfer/transformation processes into a single, reported value.

In the current study, atrazine was below lower detection limits in all sediment and plant samples collected during the sampling regime. (Mean percent organic matter in constructed wetland sediment was 1.6%.) Atrazine has, however, been reported to partition to both sediment and plant phases in other studies (Jones et al., 1982; Jones and Estes, 1984; Buhler et al., 1993; Gilchrist et al., 1993; Barriuso et al., 1994; Fairchild et al., 1994; Ma and Selim, 1994; Detenbeck et al., 1996; Kruger et al., 1996). Forney and Davis (1981) reported that when concentrations of atrazine are present in both sediment and water phases, phytotoxicity was generally determined by the concentration in the water. They also found that atrazine in the sediment at concentrations of less than 1000 µg/l did not adversely affect plants.

Results from this research indicate when targeted application concentrations are doubled, observed aqueous half-lives at least double. Reported literature values of aqueous half-lives of atrazine range from 8 to 41 days (Fairchild et al., 1994; Detenbeck et al., 1996). Values for wetlands with targeted concentration of 73 µg/l fell within this range, and wetlands with targeted concentration of 147 µg/l only slightly exceeded this range (46 and 48 days).

Currently, little research has been published concerning the value of constructed wetlands to serve as ‘buffers’ between agricultural fields and receiving water bodies. However, investigations into restoration efforts of riverine and prairie pothole wetlands to serve as means of treatment for agricultural runoff have been initiated (Detenbeck et al., 1996). Klaine et al. (1988) reported that almost 90% of atrazine discharged from the first storm event following application was done so in the first 65% of the runoff. They suggested that if this runoff could be contained in some detaining structure with sufficient time for atrazine degradation, up to 90% of atrazine typically entering a receiving stream via agricultural runoff could potentially be reduced. The current study reports that after 35 days, an average of 52% (for all wetlands of both targeted concentrations) of measured atrazine is transferred or transformed.

The next problem to address concerns specific wetland size required for effective mitigation. This question is dependent upon the target threshold concentration allowable to enter aquatic receiving systems. Based on current findings, it would not be recommended to implement constructed wetlands as sole best management practices (BMPs) on smaller agricultural fields.

Table 3
Transport of measured atrazine mass within constructed wetland mesocosms 35 days post-atrazine application

<table>
<thead>
<tr>
<th>Wetland</th>
<th>Targeted concentration (µg/l)</th>
<th>Inflow</th>
<th>Transect 2</th>
<th>Transect 3</th>
<th>Outflow</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>73</td>
<td>10</td>
<td>24</td>
<td>32</td>
<td>34</td>
</tr>
<tr>
<td>3</td>
<td>147</td>
<td>23</td>
<td>35</td>
<td>24</td>
<td>18</td>
</tr>
<tr>
<td>5</td>
<td>73</td>
<td>34</td>
<td>29</td>
<td>15</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>147</td>
<td>29</td>
<td>18</td>
<td>28</td>
<td>25</td>
</tr>
</tbody>
</table>

* Percentages are based on 100% of the measured atrazine mass in each wetland, not necessarily 100% of the originally applied atrazine.
(e.g. 4 ha). For larger fields, it becomes a two-fold question of economics and potential risk. Farm managers must examine the value of land converted into wetlands, while weighing ecological (and potentially economical) benefits. Another problem that may arise with constructed wetlands to mitigate herbicide runoff is that, unlike insecticides, herbicides attack plants. Serious consideration must be given to implementing such wetland treatment of herbicides, so as not to inadvertently damage plants within wetlands. Plants are an important wetland macrofeature (especially for sorption) aiding in transfers of pesticide-associated runoff.

Use of constructed wetlands for atrazine-associated runoff mitigation must be carefully designed so as to maximize transfers and transformations, while minimizing effects to downstream aquatic receiving systems, as well as minimizing effects to the wetland itself. Economical and ecological benefits and risks must be thoroughly considered before implementing constructed wetlands as sole BMPs in agricultural systems.

5. Disclaimer

All programs and services of the US Department of Agriculture (USDA) are offered on a non-discriminatory basis without regard to race, color, national origin, religion, sex, marital status, or handicap. Mention of a pesticide in this paper does not constitute a recommendation for use by the USDA nor does it imply registration under FIFRA as amended. Names of commercial products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the USDA.

Acknowledgements

Authors thank P. Rodrigue of the USDA NRCS Wetland Science Institute for partial funding. Special thanks to M.M. Holland and staff of the University of Mississippi Field Station, G.M. Huddleston III, and W.B. Gillespie Jr. Thanks also to J.D. Maul and R.E. Lizotte Jr. for reviewing earlier drafts of the manuscript.

References


