FATE AND EFFECTS OF THE HERBICIDE ATRAZINE IN FLOW-THROUGH WETLAND MESOCOSMS

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Abstract—Wetland mesocosms were exposed to increasing concentrations of atrazine over time at levels typical of midwestern surface waters following spring runoff (15 to 75 μg/L). Atrazine had a half-life of 8 to 14 d in the 230-m-long wetlands. End points measured included nutrient levels; periphyton biomass; periphyton productivity and respiration; growth of selected macrophytes; and survival and growth of Daphnia magna (15, 25 μg/L atrazine), Rana pipiens (15, 25 μg/L), and Pimephales promelas larvae (25 to 75 μg/L) and adults (50, 75 μg/L). Interaction between nutrient status or grazing intensity and atrazine effects were measured using periphyton enrichment and grazing exclosure experiments. Only periphyton, Ceratophyllum demersum, Zizania aquatica, and Daphnia were significantly affected by atrazine at any of the concentrations tested. Periphyton net productivity was significantly depressed by incubation in treated water as compared to control water at ≥25 μg/L atrazine (9 to 27-d exposures). In response, dissolved nutrient concentrations increased in treated mesocosms after 14 d. Ceratophyllum length/weight ratios increased after 6-d exposures to 50 μg/ L atrazine, while Zizania senesced prematurely during treatments of 50 or 75 μg/L atrazine (97 d of cumulative exposure). Periphyton developed resistance to atrazine only at concentrations ≥50 μg/L. Atrazine effects on periphyton composition varied with the N:P supply ratio. Daphnia magna survival was significantly depressed at 15 μg/L atrazine (48-h exposures).

Keywords—Atrazine Wetlands Fate Effects Mesocosms

INTRODUCTION

The herbicide atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) has been detected in a wide range of surface waters and ground water [1,2]. Throughout 10 midwestern states, atrazine has been detected in 55% of basins sampled at levels exceeding the maximum contaminant level for drinking water (3 μg/L) during the postplanting period (May–June; median = 3.8 μg/L, maximum = 108 μg/L) [2]. Peaks in triazine concentrations (including atrazine, simazine, and others) of 5 to 105 μg/L typically coincided with streamflow peaks, with greatest concentrations occurring during the first storm following application of herbicides and gradually diminishing throughout the summer. Atrazine levels in riverine systems were elevated over periods of weeks to months, because inputs throughout the watershed were asynchronous. Peak atrazine concentrations in other aquatic systems have ranged from 5 μg/L to over 1 mg/L, the latter in Kansas farm ponds adjacent to treated fields [1,3]. The persistence of atrazine in the environment varies greatly among systems. Estimated half-lives for atrazine range from approx. 2 weeks in estuarine sediments to approximately 1 year in agricultural soils [4]. Thurman et al. [2] used the seasonal ratio of deethylated atrazine to atrazine in stream and river waters relative to that in runoff and ground water to demonstrate that alluvial ground water was recharged with pesticide-laden water during bankful stage in spring, which then served as a source of contamination to lotic systems in the fall. Thus, aquatic systems are being exposed to short-term pulses of atrazine as well as to long-term low-level concentrations.

Ecological effects of atrazine have been studied in laboratory bioassays [5,6], microcosms [7], and field mesocosms within ponds, lakes, streams, and marshes [8–12]. Based on the desire to bracket LC50 values derived from laboratory acute toxicity assays, most field studies have been carried out at relatively high exposure regimes, e.g., ≥100 μg/L atrazine, and thus have not been designed to detect effects of long-term low-level exposures. However, a 3-year study of treated ponds in Kansas detected direct effects of atrazine on periphyton, phytoplankton, and macrophytes, as well as indirect effects on abundance or growth of invertebrates, tadpoles, and fish, at levels as low as 20 μg/L atrazine [8]. Other studies carried out at higher triazine exposure levels (24 to 500 μg/L atrazine, 1 mg/L simazine) have suggested impairment of ecosystem functions such as nutrient uptake and dissolved oxygen production [8,11,12].

Freshwater emergent marshes, which form a buffer between agricultural uplands and other surface waters, might be particularly vulnerable to the effects of herbicide runoff or drift from agricultural fields. Restoration of riverine and prairie pothole wetlands is being investigated as a means of treating agricultural runoff and protecting downstream surface waters from the effects of nonpoint-source pollutants. Because secondary productivity, habitat functions, and water-quality improvement functions of wetlands are linked to their vegetative structure and high primary productivity, these functions may be vulnerable to long-term exposure to atrazine and other pesticides.

This study was designed to examine potential long-term direct and indirect, lethal and sublethal effects of relatively low-level atrazine exposure to components of wetland communities. Use of flow-through wetland mesocosms allowed us to determine the fate of atrazine moving through the wetlands as well.
as to maintain a consistent exposure regime. Studies were focused on growth and productivity of those ecological components expected to be most vulnerable to atrazine exposure, i.e., periphyton biomass and production, macrophyte cover and growth rates, and growth rate and development of vertebrate grazers. The potential for periphyton communities to develop resistance or tolerance to atrazine, as has been described for phytoplankton, also was examined [13]. Interactions between nutrient limitation or grazing intensity and sensitivity of periphyton communities to atrazine were examined through enrichment bioassays and exclosure experiments. Finally, nutrient levels in water were monitored to determine the effects of atrazine on nutrient uptake.

METHODS

Study site

Experiments were carried out in the downstream wetland portions of four of the eight outdoor experimental stream mesocosms located at the U.S. Environmental Protection Agency (EPA) Monticello Ecological Research Station (MERS) in Monticello, Minnesota, USA [14]. The MERS streams are provided with water from the Mississippi River. In 1987, approx. 90% of the flow was diverted from the lower portion of half of the streams to form four flow-through wetland mesocosms of 230 m length, each with four pools and four “rifles” and a flow of approx. 76 L/min. Stream mesocosms were originally constructed with an alternating pool (30 m3 of approx. 76 L/min. Stream mesocosms were originally constructed with an alternating pool (30 m x 3 m x 80 cm) and riffle (30 m x 2 m x 15 cm) sequence. Organic debris has accumulated over the gravel substrate in rifle sections of the wetland mesocosms. The MERS wetlands have become vegetated through planting (Typha latifolia, Zizania aquatica) and natural succession. Dominant emergent plants consist of cattail (Typha spp.), reed canary grass (Phalaris arundinacea), and wild rice (Zizania aquatica, fourth pools only). Dominant submerged vegetation consists of waterweed (Elodea canadensis), pondweed (Potamogeton spp.), and coontail (Ceratophyllum demersum), and floating-leaved vegetation is dominated by duckweed (Lemna minorn). Vertebrate grazers occurring naturally in the wetlands include tadpoles (Rana pipiens) and fathead minnows (Pimephales promelas).

Exposure regime

Two wetland mesocosms were treated with atrazine and two were controls. Treated mesocosms were exposed using a stock solution made of well water and 30 mg/L commercial grade atrazine (AATrex Nine-O [Ciba-Geigy, Greensboro, NC, USA], 85% active ingredient, water-dispersable granule). Treatments consisted of a stepped exposure regime of four increasing concentrations: 15 μg/L (May 18–June 1), 25 μg/L (June 2–July 15), 50 μg/L (July 16–August 17), and 75 μg/L nominal (August 18–September 4). The treatment regime was designed to allow a series of in situ bioassays to be conducted at a series of increasing concentrations until lowest-effect concentrations could be found for a particular end point; it was not designed to mimic a typical time series for atrazine exposure in a natural aquatic ecosystem in an agricultural setting.

Atrazine sampling and analysis

Water samples were collected weekly at the upper reach, middle reach, and outlet of each wetland. Standard solutions were made with Supelco (Bellefonte, PA, USA) standard reference solution. Samples were concentrated with a C18 solid-phase extraction column (SPE-C18 Fisher Scientific Co., Springfield, NJ, USA), and atrazine was eluted with 2 ml of ethyl acetate isooctane (1+9) [15]. Sample extracts were analyzed using a Hewlett-Packard 5840 gas chromatograph with a fused silica capillary column (25 m x 0.32 mm internal diameter) using helium as the carrier gas. Injector and detector temperatures were 200 and 300°C. The column temperature was programmed to start at 85°C (1 min) and increase to 250°C (10°C/min). Average atrazine recovery in spiked samples was 106% (78–127%, n = 24).

Three replicate sediment samples were collected from the third pool of each wetland prior to atrazine exposure and at the end of each exposure regime using an Ekman dredge. After centrifuging to remove pore water, samples were dried at 75°C and extracted with 90% methanol [16]. Sediment extract solutions and pore water were prepared for analysis using SPE-C18 as described above.

Atrazine fate modeling

The equilibrium coefficient, K, and rate coefficient, k, for atrazine adsorption and degradation vary linearly with the organic carbon content of soils or sediment [17]. The average organic matter content of MERS wetlands is 8.6%. Assuming that sediment organic matter is composed of 50% carbon, the equilibrium and degradation rate coefficients for the MERS wetland mesocosm sediments were predicted to be 51.11 and −9.983 x 10−3 d−1, respectively [17]. Atrazine concentrations in sediment were predicted using a spreadsheet model based on the Freundlich sorption equation [17]:

\[ C_{sed} = 51.11C_{aq}^{0.705} \]

where

\[ C_{sed} = \text{atrazine concentration in the sediment (μg/kg), and} \]
\[ C_{aq} = \text{atrazine concentration in the water column (μg/L).} \]

The first-order rate coefficient for degradation of atrazine in these systems was estimated using plots of log atrazine concentration versus estimated water retention time (pool or riffle volume/flow rate) at three atrazine sampling points. The slope of these plots corresponds to −k, and the degradation half-life can be estimated as −0.693/k.

Water-quality sampling and nutrient analysis

Temperature and pH (Corning C107 meter), dissolved oxygen (Winkler method [18]), and specific conductivity (Beckman RB4-250) were monitored weekly at early morning and midafternoon at the middle of the second pool in each of the four wetland mesocosms. Nutrients were analyzed to test the hypothesis that nutrient levels would increase following depression of algal and/or plant growth by atrazine. Water samples were collected weekly, filtered (0.45 μ) immediately for dissolved nutrients, and stored frozen (nitrogen, phosphorus) or at 4°C following addition of phosphoric acid (0.1% v/v, carbon samples). Nutrients were analyzed with a Lachat Quikchem AE autoanalyzer by the ascorbic acid method (soluble reactive phosphorus), the salicylate-hypochlorite method (ammonium), or cadmium reduction techniques (nitrate + nitrite) [19]. Total or dissolved nitrogen and phosphorus were measured following an alkaline persulfate digestion of filtered and unfiltered samples [20]. Dissolved and total organic carbon were analyzed using an Ionics carbon analyzer.
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Table 1. End points measured in control and atrazine-treated channel waters. With the exception of measurements on detrital accumulation and senescence of wild rice growing within each channel, measurements were made on organisms colonized or grown outside of treatment channels, then incubated within treatment or control wetlands during specific treatment regimes.

<table>
<thead>
<tr>
<th>Ecosystem component</th>
<th>End point measured</th>
<th>Conc. tested</th>
<th>Exposure (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Nutrients</strong></td>
<td>Water column concn.</td>
<td>15–75 µg/L</td>
<td>14–43</td>
</tr>
<tr>
<td><strong>Detritus</strong></td>
<td>Accumulation</td>
<td>75 µg/L a</td>
<td>106</td>
</tr>
<tr>
<td><strong>Periphyton</strong></td>
<td>Biomass</td>
<td>15–75 µg/L</td>
<td>5–12</td>
</tr>
<tr>
<td></td>
<td>Presence/absence of small herbivores</td>
<td>2–5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>With and without nutrient enrichment</td>
<td>28</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Productivity (O₂ production)</td>
<td>9–27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Atrazine resistance</td>
<td>9–27</td>
<td></td>
</tr>
<tr>
<td><strong>Submerged macrophytes</strong></td>
<td>Growth (wet and dry weight, length)</td>
<td>15–75 µg/L</td>
<td>11–19</td>
</tr>
<tr>
<td><strong>Waterweed (Elodea canadensis)</strong></td>
<td>50–75 µg/L</td>
<td>6–8</td>
<td></td>
</tr>
<tr>
<td><strong>Coontail (Ceratophyllum demersum)</strong></td>
<td>Growth (wet and dry weight change), browning (senescence)</td>
<td>15–25 µg/L</td>
<td>19</td>
</tr>
<tr>
<td><strong>Emergent macrophytes</strong></td>
<td>15–50 µg/L</td>
<td>83</td>
<td></td>
</tr>
<tr>
<td><strong>Cattail (Typha latifolia)</strong></td>
<td>75 µg/L a</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td><strong>Wild rice (Zizania aquatica)</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td><strong>Grazers</strong></td>
<td>Daphnia magna</td>
<td>Survival</td>
<td>15–25 µg/L</td>
</tr>
<tr>
<td></td>
<td>Tadpoles (Rana pipiens)</td>
<td>Metamorphosis, growth, survival</td>
<td>15–25 µg/L</td>
</tr>
<tr>
<td></td>
<td>Fathead minnows (Pimephales promelas)</td>
<td>Growth, survival</td>
<td>50–75 µg/L</td>
</tr>
<tr>
<td><strong>Larvae</strong></td>
<td>Survival</td>
<td>25–75 µg/L</td>
<td>7</td>
</tr>
</tbody>
</table>

*a* Cumulative effect, 13 d (15 µg/L) + 43 d (25 µg/L) + 32 d (50 µg/L) + 17 d (75 µg/L).

**Sediment characterization**

The top 3 or 4 cm of replicate cores from the middle pool of each wetland was removed and analyzed for bulk density (n = 3) and organic content (n = 5) [18, 21]. Following the disappearance of metaphytic mats of algae and detritus in treated wetlands during August, the depth of detritus accumulation over the gravel substrate was measured in five random locations of the second riffle of each wetland as an index of prior growth and deposition.

**Periphyton colonization**

Periphyton colonization was conducted on thin acetate strips (23 cm²) attached to the upper surface of a concrete brick for exposure periods of 5 to 12 d during each exposure regime (Table 1). In two of the tests (50- and 75-µg/L exposures), precolonized strips were placed inside individual glass tubes during 2- or 5-d exposures in test mesocosms. Half of the tubes (n = 4 or 5) were covered at both ends with Nitex netting (80-µm mesh) to exclude grazer invertebrates, and the other half were open-ended controls.

At the end of each exposure period, periphyton strips were analyzed for chlorophyll biomass and ash-free dry weight [18, 22]. Chlorophyll a, b, c, phaeophytin, and carotenoid concentrations were calculated from absorbance measurements [23].

**Nutrient enrichment assays**

Nutrient enrichment bioassays were conducted to determine which nutrients were limiting periphyton growth and whether atrazine effects varied under different nutrient limitation regimes. Bioassays were conducted during the 15- and 25-µg/L exposure regimes using the inverted pot method [24]. Nutrient enrichment treatments included addition of 1.0 M NH₄Cl (+NH₃), 2.5 M NaNO₃, 0.05 M KCl (+NO₂), 0.05 M KH₂PO₄, 2.5 M NaCl (+PO₄), or 2.5 M NaNO₃, 0.05 M KH₂PO₄, (+NO₂,+PO₄) to a 4% agar solution. Control pots were filled with 4% agar plus 0.05 M KCl + 2.5 M NaCl. Three pots of each nutrient treatment and three control pots were incubated in a riffle section of each wetland for 28 d, from May 18 to June 15. At the end of the experiment, subsamples for chlorophyll and ash-free dry weights were processed as described above.

**Periphyton productivity and assays for atrazine tolerance and resistance**

Periphyton strips were allowed to colonize for 9 to 27 d in each of the wetlands as described above. Five strips from each wetland were incubated for primary productivity measurements in filtered control water, and five were incubated in filtered atrazine treatment water. Periphyton productivity was measured using the light/dark bottle technique following Wetzel and Likens [23], except that dark incubations were performed on the same set of bottles immediately following light incubations. Dissolved oxygen readings were measured using a YSI Model 58 meter and BOD probe.

Periphyton productivity and respiration data measured under ambient conditions (control water for control wetland periphyton and atrazine-treated water for treatment mesocosm periphyton) were used to test the hypothesis that long-term atrazine exposure has no effects on productivity or respiration. End points included periphyton chlorophyll a, net primary production (NPP), gross primary production (GPP), specific NPP (NPP/µg chlorophyll a), specific GPP, and respiration. Data from reciprocal “transplants” were used to test the resistance/tolerance hypothesis, that productivity will not be reduced more by atrazine for periphyton grown under control conditions than for previously exposed periphyton.

**Macrophyte growth and senescence analyses**

Potted cattails were tested during the first three exposure regimes (15–25 and 50 µg/L atrazine; Table 1). Cattails were grown in 10-cm-diameter clay pots from seeds germinated from a single seed spike of T. latifolia. Seedlings were grown in the laboratory and subsequently in a riffle of a MERS stream not...
used in this study. On May 19, 14 plants were placed in the second pool of each mesocosm, with the soil surface 3 to 5 cm below the water. Response variables measured for each plant were number and length of leaves, browning of leaf tips, and wet and dry weights of above-ground and below-ground biomass. Measurements were made on July 7 (six to seven plants/wetland) for the 15- to 25-μg/L exposure regimes and on August 12 (five to seven plants/wetland) for the 50-μg/L exposure regime.

Five-centimeter-long shoots of Elodea canadensis (including the terminal bud) were collected from a MERS stream not used in the atrazine study. Initial and final wet and dry weights and main plus lateral shoot lengths were determined for plants in each test [18]. Ten plant segments were suspended in large mesh polypropylene bags in either the second riffle or second pool for a period of 11, 12, or 19 d during the 25-, 50-, and 75-μg/L treatment regimes, respectively.

Toxicity testing with Ceratophyllum demersum was similar to that for Elodea. Fifty-five-millimeter-long plant segments with terminal buds were grown in the second pool in large mesh polypropylene bags. Ten plants/wetland were exposed for 8 d during the 50-μg/L treatment regime, and eight plants/wetland were exposed for 6 d during the 75-μg/L treatment regime. Initial and final dry weights and lengths were measured.

Qualitative observations of vegetative cover and vigor of natural populations of duckweed, watermeal, reed canary grass, and wild rice in the MERS wetlands were made throughout the experiment. After early senescence of wild rice was observed in the treated wetlands, five plants were selected randomly from the fourth pool of each wetland mesocosm. All leaves that had a minimum width of 4 cm were removed and pooled for each mesocosm. From this pool, five leaves were randomly selected, and from each of these leaves a 5-cm-long section was cut from the middle of each leaf (20 to 25 cm²). Each section was extracted and analyzed for chlorophyll a as described above for periphyton.

**Tadpole and minnow growth**

Leopard frog tadpoles (*Rana pipiens*; mean length = 49 ± 5 mm, mean weight = 1.3 ± 0.3 g) were collected in stream 2 on June 4 upstream of atrazine inputs. In each wetland, 20 tadpoles were placed in a wooden-frame cage (122 cm long × 91 cm wide × 91 cm deep) covered with 0.3-cm-mesh plastic screen. The cage was placed in the second pool—third riffle interface of each wetland in 30-cm-deep water. End points measured at the end of 41 d included stage of metamorphosis and survival (Table 1). Tadpoles were allowed to feed ad libitum in the cages.

Juvenile fathead minnows (*Pimephales promelas*; mean weight = 0.12 ± 0.04 g, mean length = 25 ± 2 mm) obtained from the U.S. EPA Environmental Research Laboratory—Duluth were tested at the first pool—second riffle interface in the same type of cages as described above. Fish were acclimated to river water in a holding tank at MERS for 2 d prior to being placed in cages. A random sample was selected for testing in each wetland mesocosm for 10 d in the 50-μg/L treatment regime (June 30–August 10; n = 25) and for 13 d in the 75-μg/L treatment regime (n = 22). End points included minnow survival, length, and weight.

**Interaction of solar ultraviolet light with atrazine**

Bioassays were done in situ in the four MERS wetlands to test the hypothesis that atrazine toxicity is enhanced by exposure to solar ultraviolet light (Table 1). Animals were incubated in plastic jars that had two holes cut in their sides for the exchange of water and food. Holes were covered with 80-μm mesh. Jars were suspended from clear acrylic racks at a depth such that they each held 100 ml. Each rack held five jars; within each wetland one rack of jars was exposed to sunlight and one rack was held in full shade.

Bioassays were performed using *Daphnia magna* as test organisms from May 20 to 22 (15 μg/L atrazine) and from June 9 to 11 (25 μg/L atrazine). Bioassays using fathead minnow larvae were done on June 1 to 8 and June 18 to 25 (25 μg/L), July 17 to 25 and July 27 to August 3 (50 μg/L), and August 18 to 25 (75 μg/L atrazine). In each bioassay, 10 animals were counted into the jars in the laboratory over the course of a few minutes before they were placed into the racks in wetland pools.

*Daphnia magna* were obtained from the stock culture maintained at the University of Minnesota Cooperative Fisheries and Wildlife Unit in St. Paul, Minnesota, USA. Gravid females were obtained 1 d prior to the first *Daphnia* experiment and held for a day to release all of the neonates. *Daphnia* were cultured at MERS between the first and second *Daphnia* bioassay; the culture was fed every other day using food (yeast and ceraphyll) provided by the culture facility at the Cooperative Fisheries and Wildlife Unit. For both *Daphnia* experiments, a mixture of neonates less than 24 h old and similarly sized individuals of unknown age were used because not enough neonates were produced. The *Daphnia* bioassays were 48-h acute bioassays which followed the methods of the EPA [25] for effluent and pure-compound testing except that the animals were incubated in situ in the wetlands. No food other than what could pass through the 80-μm mesh on container sides was provided during the test.

Fathead minnow larvae were obtained from the culture facility at the U.S. EPA Environmental Research Laboratory—Duluth. Newly hatched larvae were picked up at the laboratory in midmorning on the day an experiment began and were transported to MERS (3 h), where they were allowed to equilibrate in MERS stream water at wetland temperatures for a few hours. There was almost never any mortality during transportation and temperature equilibration. Larvae were sorted into test containers using a pipette. Larvae were always in the wetlands by 1700 h of the day they were picked up at the laboratory. Care was taken to choose only healthy-looking larvae for bioassays. Fathead minnow larval response to atrazine was measured using the 7-d survival and growth bioassay [25]. Ten animals were incubated in each chamber; no food other than what could pass through the 80-μm mesh on the container sides was provided during the test. Survival was the only end point measured (number of individuals surviving in each incubation jar).

**Statistical analysis**

Results from the above experiments were analyzed using analysis of variance (ANOVA) techniques [26]. Statistical tests for analyses requiring a more sophisticated design than one-way ANOVAs are described in Table 2. All tests for significance were conducted using an alpha level of 0.05 unless otherwise noted. For all analyses, data were tested for normality using Wilks–Shapiro statistic [26] and for homogeneity of variance using Bartlett’s test [27]. Data were log-transformed where necessary to meet model assumptions (normality and homogeneity of variance), except for percent survival data, which were arcsine, square-root transformed.
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Table 2. Statistical tests used in analysis of experimental results

<table>
<thead>
<tr>
<th>Independent variables</th>
<th>Dependent variable(s)</th>
<th>Test/design</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atrazine</td>
<td>Pretreatment nutrients</td>
<td>1-way MANOVA</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Nutrients</td>
<td>Repeated-measures ANOVAs</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Periphyton biomass (pigment concns. on clay pots)</td>
<td>3-way MANOVA</td>
</tr>
<tr>
<td>Phosphate</td>
<td>Periphyton biomass (pigment concns. on clay pots)</td>
<td>2-way MANOVA</td>
</tr>
<tr>
<td>Atrazine × nutrient</td>
<td>Periphyton chlorophyll a, NPP, NPP/μg chlorophyll a, GPP, GPP/μg chlorophyll a</td>
<td>1-way ANOVA</td>
</tr>
<tr>
<td>Incubation exposure</td>
<td>Periphyton respiration</td>
<td>Mixed-model 3-way MANOVA</td>
</tr>
<tr>
<td>Atrazine</td>
<td>Periphyton productivity</td>
<td>Fixed effects = colonization, productivity treatments</td>
</tr>
<tr>
<td>Nutrient addition</td>
<td>Typha above-ground biomass</td>
<td>Random effects = mesocosm replicate MANOVA</td>
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<tr>
<td>Atrazine</td>
<td>Typha below-ground biomass</td>
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<td>Atrazine</td>
<td>Elodea stem length</td>
<td>MANOVA</td>
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<td>Atrazine</td>
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<tr>
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<td>Ceratophyllum stem length</td>
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<td>Ceratophyllum biomass</td>
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<td>Atrazine</td>
<td>Daphnia survival</td>
<td>Split plot/ANOVA</td>
</tr>
<tr>
<td>Sunlight</td>
<td>Fathead minnow survival</td>
<td>Split plot/ANOVA</td>
</tr>
</tbody>
</table>

ANOVA = analysis of variance; GPP = gross primary productivity; MANOVA = multivariate analysis of variance; NPP = net primary productivity.

RESULTS AND DISCUSSION

Atrazine partitioning in wetland mesocosms

Control wetlands had an average atrazine concentration of 0.69 μg/L, which probably originated from agricultural runoff into the Mississippi River. It is possible that exposure to background levels of atrazine in the mesocosms would have selected for strains of primary producers that were resistant to atrazine. However, our studies showed evidence of development of resistance to atrazine by periphyton at 50 ppb but not at 25 ppb, suggesting that exposure to much lower concentrations would have been insufficient to select for resistance (see below.) Atrazine concentrations in treated wetlands 230 m downstream of inputs ranged from 78 to 96% of concentrations at the head of wetlands (Table 3). Analyses of bulk sediment and pore-water concentrations showed that measurable partitioning of atrazine into sediments was occurring (Table 3).

Atrazine concentrations in sediment at the end of the latter three exposure regimes were 18 to 43% lower than those predicted using the Freundlich sorption equilibrium equation (Table 3). Pore-water atrazine concentrations also were lower than those measured in the water column, suggesting that diffusion of atrazine into the sediments was limiting adsorption within the stratum sampled.

Losses of atrazine in the water column between the second and fourth pools were greater than those predicted by kinetic models. Predicted half-lives of atrazine in the wetland mesocosms, based on first-order rate coefficients estimated from the organic matter content of wetland sediments [17], were 36 to 37 d, about three times those calculated using concentration and retention time data (8 to 14 d; Table 4).

Low model predictions of atrazine loss rates within the wetlands could have been the result of spatial heterogeneity in organic carbon content of surficial sediments. Kadlec and Alvord [17] found that the highest rates of atrazine degradation in the Des Plaines constructed wetlands were associated with cattail litter. Previous investigators have demonstrated that the carboxylic groups in humic acids of organic sediments (and presumably plant litter) are responsible for binding atrazine and catalyzing chemical hydrolysis to hydroxyatrazine [28]. Areas of greater plant litter accumulation than those sampled for sediment analysis could have accounted for a disproportionate amount of atrazine adsorption and degradation.

Periphyton bioassays

Gross productivity was significantly reduced in treatment wetlands at the lowest exposure level (15 μg/L), and specific GPP (GPP/μg chlorophyll a) was reduced at the highest exposure level (75 μg/L). Respiration was either significantly reduced by atrazine treatments (25 μg/L) or significantly stimulated (75 μg/L). Neither chlorophyll a biomass nor ash-free dry weight were significantly affected by any of the atrazine treatments.

Only four previous studies on periphyton response to atrazine have examined effects following long-term exposures at concentrations ≤75 μg/L atrazine. The lowest effect level of atrazine on periphyton biomass or productivity reported in field studies was 24 ppb atrazine [11]. However, Krieger et al. [11] found an interaction between temperature and atrazine effects; periphyton biomass was significantly affected at 24 ppb atrazine when exposed at 25°C but not at 10°C. Lynch et al. [29] found no significant effect of 25 ppb atrazine on periphyton biomass, productivity, or respiration in artificial streams, but their studies were carried out at ≤15.5°C. The lack of significant effects reported at lower temperatures may be the result of the increased dominance of diatoms at lower temperatures; diatoms have a relatively greater tolerance to atrazine than some other taxa [9]. Jurgensen and Hoagland [1] also found no significant effect of 30 ppb atrazine on biomass or cell densities of dominant species of periphyton in artificial streams, but in their studies exposure periods consisted of only 24-h pulses.
Nutrient enrichment bioassays

We found a significant multivariate effect of nutrient treatments on periphyton pigment concentrations (Wilks’ lambda) but no effect of atrazine addition (15 to 25 μg/L) or nutrient × atrazine treatment interactions. Periphyton biomass (chlorophylls a, b, and carotenoids) was stimulated by N + P or by nitrogen additions alone (NO₃ or NH₄) as compared to controls. A significant univariate interaction was found between the effects of atrazine and the effect of phosphorus additions. Atrazine was more effective in reducing periphyton carotenoid/chlorophyll a ratios under phosphate enrichment conditions (Fig. 1).

These results suggest that all MERS wetlands were nitrogen-limited. The greater reduction in carotenoid/chlorophyll a ratios in atrazine-treated wetlands compared to control wetlands when substrates were enriched with phosphate suggests that nutrient limitation may be important in determining the relative sensitivity of periphyton communities to atrazine. With the addition of phosphate, nitrogen limitation may have become more extreme and the community may have shifted to dominance by greens and/or blue-greens; exposure to atrazine would have selected against greens and blue-greens and decreased the ratio of carotenoid/chlorophyll a pigments. Primary producers in wetlands tend to be nitrogen-limited rather than phosphorus-limited; thus, shifts in periphyton community composition may be expected under low atrazine concentrations (15 to 25 μg/L).

Table 3. Mean measured and predicted atrazine concentrations in surface water, sediment pore water, and bulk sediment of treated wetland channels. Predicted sediment concentrations were based on applications of the Freundlich adsorption equation and regressions relating parameters to organic carbon content of sediments (from Kadlec and Alvord [17]).

<table>
<thead>
<tr>
<th>Nominal concn. of atrazine in water column</th>
<th>15 μg/L</th>
<th>25 μg/L</th>
<th>50 μg/L</th>
<th>75 μg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Measured surface water concns (μg/L) atrazine</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Upper</td>
<td>17.9 ± 1.9</td>
<td>26.2 ± 1.3</td>
<td>53.5 ± 7.0</td>
<td>85.0 ± 12.2</td>
</tr>
<tr>
<td>Middle</td>
<td>16.0 ± 0.2</td>
<td>26.4 ± 0.7</td>
<td>47.3 ± 0.7</td>
<td>78.5 ± 4.6</td>
</tr>
<tr>
<td>Lower</td>
<td>15.4 ± 0.6</td>
<td>22.7 ± 2.7</td>
<td>47.8 ± 2.0</td>
<td>73.9 ± 5.6</td>
</tr>
<tr>
<td>Measured pore-water atrazine concn. (μg atrazine/L)</td>
<td>0.87</td>
<td>2.6</td>
<td>10.8</td>
<td></td>
</tr>
<tr>
<td>Measured bulk sediment concn. (μg atrazine/g dry wt.)</td>
<td>0.33</td>
<td>0.88</td>
<td>0.81</td>
<td></td>
</tr>
<tr>
<td>Predicted bulk sediment concn. (μg atrazine/g dry wt.)</td>
<td>0.58</td>
<td>1.07</td>
<td>1.43</td>
<td></td>
</tr>
</tbody>
</table>

Development of resistance and tolerance in periphyton communities

At each exposure level ≥25 μg/L, there was a significant depression in specific NPP (mg dissolved oxygen [DO]/h/μg chlorophyll a) for periphyton strips incubated in treated versus control water. During the 50-μg/L exposure period, periphyton that had been growing in control mesocosms experienced a significantly greater reduction in GPP when incubated in treatment water than did periphyton that had been growing in treated wetlands (Fig. 2). This is evidence for the development of resistance and/or a shift in community composition to less sensitive species. Investigators have successfully selected for atrazine-resistant strains of Chlamydomonas reinhardii and Nannochloropsis oculata mutants [13]. Atrazine-resistant mutants demonstrate a reduced capacity for atrazine binding to thylakoid membranes, with a nonmendelian inheritance pattern characteristic of chloroplast genes. While some of the atrazine-resistant Chlamydomonas mutants have a reduced growth rate and rate of electron transfer from reduced Q to B in photosystem II, this is not true for all strains. Thus, atrazine resistance in algae does

Table 4. Estimated and predicted first-order atrazine loss rate and half-life. Values were estimated as the slope of plots of ln[atrazine concentration] versus water retention time for three stations along the wetland mesocosms. Predicted values were based on equations relating degradation rate, k, to organic carbon content of sediments (from Kadlec and Alvord [17]).

<table>
<thead>
<tr>
<th>Meso-com</th>
<th>Estimated mean k, d⁻¹ (range)</th>
<th>Estimated half-life, d (range)</th>
<th>Predicted k, d⁻¹</th>
<th>Predicted half-life, d</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.0830 (0.0497–0.145)</td>
<td>8.4 (4.8–13.9)</td>
<td>0.0193</td>
<td>35.9</td>
</tr>
<tr>
<td>5</td>
<td>0.0489 (0.0175–0.118)</td>
<td>14.2 (5.9–39.6)</td>
<td>0.0189</td>
<td>36.7</td>
</tr>
</tbody>
</table>
than did periphyton that had been growing in treated mesocosms (sensu significantly greater reduction in GPP when incubated in treatment water that had been growing in control mesocosms experienced a significantly greater reduction in GPP when incubated in treatment water than did periphyton that had been growing in treated mesocosms (p < 0.05).

A paradoxical effect occurred at the highest treatment level. Specific NPP (mg DO/µg chlorophyll a) was significantly lower for periphyton from each treated or control wetland when incubated in the atrazine-treated water than when incubated in control water. However, NPP per strip was higher overall for periphyton from atrazine-treated wetlands than for periphyton from control wetlands because chlorophyll biomass levels per strip were higher in atrazine-treated wetlands. This could have been caused by a reduction in macroinvertebrate grazing pressure in atrazine-treated wetlands. However, grazing exclusion experiments showed no interaction between atrazine and grazer exclusion effects. Alternatively, this phenomenon could have been caused by greater shading in control wetlands than in treated wetlands from metaphyton (floating filamentous algae). Although metaphyton biomass was not directly measured over the course of the experiment, metaphyton development was visibly greater in control wetlands than in treated wetlands during the 75-µg/L treatment regime. In addition, the depth of detritus that accumulated over the gravel substrate of “riffle” sections was twice as great in control wetlands (40 to 47 mm) as in treated wetlands (18 to 24 mm, p < 0.05). Fromm [31] also observed the disappearance of floating metaphyton mats of filamentous green and blue-green algae in divided ponds treated with 200 ppb atrazine. Floating metaphyton can be expected to be especially vulnerable to the effects of atrazine given the tendency of atrazine to become concentrated up to 110 times in the organic surface water film [33].

Previous investigators have measured differential effects of triazine herbicides on different periphyton communities within a marsh ecosystem. Treatment of marsh mesocosms with two triazine herbicides (2.0 mg/L simazine, 0.01 mg/L terbutryn) produced only short-term (2-week) depressions in photosynthesis by haptobenthic communities (i.e., those colonizing solid substrates) but produced long-term (84-d) depressions in photosynthesis for herpobenthic communities (i.e., those colonizing soft substrates) [32]. The apparent development of tolerance by haptobenthic communities was found to coincide with the replacement of large filamentous chlorophytes by smaller diatom species.

Indirect effects on water quality parameters

Maximum DO levels in treated wetlands at 15 µg/L atrazine (5.6 mg/L DO) were significantly lower than those in control wetlands (7.3 mg/L DO). This is consistent with the measured reduction in periphyton gross productivity at 15 µg/L atrazine. Nutrient concentrations measured at the midpoint of MERS wetlands were not significantly different between controls and treatment wetlands prior to atrazine additions (two-sided test). However, ammonium and total dissolved phosphorus (at 15 µg/L atrazine), total dissolved nitrogen (at 25 to 50 µg/L atrazine), and orthophosphate (at 50 µg/L atrazine) were significantly higher in treated wetlands than in control wetlands (one-sided test). By the last treatment regime of 75 µg/L atrazine, ammonium and orthophosphate levels in treatment mesocosms (A) exceeded those in control mesocosms (C) by >50%, but high within-treatment variability prevented detection of significant differences (Figs. 3a,b). Mean ammonium and orthophosphate levels in treated wetlands would have had to exceed levels in control wetlands by 58% and 74%, respectively, in order to be judged significantly different by a one-way ANOVA at the 0.05 level with a probability of 0.90.

Investigators have measured significant increases in nitrate, ammonium, orthophosphate, and/or silica following exposures of 50 to 155 ppb atrazine in small aquatic mesocosms [7], artificial streams [11], or limnocorrals [10]. Krieger et al. [11] speculate that during storm runoff events, pulses of atrazine (>100 ppb) in small streams draining into Lake Erie coincide with nutrient pulses and thus may be reducing the nutrient uptake capacity of attached algae during a critical period. Likewise, Goldsborough and Robinson [12] measured the effect of another triazine herbicide, simazine, on the net flux of nutrients from marsh sediments, as mediated by benthic algae, by comparing nutrient concentrations in enclosures with sealed (no sediment exposure) versus unsealed bottoms (with exposure to sediments). They found a significant increase in nutrient flux from sediments at 1.0 mg/L and 5.0 mg/L treatments but not at 0.10 mg/L simazine. Atrazine is much more toxic than simazine; thus, the same effects would be expected at lower concentrations.

Our results support the hypothesis that reductions in periphyton productivity caused by exposure to atrazine can have significant effects on the capacity for nutrient uptake in aquatic ecosystems. Furthermore, results of the nutrient enrichment experiment demonstrate that effects of atrazine cannot be mitigated by increased nutrient supply expected during peak runoff events. In fact, our results suggest that periphyton biomass could respond more to atrazine exposure if the shift in nutrient supply ratio favors algal taxa which are more sensitive to atrazine. Increased ammonium and dissolved nitrogen concentrations in treated wetlands relative to controls were consistent with the observed decrease in periphyton productivity and evidence for nitrogen-limited growth for periphyton. Although no significant
Macrophyte bioassays

No significant effect of atrazine on cattail above-ground or below-ground biomass at 15 to 50 \( \mu \text{g/L} \) or on \textit{Elodea} biomass or stem length at 15 to 75 \( \mu \text{g/L} \) atrazine was observed. In both cases, there were strong within-treatment (inter-wetland) differences that limited the power of the tests. Bioassays with coontails, however, demonstrated a significant multivariate effect on stem length and dry weight at 50 \( \mu \text{g/L} \) atrazine, although neither stem length nor dry weight was affected individually. Plant segments grown in treated wetlands were relatively elongated (i.e., had greater stem length/weight ratios) as compared to those grown in control wetlands. Our finding of stem elongation for coontail at concentrations of 50 \( \mu \text{g/L} \) atrazine is consistent with results of studies by Kemp et al. [34], who measured stem elongation in \textit{Potamogeton perfoliatus} and \textit{Myriophyllum spicatum} under exposures to atrazine levels of 5 to 50 ppb. They suggested that stem elongation was a compensation mechanism, analogous to the response of \textit{Potamogeton} under light limitation.

Previous investigators have demonstrated a long-term decline in the biomass of \textit{Typha} following field exposures to 100 \( \mu \text{g/L} \) atrazine but no significant effects following exposures to 20 \( \mu \text{g/L} \) [8]. Our study results do not refute the establishment of 100 \( \mu \text{g/L} \) atrazine as the lowest effect level with respect to cattail growth or biomass.

Hofmann and Winkler [35] measured a slight stimulation in photosynthesis of \textit{Myriophyllum spicatum} and \textit{Elodea canadensis} at low levels (5 to 10 ppb) over 1 to 20 d of exposure, but they also measured 200-fold increases in respiration rate that more than offset the increases in photosynthesis. No data are available from the literature concerning the effects of atrazine on growth of \textit{Ceratophyllum demersum} or on growth or condition of \textit{Zizania aquatica}.

Laboratory studies of the effects of atrazine on other submerged macrophytes have demonstrated 50% reductions in photosynthesis at levels of 53 to 1,040 ppb atrazine for most species [36,37]. Significant short-term decreases in net productivity have been measured for several species of \textit{Fontinalis} at much lower levels (2 to 10 ppb [35]). Significant reductions in growth or biomass have been measured at atrazine levels of 50 to 100 ppb for \textit{Potamogeton} and \textit{Myriophyllum} [34] and at 12 ppb for \textit{Vallisneria} [38].

In one of the few field studies of the effects of atrazine on macrophytes in ponds, DeNoyelles et al. [8] demonstrated a shift in community composition at treatment levels of 20 to 100 ppb, from one dominated by \textit{Potamogeton} or \textit{Najas} to one dominated by the more resistant macroalga \textit{Chara}. The authors speculated that \textit{Chara} was favored under conditions of reduced epiphyton growth because it tends to disappear from farm ponds as eutrophication proceeds and epiphytic growth increases. Overall, biomass of submerged macrophytes decreased at \( \geq 100 \) ppb in the absence of grass carp or at 20 ppb atrazine in the presence of grass carp as compared to control ponds without atrazine. In contrast, in the present study, epiphytic biomass was not significantly reduced, and macrophyte grazers such as grass carp were not present in the system. Thus, it is reasonable to expect macrophytes in the MERS wetlands to be less sensitive to atrazine than those in the ponds studied by DeNoyelles et al. [8].

Premature senescence of wild rice

Wild rice (\textit{Zizania aquatica}) plants were visibly more senescent in treated wetlands than in control wetlands by August 12, the end of the 50-\( \mu \text{g/L} \) exposure regime. Chlorophyll \( a \) content of wild rice leaves of plants collected from treated wetlands on August 25 was only 25% that of plants from control mesocosms.

Vertebrate bioassays

No significant effects of atrazine on fathead minnow growth or tadpole growth or development were detected. Measures of tadpole development, such as percent adult appearance (11% of adults in controls, 26 to 42% of adults in treated wetlands) and length of back legs (2.7 to 3.1 mm in controls, 3.5 to 3.8 mm in adults in treated wetlands), tended to be accelerated in atrazine-treated mesocosms (\( p < 0.10 \)), but intermesocosm variability was too great to detect differences. Percent adult appearance and length of back legs in tadpoles from treated wet-
lands would have had to exceed values for tadpoles in control wetlands by 91% and 47%, respectively, in order to be judged significant at the 0.05 level with a probability of 0.90.

Based on the results of Birge et al.'s [6] laboratory bioassays of Rana pipiens embryos 0 to 4 d posthatching (LC50 = 7.68 mg/L), direct toxic effects on tadpoles were not expected at the atrazine levels tested in our study. Likewise, Macek et al. [5] demonstrated in laboratory bioassays that fathead minnows are relatively insensitive to direct effects of atrazine (maximum acceptable toxicant concentration [MATC] = 0.21 to 0.52 mg/L). However, Kettle et al. [39] found a significant decrease in biomass of Rana catesbiana tadpoles in treated ponds at the end of 805 d of exposure to only 20 μg/L atrazine. The investigators attributed the decrease in overall biomass to loss of macrophytes as spawning areas and refugia from predators as well as loss of periphyton food resources. The lack of demonstrated direct or indirect effects on Rana pipiens tadpoles in our study at slightly higher levels of atrazine (25 μg/L) may be due to the following: 1) tadpoles were stocked into the wetlands, thus bypassing effects on spawning habitat, 2) the incubation cages provided protection from predation, and 3) Rana catesbiana is more sensitive to atrazine [39]. The LC50 for Rana catesbiana is 410 μg/L [6]. Our study did demonstrate that the food web is not significantly affected by 25 μg/L atrazine for tadpoles or by 50 to 75 μg/L atrazine for fathead minnows over shorter exposure periods (10 or 41 d).

In situ bioassays to test interaction of solar ultraviolet light with atrazine

The only significant effects of atrazine or sunlight on Daphnia magna survival were found in the first D. magna bioassay at 15 μg/L atrazine. Both atrazine exposure and sunlight exposure significantly decreased D. magna survival, but there was no significant interaction between these two stressors. At the higher atrazine concentration (25 μg/L) present during the second D. magna bioassay, there was no apparent effect of atrazine on survival. No significant effects of either atrazine or sunlight on fathead minnow larvae at any of the atrazine concentrations present during the fathead minnow bioassays (25 to 75 μg/L) were observed.

There is no reason to expect that physical or chemical characteristics were responsible for the mortality that was measured during the first D. magna bioassay. Dissolved oxygen minima were no lower during that bioassay than during any of the other bioassays and the temperature was lower. The atrazine concentration measured in the treated wetlands on May 22 was 12.9 μg/L, a concentration much lower than those present during the other bioassays. It is possible that less food was available in the water column early in the season and that food limitation and atrazine produced synergistic effects on Daphnia magna survival. Maximum DO levels were significantly depressed during the 15 μg/L treatment, suggesting that systemwide productivity was affected.

Atrazine absorbs some ultraviolet wavelengths that are found in sunlight; thus, there is a chance that atrazine toxicity is potentiated in the presence of solar ultraviolet light [40]. However, our results did not support this hypothesis as there was no significant interaction between atrazine effects and sunlight effects. The potential phototoxicity of atrazine could have been mitigated by the presence of naturally occurring humic acids. Oris et al. [41] found that relatively small amounts of dissolved humic acids (0 to 3 mg/L) significantly mitigated the photoinduced toxicity of anthracene to Daphnia magna; most of the reduction in phototoxicity could be accounted for by the reduction in body anthracene concentration related to reduced bioavailability of anthracene when bound to humic acids. The cause of the independent effect of sunlight on D. magna survival is unknown but might be related to the formation of carbonyl compounds such as formaldehyde from ultraviolet-induced photodegradation of naturally occurring humic acids [42]. Increased mortality in control populations exposed to ultraviolet light also was observed in work by Davenport and Spacie [40].

Conclusions

Results of our wetland mesocosm studies could not be predicted a priori based solely on results of laboratory bioassays reported in the literature. For example, the decrease in light limitation following reductions in metaphyton mats stimulated net biomass accumulation for epiphytic periphyton at 75 μg/L atrazine, even though epiphyton productivity was still repressed at these levels. In addition, the probability of developing resistant strains or of producing shifts in community composition to more tolerant species could not be predicted by laboratory studies. Results of this field study and others also demonstrate that ecosystem sensitivity to atrazine can be affected by abiotic parameters such as temperature and nutrient supply ratios, as well as by the intensity of biotic controls (e.g., grazing intensity) in a system.

Atrazine concentrations typical of those observed in surface waters exposed to agricultural runoff are sufficiently high to produce significant effects on wetland primary producers, even before effects are detected on higher trophic levels. Among the ecological end points tested, periphyton productivity was the most sensitive. Effects of atrazine on periphyton production were observed at treatment levels as low as 15 μg/L. However, periphyton communities can develop partial resistance to atrazine at levels of 50 μg/L, either through a shift in dominant species or through selection for resistant strains. Increased dissolved nutrient concentrations were detected as an indirect effect of atrazine exposure, probably related to reductions in periphyton productivity. The coincidence of atrazine peaks with peak nutrient loadings could limit the water-quality improvement function of wetlands in agricultural landscapes by reducing periphyton growth and nutrient uptake. The most sensitive macrophyte in the MERS wetlands, wild rice, exhibited early senescence at atrazine levels of 50 to 75 μg/L. Wild rice in freshwater estuaries of the Great Lakes may be detrimentally affected by prolonged exposure to atrazine as well as by other stressors, such as increased turbidity related to agricultural land use upstream.

The net effect of atrazine and other triazine herbicides on natural or constructed wetlands and other aquatic systems will depend on the magnitude and duration of exposure. The relatively short half-life (8 to 14 d) of atrazine in systems with highly organic sediments and organic litter layers like the MERS wetlands suggests that headwater wetlands and wetlands associated with low-order streams will probably be exposed to fairly short-term pulses of high concentrations of atrazine associated with runoff events. In these systems, periphyton and macrophytes probably will recover quickly as long as atrazine levels remain below 50 to 100 μg/L, but water-quality improvement functions of wetlands may be impaired. Wetlands associated with higher-order streams can be expected to receive long-term atrazine exposures at lower levels because of the asynchrony of runoff events throughout a watershed and the recharge of streams with contaminated ground water from the alluvial plain. In these systems, it is more likely that effects on the more sensitive macrophyte species, shifts in periphyton community...
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REFERENCES


