

# Diazinon Mitigation in Constructed Wetlands: Influence of Vegetation

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**Abstract** In intensively cultivated areas, agriculture is a significant source of pesticides associated with storm runoff. When these pollutants enter aquatic receiving waters, they have potential to damage nearby aquatic ecosystems. Constructed wetlands are a best management practice (BMP) designed to help alleviate this potential problem. A constructed wetland system (180×30 m) comprised of a sediment retention basin and two treatment cells was used to determine fate and transport of a simulated storm runoff event containing the insecticide diazinon and suspended sediment. Wetland water, sediment, and plant samples were collected spatially and temporally over 55 d. Results indicated that 43% of the study's measured diazinon mass was associated with plant material, while 23 and 34% were measured in sediment and water, respectively. Mean diazinon concen-

trations in water, sediment, and plants for the 55-d study were  $18.1 \pm 4.5$   $\mu\text{g/l}$ ,  $26.0 \pm 8.0$   $\mu\text{g/kg}$ , and  $97.8 \pm 10.7$   $\mu\text{g/kg}$ , respectively. Aqueous concentrations fluctuated in the wetlands between 51–86  $\mu\text{g/l}$  for the first 4 h of the experiment; however, by 9 h, aqueous concentrations were approximately 16  $\mu\text{g/l}$ . During the 55 d experiment, 0.3 m of rainfall contributed to fluctuations in diazinon concentrations. Results of this experiment can be used to model future design specifications for mitigation of diazinon and other pesticides.

**Keywords** Agricultural runoff · BMP · Pesticides · Phytoremediation · Retention

## 1 Introduction

According to the US Environmental Protection Agency (US EPA 2004a), over 441 million kg of conventional pesticides (e.g. herbicides, fungicides, insecticides, etc.) were used in the US in 2001. Of that total, 77% were used in agricultural applications, and 11% were used for home and garden purposes. Through storm runoff, spray drift, or accidental spills, pesticides have the potential to contaminate surface and ground water resources. Increased scrutiny of the US water quality 303(d) program led to a renewed focus on the Total Maximum Daily Load (TMDL) program, originally enacted as part of the 1972 Clean

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Water Act. Approximately 1,200 water body impairments across the US are attributed to pesticides (US EPA 2004b). While agriculture is often targeted as the primary source of these pesticides, many overlook urban use contributions. Studies from the US Geological Survey (USGS) indicated 99% of major US urban streams are contaminated by at least one pesticide, while slightly over 70% are contaminated with five or more pesticides (Gilliom 2001). Insecticides make up approximately 10% of both the US and world pesticide markets and between 1982–2001, the average annual insecticide expenditure in the US was \$2.4 billion (US EPA 2004a). When many organochlorine insecticides were banned, their replacement pesticides, organophosphates (OP), increased in usage. However, with the 1996 passage of the Food Quality Protection Act, OP insecticides became the primary target group for US EPA's re-registration process. Although OP insecticide usage is down 45% since 1980 (from 55 to 33 million kg in 2001), their share of percent total insecticide applied has actually increased from 58% (1980) to 70% (2001) (US EPA 2004a).

Diazinon [O,O-diethyl-O-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate] is a non-systemic OP insecticide with agricultural and veterinary uses. Residential, lawn, and garden uses of diazinon were phased out effective December 31, 2004. Still, diazinon is the third most commonly used OP in the US, and over 390,000 kg of diazinon active ingredient were used in 2002 (Gianessi and Reigner 2006). In California, diazinon is used for treatment of overwintering insects in almonds (*Prunus dulcis*) and other stonefruit orchards. From 1993 to 2002, almost five million kg of diazinon were used in California, with an average annual application of 484,000 kg (California DPR 2003). While diazinon is an effective insecticide, the timing of California's dormant season applications coincides with the wettest months of the year (December through March), resulting in detection of diazinon in California Central Valley water from dormant orchard storm runoff for over 10 years (de Vlaming et al. 2000). Diazinon is also one of the three most frequently detected insecticides in US surface waters (Larson et al. 1997, 1999; Holmes and de Vlaming 2003).

Many best management practices (BMPs) have been suggested to help alleviate pesticide runoff into downstream aquatic receiving systems. One such edge-of-field BMP is constructed wetlands. Wetlands

have long been known for their capacity to improve water quality, and recent studies have indicated their success with mitigating agricultural runoff (Wolverton and Harrison 1973; Higgins et al. 1993; Cole 1998; Rodgers et al. 1999; Moore et al. 2002; Schulz et al. 2003a, b; Schulz 2004). Vegetation is an important component of constructed wetlands. Plants provide stabilization of bed sediments, surface area for microbial attachment and growth, and physical filtration (Brix 1994). The presence of organic matter associated with wetland plants also aids in pesticide mitigation by increasing their potential to transfer from the water to plant material. Other studies have focused on benefits of vegetation in decreasing diazinon concentrations in runoff. For example, using inter-row vegetative filter strips, 37% of applied diazinon remained within the vegetated filter strip that provided 50% coverage. When coverage of the inter-row filter strip was increased to 100%, 88% of applied diazinon remained in the filter strip (Watanabe and Grismer 2001). Total runoff pesticide loading in areas supporting ground cover crops could be reduced by approximately 50% (Watanabe and Grismer 2001). This same study recommended that potential diversion of runoff water through wetlands (or other practices aimed at increasing hydraulic residence time) may successfully mitigate effects of pesticides entering downstream aquatic receiving systems. The objective of this research was to evaluate the use of a constructed wetland system for mitigating diazinon runoff from sources such as dormant orchard spray applications, irrigation tailwater runoff, or row crop storm runoff. A constructed wetland in the Mississippi Delta, USA, was used to accomplish the objective.

## 2 Materials and Methods

### 2.1 Study Site Description

Beasley Lake watershed, in Sunflower County, Mississippi, comprises 850 ha of land surrounding a 25 ha oxbow lake (Locke 2004). Adjacent to the southeast corner of Beasley Lake, a 180×30 m constructed wetland system was established in spring 2003. The system consisted of an initial sediment retention basin, followed by two individual cells (Weaver et al. 2004). Ten stations at distances from inflow of 1 m (site 1),

10 m (site 2), 15 m (site 3), 30 m (site 4), 60 m (site 5), 85 m (site 6), 90 m (site 7), 120 m (site 8), 150 m (site 9), and 170 m (site 10) were established within the constructed wetland system for collection of water, sediment, and plant samples (Fig. 1).

## 2.2 Simulated Storm Runoff Event

A simulated storm runoff event was conducted on the constructed wetland system in May 2003. Diazinon 4E™ (32 g active ingredient total), suspended sediment (403 mg/l), and surface water from Beasley Lake (Table 1) were mixed together in a 7,570 L chamber for 1 h before being continuously amended into the wetland system through a metal flume at the upper end for 4 h. Amount of diazinon used was based on the recommended application rate in California (2.25 kg active ingredient/ha); wetland contributing acreage (14 ha); and assumed 1% pesticide runoff (Wauchope 1978). Simulated rainfall contributions to the storm event were based on a 1.3 cm event, with assumed rainfall runoff of 50% (~917,000 L). A pump (~3,800 L/min) transported water from the lake into the wetland system for 4 h to complete the simulated runoff event.

## 2.3 Collection of Water, Sediment, and Plant Samples

Grab samples of wetland water were collected in 1-L amber glass bottles at 15 min intervals for the first hour, then again at 1.5 h, 2 h, 3 h, 4 h, 9 h, 1 d, and 2 d at individual sampling sites indicated in Fig. 1. When available, water was also collected on days 7, 13, 27, 41, and 55 post-application at sampling sites. However, with no inflow after the 4 h simulated event, certain wetland sampling stations were dry after 7 days. After collection, samples were stored on ice and immediately returned to the laboratory for extraction

**Table 1** Pesticide concentrations ( $\mu\text{g/L}$ ) in Beasley Lake water (used as source water for storm runoff)

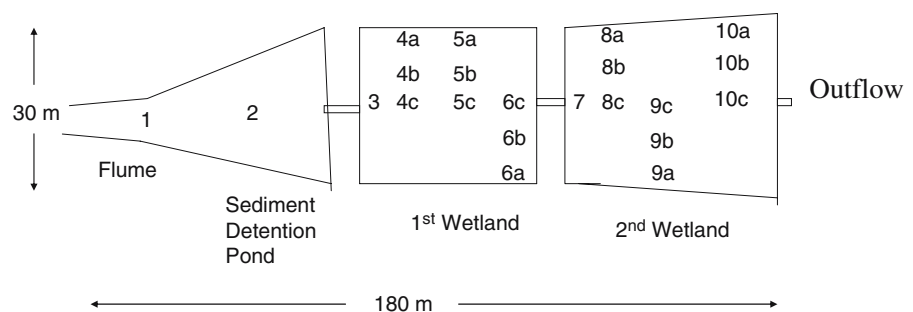
|                    | Pre-study (4/30/03) | Post-study (5/19/03) |
|--------------------|---------------------|----------------------|
| Trifluralin        | 0.000               | 0.000                |
| Atrazine           | 0.206               | 0.227                |
| Methyl parathion   | 0.015               | 0.015                |
| Alachlor           | 0.000               | 0.000                |
| Metolachlor        | 0.020               | 0.011                |
| Chlorpyrifos       | 0.000               | 0.000                |
| Cyanazine          | 0.006               | 0.002                |
| Pendimethalin      | 0.000               | 0.000                |
| Fipronil           | 0.010               | 0.011                |
| Fipronil sulfone   | 0.002               | 0.001                |
| Dieldrin           | 0.002               | 0.001                |
| pp'-DDE            | 0.004               | 0.002                |
| pp'-DDD            | 0.006               | 0.003                |
| pp'-DDT            | 0.024               | 0.014                |
| Chlorfenapyr       | 0.008               | 0.004                |
| Bifenthrin         | 0.015               | 0.006                |
| Lambda-cyhalothrin | 0.005               | 0.002                |

(within 24 h). Approximately 10 g (wet weight) of sediment and plant material were collected at 1, 3, 9, 24, and 48 h, as well as 7, 13, 27, 41, and 55 d. Sediment samples were limited to the top 3 cm, and only leaves and shoots exposed in the water column (from sediment surface to water surface) were collected as plant samples. Samples were wrapped in foil, stored on ice, and transported to the laboratory. Upon arrival, samples were stored in a freezer ( $-20^{\circ}\text{C}$ ) until being dried for analysis.

## 2.4 Diazinon Extraction and Analysis

Pesticide analyses were conducted on unfiltered water, sediment, and plants to determine diazinon

**Fig. 1** Sampling stations located within the Beasley Lake constructed wetland system. Sites with a, b, and c were collected along the same transect



concentrations in the three environmental matrices. Extraction methods used were similar to those detailed by Bennett et al. (2000). Individual water sample volumes were recorded (500–800 ml) prior to addition of 200 ml of ethyl acetate and 100 mg of KCl. Sediment and plant samples were air-dried and ground to pass through a 2 mm sieve, prior to extraction. Diazinon was analyzed using an Agilent Technologies 6890 gas chromatograph equipped with a 30 m Agilent Technologies-1 MS column (Santa Clara, CA). An Agilent electron capture detector (model G2397A) was utilized. A multi-level calibration procedure was used with standards (99.4% purity, USEPA, Research Triangle Park, NC) and updated every ninth sample. Limits of detection (LOD) in water, sediments, and plants were 0.01 µg/l, 0.1 µg/kg, and 0.1 µg/kg, respectively. Mean extraction efficiencies based on fortified samples, were >90% for water, sediment, and plants.

## 2.5 Data Analysis

Mass balances were performed using a model developed previously by Bennett et al. (2005) and Moore et al. (2006). Briefly, data on water, plant, and sediments collected along transects of the sediment detention pond, vegetated wetland cell no. 1 and vegetated cell no. 2 (Fig. 1) at each sample time point (1 h, 3 h, 9 h, 24 h, 48 h, 7 d and 13 d) were used to calculate mass balances. Because water data was unavailable due to dry conditions at some locations after 13 d, no further mass balances were derived for comparisons of the three environmental matrices (water, plant, and sediment).

Mass balances for each compartment were compared between cells and total pesticide mass in each compartment was compared to determine overall relative partitioning within the entire system. This enabled quantitative evaluation of chemical partitioning and losses that occurred over the study duration. The mass balance at a given time point, using wetland cell no. 1 as an example, was determined as:

$$m_{\text{total}(t)} = m_{\text{w}(0-70)} + m_{\text{p}(0-70)} + m_{\text{s}(0-70)} \quad (1)$$

where  $m_{\text{w}(0-70)}$ ,  $m_{\text{p}(0-70)}$  and  $m_{\text{s}(0-70)}$  reflect the total chemical mass (g) in water, plants (that part exposed in water column) and sediments over the 70 m wetland

length. Integration of chemical masses in water was performed according to the trapezoidal rule:

$$m_{\text{w}(0-70)} = \sum_{i=0}^{n-1} \left( (V_{\text{w}(i+1)} - V_{\text{w}(i)}) \cdot \left( \frac{C_{\text{w}(i+1)} + C_{\text{w}(i)}}{2} \right) \right) \quad (2)$$

where the term  $(V_{\text{w}(i+1)} - V_{\text{w}(i)})$  represents the volume of water (L) bounded by a given transect interval (i.e. 0–13, 13–46, 46–69 m etc.) and is multiplied by the average water concentration ( $C_{\text{w}}$ ) measured at the interval boundaries. Water volumes between transects were estimated using the mean water depth (0.60 m) multiplied by the surface area of the transect interval and by accounting for water displacement by plants (assuming 20% of water was displaced by plant biomass in each transect). Mass calculations for plants and sediments were similar to Eq. 2 except that concentrations were measured in units of mg/kg and the volume terms were replaced by bulk sediment mass (kg) or plant biomass (kg). In the former case, wetland surface area (m<sup>2</sup>) within a given interval was multiplied by a sediment depth of 0.01 m and converted to sediment mass by assuming a bulk sediment density of 1,773 kg/m<sup>3</sup>. Average area plant biomass (6.96 kg/m<sup>2</sup>) within a transect interval was multiplied by wetland width and interval distance to arrive at a plant biomass (kg) estimate.

## 3 Results

### 3.1 Diazinon Concentrations

Progression of diazinon transport in the water column was documented after 30 min post-exposure. Aqueous diazinon concentrations were 132 µg/l (site 1), 133 µg/l (site 4), 104 µg/l (site 5), 35 µg/l (site 6) and below detection at site 7 (Table 2). Four hours following exposure initiation, diazinon had migrated 150 m (15 µg/l) within the water phase. Outflow (180 m) aqueous concentrations were 7.5 µg/l at 6 h and 23 µg/l at 9 h. When comparing concentrations of diazinon in the entire wetland system throughout the 55 d experiment, the mean concentrations were 18.1 ± 4.50 µg/l, 26.0 ± 8.02 µg/kg (dry weight), and 97.8 ± 10.7 µg/kg (dry weight) in water, sediment, and plant compartments, respectively. Wetland plants were associated with 69% of the measured diazinon con-

**Table 2** Mean ( $\pm$  standard error) diazinon concentrations ( $\mu\text{g/L}$ ) in wetland water

| Time (days) | Sediment                   |                           |                            |
|-------------|----------------------------|---------------------------|----------------------------|
|             | Detention pond (sites 1–2) | Wetland no. 1 (sites 3–6) | Wetland no. 2 (sites 7–10) |
| 0.01        | 72.8 $\pm$ 63.0            | 65.34 $\pm$ 66.5          | ns                         |
| 0.02        | 108 $\pm$ 20.7             | 69.0 $\pm$ 60.12          | ns                         |
| 0.03        | 128 $\pm$ 27.1             | 117 $\pm$ 57.0            | 0.07 $\pm$ 0.12            |
| 0.04        | 86.4 $\pm$ 70.0            | 79.2 $\pm$ 51.4           | 0.04 $\pm$ 0.12            |
| 0.06        | 102 $\pm$ 16.0             | 91.3 $\pm$ 57.5           | 0.07 $\pm$ 0.10            |
| 0.08        | 106 $\pm$ 19.9             | 122 $\pm$ 36.8            | 0.23 $\pm$ 0.46            |
| 0.13        | 108 $\pm$ 13.2             | 107 $\pm$ 42.2            | 20.2 $\pm$ 37.6            |
| 0.17        | 35.7 $\pm$ 61.6            | 86.1 $\pm$ 44.8           | 34.4 $\pm$ 48.8            |
| 0.25        | 7.50 $\pm$ 3.90            | 64.9 $\pm$ 37.9           | 14.9 $\pm$ 21.3            |
| 0.38        | 14.5 $\pm$ 0.60            | 29.2 $\pm$ 33.0           | 10.6 $\pm$ 12.4            |
| 1           | 16.3 $\pm$ 6.90            | 34.5 $\pm$ 22.1           | 17.3 $\pm$ 21.1            |
| 2           | 0.09 $\pm$ 0.13            | 0.44 $\pm$ 1.05           | 0.01 $\pm$ 0.02            |
| 7           | 0.59 $\pm$ 0.72            | 1.68 $\pm$ 2.15           | 0.51 $\pm$ 0.80            |
| 13          | 0.93 $\pm$ 1.09            | 3.12 $\pm$ 2.86           | 2.46 $\pm$ 2.37            |
| 27          | bd                         | 0.06 $\pm$ 0              | 0.32 $\pm$ 0.79            |
| 41          | bd                         | 0.61 $\pm$ 1.36           | 0.14 $\pm$ 0.26            |
| 55          | 3.26 $\pm$ 5.16            | 0.67 $\pm$ 1.42           | 0.20 $\pm$ 0.48            |

ns=no sample collected bd=below detection limits (0.01  $\mu\text{g/L}$ ) USEPA acute and chronic water quality criteria for diazinon= 0.17  $\mu\text{g/L}$

centrations, while sediment and water were responsible for 18 and 13%, respectively. Within the first 24 h, 15% of the inflow diazinon concentration was retained in the sediment detention pond. Wetland cell 1 retained 19% of its inflow concentration, while wetland cell 2 retained 86% of its inflow concentration within the first 24 h. Diazinon concentrations in sediment and plants were less predictable throughout the 55 d experiment (Tables 3 and 4). Fluxes in sediment and plant pesticide concentrations may be related to rainfall which occurred during the 55 d. Between the 48 h and 7 d samples, 2.34 cm of rainfall was recorded. An additional 2.64 cm fell between the 7 and 13 d samples. For the 2 week period between 13 and 27 d samples, 3.48 cm of rainfall was recorded; however, the greatest amounts of rainfall occurred between 27 and 41 d samples (11.51 cm) and between 41 and 55 d samples (9.32 cm).

### 3.2 Diazinon Mass

The total nominal mass of diazinon (as active ingredient) added to the wetland system was 32 g. In comparison,

**Table 3** Mean ( $\pm$ standard error) diazinon concentrations ( $\mu\text{g/kg}$ ) in wetland sediment

| Time (days) | Sediment                   |                           |                            |
|-------------|----------------------------|---------------------------|----------------------------|
|             | Detention pond (sites 1–2) | Wetland no. 1 (sites 3–6) | Wetland no. 2 (sites 7–10) |
| 0.04        | 89.6 $\pm$ 155             | 28.1 $\pm$ 52.4           | 12.5 $\pm$ 18.4            |
| 0.13        | bd                         | 21.6 $\pm$ 43.3           | 7.93 $\pm$ 13.7            |
| 0.38        | 8.26 $\pm$ 11.7            | 216 $\pm$ 479             | 17.6 $\pm$ 21.5            |
| 1           | 0.64 $\pm$ 0.90            | 32.3 $\pm$ 63.3           | 0.10 $\pm$ 0.18            |
| 2           | bd                         | 8.35 $\pm$ 9.77           | 14.1 $\pm$ 11.7            |
| 7           | bd                         | 6.51 $\pm$ 10.3           | 115 $\pm$ 219              |
| 13          | 22.4 $\pm$ 31.7            | 2.61 $\pm$ 5.22           | 2.18 $\pm$ 3.78            |
| 27          | bd                         | 49.5 $\pm$ 70.0           | 7.66 $\pm$ 13.3            |
| 41          | bd                         | 46.7 $\pm$ 71.3           | 17.7 $\pm$ 30.7            |
| 55          | bd                         | 25.5 $\pm$ 34.6           | 28.9 $\pm$ 50.0            |

bd=below detection limits (0.1  $\mu\text{g/kg}$ )

the total calculated mass of diazinon for the entire wetland system ( $m_{\text{total (detention + wetland 1 + wetland 2)}}$ ) at the 3 h sampling point was calculated to be 104 g (Table 5). Model assumptions of wetland water volume and sediment and plant biomass can lead to overestimates of actual pesticide mass present in the system. The mass balance model used for this study has been used in similar wetland studies with success (Bennett et al. 2005; Moore et al. 2006). Mass balance calculations for different sampling times within the three cells of the wetland system showed that there were changes in component distribution occurring over the study duration (Table 5). Throughout

**Table 4** Mean ( $\pm$ standard error) diazinon concentrations ( $\mu\text{g/kg}$ ) in wetland plants

| Time (days) | Sediment                   |                           |                            |
|-------------|----------------------------|---------------------------|----------------------------|
|             | Detention pond (sites 1–2) | Wetland no. 1 (sites 3–6) | Wetland no. 2 (sites 7–10) |
| 0.04        | 90.4 $\pm$ 0               | 126 $\pm$ 35.0            | 44.2 $\pm$ 45.4            |
| 0.13        | 101 $\pm$ 0                | 232 $\pm$ 139             | 208 $\pm$ 148              |
| 0.38        | 173 $\pm$ 35.9             | 90.4 $\pm$ 24.0           | 136 $\pm$ 128              |
| 1           | 139 $\pm$ 137              | 76.8 $\pm$ 14.9           | 241 $\pm$ 123              |
| 2           | 120 $\pm$ 74.4             | 106 $\pm$ 32.1            | 119 $\pm$ 62.5             |
| 7           | 106 $\pm$ 88.6             | 35.0 $\pm$ 53.3           | 157 $\pm$ 85.8             |
| 13          | 4.40 $\pm$ 6.22            | 28.3 $\pm$ 22.6           | 147 $\pm$ 35.8             |
| 27          | bd                         | 339 $\pm$ 443             | 37.0 $\pm$ 3.44            |
| 41          | 8.99 $\pm$ 12.7            | 8.91 $\pm$ 11.4           | 74.5 $\pm$ 32.0            |
| 55          | 55.7 $\pm$ 78.8            | 5.60 $\pm$ 9.69           | 80.6 $\pm$ 0               |

bd=below detection limits (0.1  $\mu\text{g/kg}$ )

**Table 5** Diazinon mass data for Beasley Lake constructed wetland system

| Time | Cell           | Water (%) | Sediment (%) | Plants (%) | Mass (g)            |
|------|----------------|-----------|--------------|------------|---------------------|
| 1 h  | Detention pond | 95.1      | 4.70         | 0.200      | 6.11E-02            |
|      | Wetland 1      | 91.8      | 4.90         | 3.30       | 57.2                |
|      | Wetland 2      | 3.70      | 26.5         | 69.8       | 1.69                |
|      |                |           |              |            | Total Mass (g) 59.0 |
| 3 h  | Detention pond | 99.8      | N.C.         | 0.200      | 9.16E-02            |
|      | Wetland 1      | 92.7      | N.C.         | 7.30       | 53.4                |
|      | Wetland 2      | 87.5      | 0.300        | 12.2       | 50.5                |
|      |                |           |              |            | Total Mass (g) 104  |
| 9 h  | Detention pond | 73.5      | 8.80         | 17.7       | 1.18E-02            |
|      | Wetland 1      | 46.9      | 47.7         | 5.40       | 27.7                |
|      | Wetland 2      | 63.6      | 5.40         | 31.0       | 15.1                |
|      |                |           |              |            | Total Mass (g) 42.8 |
| 24 h | Detention pond | 81.3      | 0.200        | 18.5       | 1.03E-02            |
|      | Wetland 1      | 94.8      | 0.0238       | 5.20       | 20.6                |
|      | Wetland 2      | 61.5      | 0.084        | 38.5       | 18.9                |
|      |                |           |              |            | Total Mass (g) 39.5 |
| 48 h | Detention pond | 4.40      | N.C.         | 95.6       | 1.80E-03            |
|      | Wetland 1      | 8.50      | 6.80         | 84.7       | 1.81                |
|      | Wetland 2      | 0.200     | 16.3         | 83.5       | 4.36                |
|      |                |           |              |            | Total Mass (g) 6.17 |
| 7 d  | Detention pond | 32.2      | N.C.         | 67.8       | 2.44E-03            |
|      | Wetland 1      | 71.7      | 15.1         | 13.2       | 1.60                |
|      | Wetland 2      | 9.70      | 11.8         | 78.5       | 6.39                |
|      |                |           |              |            | Total Mass (g) 7.99 |
| 13 d | Detention pond | 41.3      | 57.1         | 1.60       | 8.34E-04            |
|      | Wetland 1      | 48.3      | 18.3         | 33.4       | 0.864               |
|      | Wetland 2      | 57.0      | 2.70         | 40.3       | 6.09                |
|      |                |           |              |            | Total Mass (g) 6.95 |

N.C.=not calculated  
(diazinon not detected)

the study, mass data indicated the initial cell (sediment retention basin) played a minor role in overall wetland retention. For example, total overall diazinon masses (water + sediment + plants) calculated in this portion of the wetland system, at all sampling times, were consistently below 0.10 g. On the other hand, wetland cells 1 and 2 played a more important role in this test system. At the 1 h sampling time point, the majority of overall mass was measured in wetland cell 1, where the bulk of the mass had partitioned into water (Table 5). By the 3 h sampling point, overall diazinon mass was evenly distributed between wetland cells 1 and 2, with the majority of mass still being measured within the water. This trend continued until the 48 h sample collection. At this time, overall mass had decreased to 6.16 g where the majority of mass was measured in the plants. Overall, diazinon mass in water decreased with time, while the mass of diazinon in plants remained constant throughout the study. In the

sediment retention basin, sediment played a minor role in the partitioning of diazinon (Table 5).

Only 4% of the overall diazinon water mass was located in the sediment detention pond, while wetland cell 1 had 37% of the mass, and 59% of the aqueous mass was located in wetland cell 2. Sediment pesticide masses followed a similar pattern with <1% of the overall diazinon sediment mass located in the sediment retention basin, 46% in wetland cell 1, and 54% in wetland cell 2. Diazinon plant masses were partitioned into <1% (sediment retention basin), 21% (wetland cell 1), and 79% (wetland cell 2).

Evaluating the entire 55 d exposure period, 44% of measured diazinon mass in the sediment retention basin was associated with the water column. Plants accounted for 55% of diazinon mass, while only 1% was associated with the sediment. In wetland cell 1, 34% of diazinon mass was in the water, while 36 and 30% were associated with sediments and plants, respectively. Wetland cell no. 2 had 24% diazinon

mass associated with water, 33% associated with sediments, and 43% associated with plants.

#### 4 Discussion

Diazinon's water solubility (68.8 mg/l at 20°C) and  $K_{oc}$  values (180–430) indicate the pesticide's tendency to remain in the water (Sharom et al. 1980; Watanabe and Grismer 2001). By remaining in the aqueous phase, diazinon concentrations may be detrimental to fish, invertebrates, and other fauna associated with aquatic receiving ecosystems. According to the USEPA, both acute and chronic freshwater ambient water quality criteria for diazinon are 0.17 µg/l (US EPA 2005). As demonstrated in Table 2, aqueous concentrations in wetlands were occasionally below the established criteria. However, instead of focusing on individual wetland aqueous concentrations, one should examine the final wetland cell (no. 2) aqueous concentrations. For the first 3 h of the experiment, concentrations were below the criteria. From 3–24 h sampling, concentrations exceeded the criteria, but were back below the criteria after 48 h.

Effects of technical grade diazinon in aquatic microcosms have been reported (Giddings et al. 1996). Zooplankton and macroinvertebrate taxa were affected at time-weighted average diazinon concentrations of 9.2 µg/l and greater. At concentrations of 22 µg/l and higher, total fish biomass was reduced, while survival effects were noted at concentrations of 54 µg/l and above. Other studies have reported effects of diazinon on laboratory-reared organisms. When comparing the relative sensitivity of *Ceriodaphnia dubia*, *Daphnia magna*, *Hyalella azteca*, *Chironomus tentans*, and *Pimephales promelas*, it was reported that *C. dubia* was the most sensitive of those species, with a no-observed effects concentration (NOEC) of 0.6 µg/l and a lowest-observed effects concentration (LOEC) of 0.8 µg/l. These results translated into a exposure response slope of 300% mortality/µg/l. In contrast, *P. promelas* (fathead minnow) was the least sensitive species with an exposure response slope of 0.005% mortality/µg/l (Burkepille et al. 2000). *Daphnia magna* followed *C. dubia* in sensitivity in the same study, but its exposure response slope was less pronounced (26% mortality/µg/l) than *C. dubia*. Other studies of *D. magna* reported depression of growth at concentrations above 0.05 ng/l, which

were sub-lethal (Sanchez et al. 1998). Recently, the presence of other pesticides in solution with diazinon have been documented to increase diazinon's independent toxicity. In the presence of atrazine concentrations between 40–200 µg/l, diazinon toxicity to *C. tentans* increased (Belden and Lydy 2000). When the pyrethroid esfenvalerate was present with diazinon, greater than additive toxicity was observed in *P. promelas* (Denton et al. 2003).

To alleviate potential contamination of aquatic receiving system resources surrounding agricultural areas, various management practices have been suggested for implementation. One such practice, constructed wetlands, has been successful at mitigating concentrations of pesticides leaving the agricultural production landscape (Moore et al. 2000, 2002; Sherrard et al. 2004). Biotic and abiotic factors associated with constructed wetlands work in conjunction to remediate pesticide runoff. Microbial activities in wetlands are less understood than other components, but are nonetheless integral in the remediation process. An earlier study conducted on the current constructed wetland system reported similar general enzymatic activities between sediments from the two main cells (Weaver et al. 2004). No microbial data were collected in the current study.

Another important environmental characteristic in constructed wetland systems is pH. Rapid degradation of diazinon via hydrolysis has been reported under acidic conditions (Bailey et al. 1996). In freshwater aqueous solutions, diazinon degradation has increased 2–4 times during temperature increases from 10 to 21°C (Bondarenko et al. 2004). With a mean ambient air temperature of 29°C during the current experiment and previously reported wetland water pH values of 4.85–5.21 (Weaver et al. 2004), diazinon degradation was likely increased in the constructed wetland.

To further understand fate of diazinon in this series of vegetated wetland systems, mass balance calculations were performed to determine diazinon partitioning between water, sediment and plant components. At the 3 h sample collection, it was evident that the majority of the mass of diazinon was calculated to be in the water (Table 5). This mass was evenly distributed between wetland cells 1 and 2, indicating that advection was a major process occurring in these wetland systems. By 9 h, the mass in water was still evenly distributed between wetland cells 1 and 2, but the overall mass throughout the

system had decreased from 104 to 42.8 g indicating a reduction of greater than 50%. This major loss was likely due to advection since diazinon was measured at the outflow of wetland cell 2 between the 3 and 9 h sampling points. Interestingly, at the 24 h sampling collection, overall mass within the system was similar to what was measured at the 9 h sampling point indicating the wetland system was retaining the remaining diazinon mass (Table 5). After the 24 h sampling point, the mass of diazinon in water was reduced by two orders of magnitude, while the plant component remained consistent and the sediment component partitioning was minimal. This trend continued throughout the study. These data show diazinon was being degraded in the wetland system, since diazinon mass was decreasing after the 24 h sampling period and diazinon was no longer measured in the outflow of the wetland system.

It was expected that aquatic macrophytes would play a more important role in the retention of diazinon in this test system since they were effective in a previous study using the organophosphate insecticide, methyl parathion (Moore et al. 2006). In that study, a 5.5×50 m vegetated wetland dominated by the aquatic macrophyte, *Juncus effusus*, was shown to successfully reduce methyl parathion concentrations to 0.1% of the inflow concentration within a 20 m reach. Furthermore, methyl parathion was not detected in the outflow. In the current study, overall retention of diazinon by aquatic macrophytes was not as evident. There are several possibilities as to why this difference in plant sorption was evident. Perhaps *Polygonum amphibium* (dominant macrophyte in wetland cell 2), was simply not as effective in sorbing diazinon as was the case with methyl parathion and *J. effusus* in the above study. Alternatively, surface sorption sites may have been saturated with diazinon throughout the study. Evidence for this is indicated by calculated mass data where after the 3 h sampling period, the diazinon mass in plants remained relatively consistent throughout the study (7.00 g±0.861) until the 13 d sampling period. Also, reported  $K_{oc}$  values for methyl parathion are 3–5 times greater than those in diazinon, which may account for increased methyl parathion plant sorption. Further plant-pesticide specific studies are needed to address this concern.

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