Atrazine fate processes in a constructed emergent marsh: 1998 research updates

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Introduction

Atrazine (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine) is a widely used herbicide, used to selectively control broadleaf weeds in a variety of agricultural crops, including corn (*Zea mays* [L.]), sorghum (*Sorghum bicolor* [L.]), and turfgrass, by blocking photosynthetic pathways (WSSA, 1994). It is known to migrate from the point of application into surface waters through two primary routes, surface runoff (Paterson and Schnoor, 1992) and field tile drainage (Buhler et al., 1993; Southwick et al., 1990). Regardless of the source, atrazine is a common contaminant in surface waters, particularly in states with abundant croplands (Pereira et al., 1990; Baker and Richards, 1990). Atrazine was the most persistent and frequently detected herbicide observed by Goolsby et al. (1991), who detected atrazine in 98% of surface water samples from 132 streams in the upper midwestern United States. Frank et al. (1990) found atrazine and deethylatrazine (DEA, an atrazine degradation product) in 89 to 100% of raw water samples at a Dresden, Ontario, Canada, drinking water source (Sydenham River) over a seven-year period. In 1991, the annual mass transport of atrazine in the Mississippi River, which discharged into the Gulf of Mexico, was conservatively estimated at 160 tons (Periera and Hostettler, 1993).

From a human health perspective, there is concern regarding atrazine in surface water and groundwater used as drinking water sources, since numerous studies have identified concentrations that exceed the U.S. EPA drinking water maximum contaminant level (MCL) of 3 µg/L (Kadlec and Alvord, 1992; Masse et al., 1994; Baker and Richards, 1991; Jayachandran et al., 1994; Pereira and Hostettler, 1993; Thurman et al., 1991). Although there is on-going scientific discussion over whether this MCL is reflective of true risks (Baker and Richards, 1991; Richards et al., 1995; Powers, 1996; Richards and Baker, 1990), the reduction of atrazine levels in surface waters is desirable, given the significant implications of this herbicide in water treatment processes and a relative lack of information on the human health and ecological impacts associated with atrazine degradates, such as DEA, deisopropylatrazine (DIA), hydroxyatrazine (HA) and several other hydroxy analogs. No MCLs or health advisories have been established for these breakdown products (U.S. EPA, 1995). In addition, atrazine has recently come under scientific scrutiny as a potential endocrine disrupter or "estrogen-mimic" that may cause genetic damage to exposed organisms (Crain et al., 1997; Cooper et al., 1996).

Removal of atrazine in conventional water treatment facilities typically involves expensive or slow and inefficient technologies, including ozonation, activated carbon absorption, microbial action, hydrolysis, and photodecomposition (as discussed in Pelizzeti et al., 1990). Several studies have found that sediment removal at water treatment plants is ineffective in pesticide removal, and that pesticide concentrations in finished water are very similar to the concentrations in the raw water supplies when conventional water treatment practices are used (Frank et al., 1990; Miltner et al., 1989 Meakins et al., 1994). Miltner et al. (1989) reported only 10 to 20% removal of atrazine under this treatment. Frank et al. (1990) reported no reduction in atrazine concentrations when raw water was treated with 5 mg/L powdered charcoal.

Preventing the migration of atrazine into surface waters could eliminate the need for these costly removal technologies and could also alleviate potential stresses to aquatic communities. Wetlands are known to be effective in removing or reducing concentrations of numerous types of pollutants, and several studies have shown that wetlands and vegetative riparian buffer strips have the capacity to reduce atrazine concentrations (Alvord and Kadlec, 1996; Kadlec and Alvord, 1992; Paterson and Schnoor, 1992). Restoration or creation of wetlands adjacent to rivers has been proposed as a means of treating agricultural runoff and protecting downstream surface waters from the effects of non-point pollutants (Detenbeck et al., 1996; Cooper, 1993; Baker, 1992; Mitsch, 1992). If pesticides are effectively filtered and processed in wetlands, their impacts are not realized in receiving lakes, rivers, streams, and reservoirs (Rodgers and Dunn, 1992; Gilliam, 1994).

The Olentangy River serves as the principal source of water for the constructed wetlands at the Olentangy River Wetlands Research Park (ORWRP). Due to the agricultural activity within the Olentangy River watershed, and the fact that the wetlands at the ORWRP rely on the Olentangy River as the primary source of water, atrazine frequently enters these wetlands, particularly following heavy precipitation events. Based on a preliminary study to identify the presence and distribution of atrazine in Wetland 1 (W1), it appears likely that atrazine concentrations are reduced from inflow to outflow (Dilley et al., 1996). In 1998, field monitoring was begun on W1, a 2.5-acre, reniform (kidney-shaped) emergent marsh, to observe trends in atrazine concentrations and to research specific factors that may

influence atrazine fate and transport within the wetland. The existence of a wealth of hydrological, biological, and chemical data for the wetlands collected by other researchers makes the ORWRP an ideal site to assess the atrazine removal potential of wetlands and to study the processes involved.

Based on an extensive literature review and evaluation of site-specific factors, it was determined that partitioning to sediment (organic matter and clay) or settling of atrazine sorbed to suspended solids in the influent will likely remove the highest percentage of the atrazine load in W1. This was the general conclusion drawn from similar studies on the Des Plaines wetlands in Illinois (Kadlec and Hey, 1994).

A second fate mechanism, biological degradation, was also studied to determine at what rate the sediment-sorbed atrazine is degraded within the wetland system. Several studies have reported the enrichment of atrazine-degrading microbial communities over time in atrazine-exposed soils and sediments (Radosevich et al., 1995; Topp et al., 1995; Ostrofsky et al., 1997). Since atrazine is regularly detected in the Scioto River watershed (P. Orndorff, 1996, pers. comm.), and has been detected in the water of the Olentangy River (a Scioto tributary) (Dilley et al., 1996), it was suspected that the ORWRP wetlands possessed an atrazine-degrading microbial community.

The remainder of the potential fate mechanisms identified (e.g., photo/chemodegradation, metabolism by non-microbial wetland organisms) are assumed to be of little significance to the overall mass balance of atrazine in W1, based on literature sources and site-specific factors. Therefore, field and laboratory research efforts were aimed at establishing pre-study conditions at W1 (i.e., residual atrazine in sediment), measuring the sorptive capacity of W1 sediments, determining biodegradation rates, and performing extended monitoring of atrazine concentrations at the inflow and outflow of W1 to observe trends over the spring and summer months of 1998.

All studies were performed as part of on-going research at the ORWRP to evaluate the fate and transport of atrazine in wetlands and develop an interactive simulation model to illustrate these processes. The 1998 results of this effort are discussed here.

Methods

Preliminary Sampling

To establish pre-study conditions, sediment samples were taken in clusters near the inflow, at the middle, and near the outflow of W1 on February 28, 1998. Ten sediment samples were taken from each area using a small sediment coring device, consisting of a 3/4-inch inner diameter (ID) poly-vinylchloride (PVC) tube with a built-in plug ejector. This device was driven into the sediment by hand, and then retracted to pull a five-cm plug from the wetland substrate. The sediment corer was decontaminated between each cluster of samples using a soap and water wash, deionized (DI) water rinse, methanol rinse, and final DI water rinse. Each cluster of ten samples was composited, and three subsamples were taken from each composite for extraction and atrazine analysis. Sediment pH and composition (particle-size distribution and percent organic carbon) analyses were performed by staff in the soil characterization laboratory at The Ohio State University.

This sampling effort was undertaken during a time of year (pre-planting period) when atrazine concentrations were expected to be low based on usage patterns and the findings of other researchers (Goolsby, et al., 1991; Goolsby and Battaglin, 1993; Baker and Richards, 1991). Confirmatory surface water samples were also collected at this time to determine if atrazine was entering the wetland system during this non-peak season. Water samples were collected in clusters, as described for the sediment samples, and each cluster of samples was composited. The samples were taken by slowly lowering a PVC tube with a cable-mounted stopper into the wetland surface water. The stopper was retracted at the desired depth to seal the tube, trapping an integrated sample of the water column. This device was lowered to within two inches of the sediment before the stopper was pulled, so that almost the entire water column was sampled. The water samples were collected in advance of the sediment sampling, to avoid sampling material that was resuspended during the sediment coring. Both surface water and sediment samples were stored at 4°C until extraction.

Water and Sediment Analysis

Surface water subsamples (1000 mL; with 1000 µL of terbutylazine, TBZ, added as a surrogate to determine recovery efficiency) were extracted by liquid-liquid extraction with methylene chloride and passed through a drying column packed with glass wool and sodium sulfate. The extracted samples were evaporated to dryness at 40°C and then redissolved with 2-propanol and transferred to a 2.0 mL amber storage vial with a teflon-lined septum. All samples were stored in a freezer until analysis.

Sediment samples were extracted following methods described by Koskinen et al. (1991). Subsamples of each sediment composite were weighed, dried overnight in an oven set at 110°C, and re-weighed to determine moisture content. Triplicate 20 g subsamples were taken and placed in 50 mL centrifuge tubes, to which 20 mL of extracting solution (4:1 methanol:water [v:v]) was added. The tubes were capped, vortexed for two minutes, and allowed to stand overnight (minimum of 16 hours) at room temperature. The samples were then revortexed for 30 seconds and centrifuged. The supernatant from each sample was transferred to a clean centrifuge tube, and the sample was subjected to an additional extraction, with 30 seconds of vortexing followed by centrifugation. The supernatant was added to the previously collected supernatant and the centrifuge tube was placed in a 60°C bath to evaporate the methanol . The remaining water was passed through a C-18 Solid Phase Extraction (SPE) column connected to a vacuum

system. Each SPE column was eluted with 2.0 mL ethyl acetate and the sample was transferred to a pre-weighed amber storage vial with a teflon-lined septum. Samples were held in a freezer until prepared for GC analysis.

Analysis for both surface water and sediment samples was performed on a dual-column Varian 3500 gas chromatograph (GC) with a Varian 8100 autosampler and split/splitless injection (split ratio 25:1). Azobenzene was used as the internal standard for quantification. The carrier gas was helium at a flow rate of 1 mL min^{-1}. The initial and final column temperatures were 120°C and 250°C, respectively, and the total run time was 62.5 minutes.

Sorption to Sediment

To measure sorption to sediment and calculate the partitioning coefficient (K_d), three additional 3-g subsamples (wet weight, approx. 2.15 g dry weight) were taken from the each of the composited February 28 sediment samples from W1 (near the inflow, middle, near the outflow) and combined with 29.5 mL of water from the corresponding composite sample in a polyallomer centrifuge tube. These water/sediment subsamples were spiked to a concentration of 0.1 mg/L atrazine by adding 0.5 mL of a 6 mg/L atrazine solution, consisting of a 500 ppm reagent-grade atrazine standard (in methanol) diluted to the final concentration in organic-free water. This addition resulted in a 1:10 ratio of sediment to liquid (w solid:v liquid), comparable to the ratio of water to the "active layer" of sediment for atrazine adsorption (based on studies by Topp et al., 1995; Bacci et al., 1989) expected for W1.

After a 48-hour equilibration period under constant shaking, these samples were centrifuged and the supernatant was analyzed using reverse-phase high performance liquid chromatography (HPLC) with UV detection (223 nm) to quantify the dissolved (non-sorbed) atrazine. The difference between the known spike concentration (0.1 mg/L) and this detected water concentration was assumed to represent the portion of atrazine sorbed to the sediment. From this, the K_d value was derived for each sediment composite using the following equation (Wauchope and Myers, 1985):

$K_d = (x/m)/C_e$,

where x/m is the amount of herbicide x (µg) adsorbed by mass m of soil (g dry weight) at equilibrium with solution concentration C_e (mg atrazine/L) Using the calculated K_d values and the organic carbon data for each sediment composite, an organic carbon partitioning coefficient (K_{oc}), was calculated using the following formula (Wauchope and Myers, 1985):

$K_{oc} = K_d/f_{oc}$

where f_{oc} is the fraction by weight of organic carbon (OC) in the sediments. This coefficient is useful in making predictions about atrazine fate in W1.

Biodegradation

Fifteen water and sediment samples from across W1 were collected on April 29, 1998, using the techniques previously described for the preliminary sampling. In the laboratory, these samples were composited (one water composite and one sediment composite) and 2.5 g (wet weight) subsamples of sediment and 2.5 g subsamples of water were placed in biometer flasks, following methods described by Ostrofsky et al. (1997). The biometers are 60 ml serum bottles sealed with rubber septum and capped with an Al-ring. The controls were sterilized by autoclaving at 121°C for 20 minutes. Each biometer was spiked with 1 ppm radiolabelled atrazine with an activity of 0.1 µCi. Half of the biometers were spiked with (^{14}C-ethyl)-atrazine (side-chain labelled), half with (U-^{14}C-ring)-atrazine (ring-labelled). The air in the biometer headspace was then purged with filter-sterilized nitrogen in half of each of these sets to produce anaerobic conditions. The complete set of biometer treatments consisted of:

three side-chain-labeled aerobic
three side-chain-labeled anaerobic
three ring-labeled aerobic
three ring-labeled anaerobic
two side-chain-labeled aerobic controls
two side-chain-labeled anaerobic controls
two ring-labeled aerobic controls
two ring-labeled anaerobic controls

These 20 biometers were sealed in Ziploc™ bags with disposable absorbent padding at the base of the bag (a safety requirement) and placed in a submersible plastic-coated heavy-wire rack. A sturdy rubber washer, with an inner diameter approximately the size of the neck of the biometer flask, was stretched over the aluminum collar of each biometer to hold the biometers in an upright and stable position, approximately three inches above the concrete base of the rack.

The rack was taken to the ORWRP on April 29, 1998, and lowered on a rope to the bottom of W1 near the main boardwalk. This placement allowed the rack to rest at a water depth of approximately two feet, in an effort to simulate the temperature and light conditions that influence biological activity in the wetland system. The rack remained in W1 for 93 days.

Mineralization of the radio-labeled atrazine in the sealed biometers was monitored by trapping $^{14}CO_2$ formed during the degradation of the ^{14}C-labeled atrazine. The $^{14}CO_2$ was trapped in 1 mL of 1 M KOH in 1.5 ml glass vials that were suspended by a loop of wire in the headspace in each biometer. This KOH trapping solution was collected and replaced with 1 mL of fresh solution on days 6, 13, 20, 27, 37, 47, 57, and 69 of the incubation period. The final collection occurred on day 93 of the incubation. The collection was performed using disposable syringes and needles to retrieve the solution from each biometer and transfer it to a scintillation vial. Collection syringes were used only once in order to prevent cross-contamination of samples. A separate syringe was used to replenish the KOH solution for each biometer. In the anaerobic samples, the needle was driven through the thick stopper-like septum, so that the system remained sealed and minimal oxygen was introduced into the biometer. Aerobic samples were opened

for sample extraction and then re-sealed. Following collection, all biometers were again sealed in their bags, placed in the rack, and returned to the wetland.

In the laboratory, 10 mL of scintillation cocktail (Scintiverse BD; Fisher Scientific) was added to the vials and the samples were counted on a Beckman LS8000 liquid scintillation counter.

Inflow/Outflow Monitoring

Starting on May 15 and continuing through July 13, 1998, water samples (40 mL or greater) were collected at the inflow and outflow of W1 at least once per day. Following storm events, sampling frequency was generally increased to two or three times per day over a 48-hr period to catch possible sudden changes in atrazine concentrations. Samples were analyzed with the Atrazine RaPID Assay (Strategic Diagnostics; Newark, Delaware) using the immunoassay technique described in Dilley (1996). A spectrophotometric reading was used to determine the triazine compound concentration (assumed to be predominantly atrazine, based on usage records) for each sample. To conserve reagents, small subsets of the samples were initially analyzed. If these results indicated high variability between the samples or high concentrations of atrazine, samples collected during intermediate dates were also analyzed to elucidate trends in atrazine concentration.

Results and Discussion

Preliminary Sampling

No atrazine was detected in the preliminary sediment samples (detection limit = 0.54±0.06 µg/kg dry weight). Surface water concentrations were low, detected at 0.119 µg/L (one sample), 0.105±0.018 µg/L, 0.106±0.015 µg/L, and 0.124±0.008 µg/L for the Olentangy River and W1 inflow, midreach, and outflow composites, respectively. These low concentrations were anticipated for the pre-planting timeframe during which the sampling was conducted. These data provided a useful frame of reference for the interpretation of the long-term monitoring carried out at W1.

Sorption to Sediment

The atrazine concentrations detected in water following the 48-hour equilibration period are shown in Table 1. The mean values for the middle and outflow composites were 0.072±0.001 and 0.069±0.009 mg/L, respectively. The inflow results indicated a mean value of 0.557±0.515 mg/L, a concentration greater than the initial spike of 0.1 mg/L. No atrazine was detected (detection limit = 0.05 mg/L) in the soil blank (unspiked sample) for this composite, so residual atrazine in the sample was ruled out as a possible cause of the high detected concentrations. This result may be related to analytical interference by organic matter in the inflow samples.

Since the results for middle and outflow composites were similar and showed good replication, these values were used to calculate an average K_d for the sediments of W1. The K_d values calculated for the middle and outflow composites were 5.52 and 6.37, respectively. The average foc for the middle composite was 0.0146±0.0002, and for the outflow, 0.0155±0.0002. Though there was a slight variation among the composites, the upper 5 cm of sediment in W1 generally contained 1.5% OC by weight. Dividing the K_d values by their respective foc values resulted in K_{oc} values of 377 and 412 for the middle and outflow composites, or an average log K_{oc} of 2.60. Reported literature values for atrazine log K_{oc} range from 1.73 to 3.17.

Table 1. Partitioning (K_d) study results at the inflow, middle and outflow of the wetland. Data in mg/L.

Sample ID	Inflow	Middle	Outflow
Replicate 1*	1.094*	0.071	0.071
Replicate 2*	0.066*	0.071	0.076
Replicate 3*	0.512*	0.073	0.059*
Mean ± SD	0.557±0.515	0.072±0.001	0.069±0.009

*Result shown is an average of the results of two HPLC runs.

Biodegradation

The results of the biodegradation experiment (average of the three replicates for each treatment) for ring-labelled and side-chain-labelled atrazine are shown in Figures 1 and 2, respectively. The results of the biometer experiments showed biodegradation to be a slow process. The ring-labelled atrazine under aerobic conditions evolved the highest amount of $^{14}CO_2$ over the 93-day incubation (approximately one-quarter of the initial activity of the stock solution added). Assuming first-order kinetics, these results indicate a rate constant, k (d^{-1}), of 0.0033 (r^2=0.95). To calculate a half-life, the following equation was used:

$t1/_2 = 0.693/k$,

where $t1/_2$ is the estimated time for biotransformation of one-half of the atrazine present and k is the calculated rate constant. Plugging the k value for the ring-labelled aerobic treatment into this equation yields a half-life of 210 days. The other treatments exhibited even slower kinetics. This indicates that biodegradation of atrazine is probably not a significant fate mechanism in W1, particularly during high-flow periods when residence times in W1 may only be one to two days (Wang et al., 1998).

Inflow/Outflow Monitoring

Several heavy precipitation events occurred during the spring sampling, and the total triazine concentrations showed some correspondingly high peaks. Total triazine concentrations, assumed to be predominantly atrazine, ranged from 0.76 to 12.77 µg/L (ppb). Daily mean flows for the Olentangy River (in cfs) recorded at USGS Gaging Station #3226800 (approximately 6.5 river miles north of the ORWRP) during the monitoring period is shown in Figure 3. Figure 4 depicts the total triazine concentrations

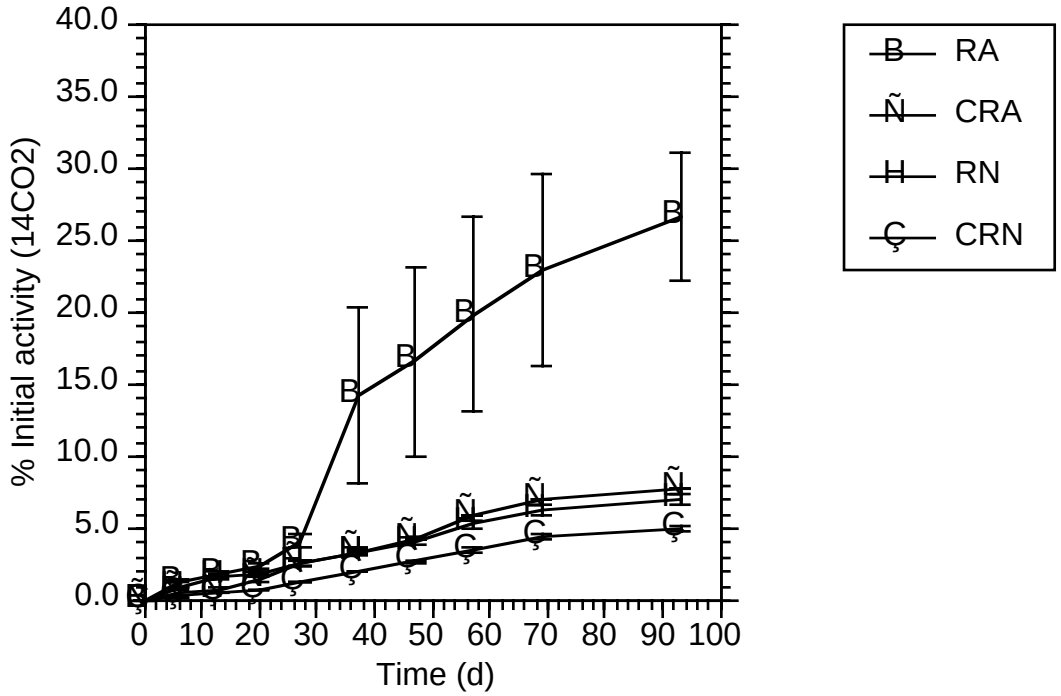

Figure 1. Cumulative evolution of $^{14}CO_2$ in ring-labelled atrazine treatments (RA = aerobic, CRA = aerobic control, RN = anaerobic, CRN = anaerobic control). Error bars reflect the standard deviation for each treatment (three samples) or control (two samples).

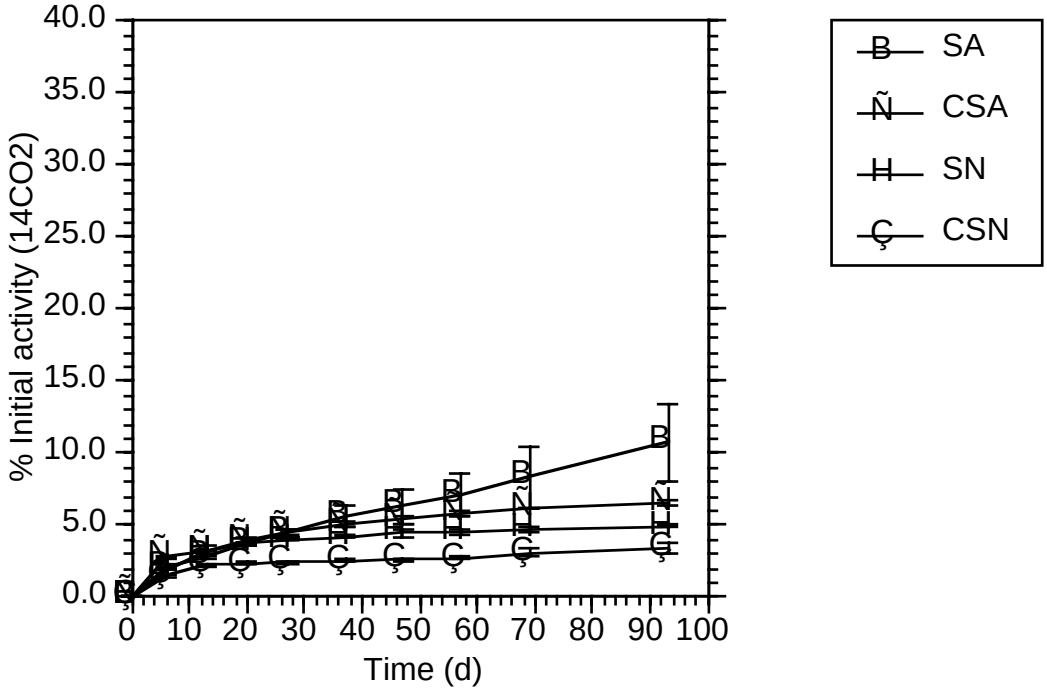

Figure 2. Cumulative evolution of $^{14}CO_2$ in side-chain-labelled atrazine treatments (SA = aerobic, CSA = aerobic control, SN = anaerobic, CSN = anaerobic control). Error bars reflect the standard deviation for each treatment (three samples) or control (two samples).

for the inflow and outflow of W1. The mean inflow and outflow total triazine concentrations were 4.69±3.37 and 4.39±3.24 µg/L, respectively. A two-sample t-test using MINITAB statistical software indicated that inflow concentrations equaled outflow concentrations (0.05 level of significance), so no significant reduction in total triazine concentrations was identified for W1. This is likely due to the relatively small size and short residence time of the wetland, which limits sorption and biodegradation within the system. A recent report on the ORWRP by Mitsch and Montgomery (1998) has attributed the "generally poor performance of the wetlands in retaining both dissolved and suspended materials" to a more consistent hydrologic pattern and lower water levels maintained in Wetlands 1 and 2. This combination of increased inflow rates and lower water levels resulted in a reduction of the nominal residence time in these wetlands, decreasing from over five days in 1996 to less than two days in 1997 (Mitsch and Montgomery, 1998). This same hydrologic pattern was maintained in 1998, as evidenced by the inflow/outflow peaks in Figure 4, which are generally staggered by two days or less.

Future Research Activities

On-going work on this research will likely include additional inflow/outflow monitoring, data analysis (e.g., a comparison of the immunoassay results with the GC results which were generated for 20% of the samples to establish a correction factor), and further evaluation of the biometer results, including an analysis of biological oxidation results to determine if ^{14}C was incorporated into microbial tissues in the biometer flasks. Since other research has shown that wetlands can be effective in reducing atrazine concentrations, the inflow/outflow monitoring may be undertaken at the billabong wetland to assess the effects of increased residence time on atrazine removal. Finally, appropriate data generated through this research will be used to develop a interactive computer simulation model to illustrate the fate and transport of atrazine in the ORWRP wetlands.

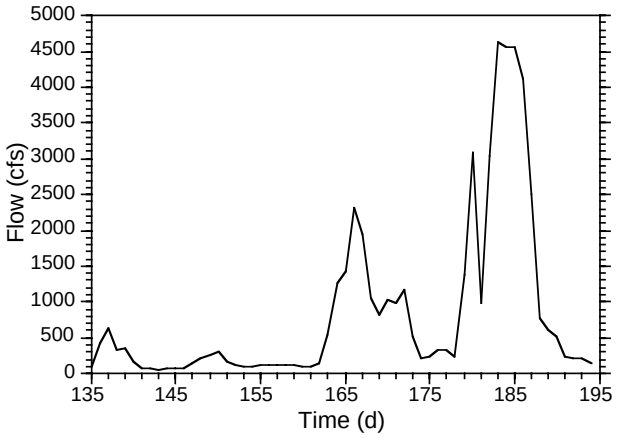

Figure 3. Mean daily flow for the Olentangy River at USGS Gaging Station #3226800 during study period of May 15 - July 13, 1998.

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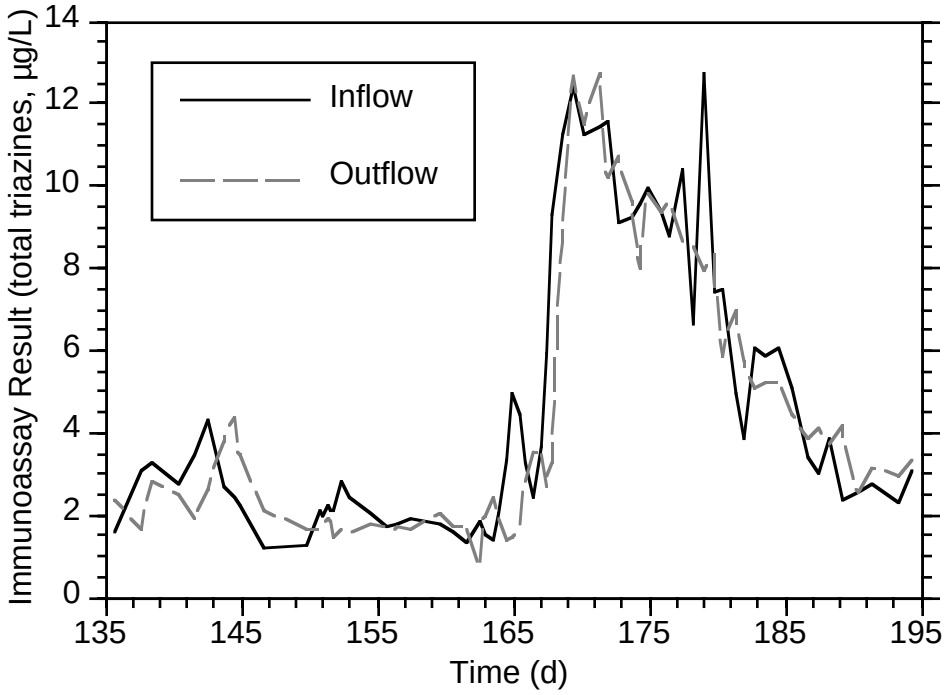

Figure 4. Immunoassay results for the inflow and outflow of Wetland 1 during study period of May 15 - July 13, 1998.

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