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Norflurazon and Simazine Removal from Surface Water Using a Constructed Wetland

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Abstract Norflurazon and simazine are pre-emergent herbicides detected frequently in surface water associated with South Florida agricultural canals and drainage water. This study investigated the potential use of a 1.34 ha constructed wetland for removing these herbicides from surface water. The total length of the wetland was 400 m and width was 35 m. A surface water flow rate of 740 L/min was maintained in the system using a pump. The plant community within the system consisted primarily of *Panicum repens, Alternanthera philoxeroides, and Bacopa caroliniana.* Norflurazon and simazine, derived from commercial formulations, were injected (51.1 g active ingredient each) directly into the water pumped into the wetland over a 2 h period. Water samples were collected from the wetland upstream of the dosing system at 3 h intervals from the beginning through 360 h and at the exit point at 1, 2, and 3 h intervals for the periods of 0–24, 25–48 and 49–360 h after dosing, respectively. The herbicides were extracted using C-18 cartridges and were analyzed by GC-TSD. The total mass of each herbicide discharged from the system was estimated by multiplying the concentration by the total volume discharged during the sampled period. Neither herbicide was detected in the inflow water during the entire study. Norflurazon was first detected at the exit 19 h after dosing and simazine after 23 h. Discharge patterns of the two herbicides differed dramatically. Norflurazon tended to bleed off from the wetland with no distinct peak concentration. However, the mobile fraction of simazine was discharged over a 58 h period. Mean/maximum/median detectable concentrations of the herbicides were 3.9 ± 1.7/8.1/3.4 μg L^{-1} for norflurazon, and 11.9 ± 6.8/23.6/12.0 μg L^{-1} for simazine, respectively. The total masses of norflurazon and simazine discharged from the exit during the 15 day study were 51.7 and 26.9 g, indicating 0% and 47.4% removal from the surface water by the system.

Keywords Triazine · Pyridazinone · Herbicide · Remediation · Wetland

Herbicide losses from agricultural production areas may potentially impact non-target aquatic plant communities due to common modes of action associated with the target and non-target species. Two commonly used herbicides in south Florida agricultural areas are norflurazon and simazine. Norflurazon is a pyridazinone herbicide that is moderately water soluble (28 mg L^{-1}) and relatively nonvolatile (2.66×10^{-9} kPa at 20°C) (Vencill 2002). Its' sorption coefficient is 700 mL g^{-1} (Ware 1992). Simazine is an *s*-triazine herbicide that is less soluble (6.2 mg L^{-1}) and is also not volatile (2.9×10^{-9} kPa at 25°C) (Vencill 2002). Its' sorption coefficient is 130 mL g^{-1} (Ware 1992). Both herbicides are used for pre/post plant control of grass and broadleaf weeds. These herbicides may also be tank-mixed together for more broad-spectrum weed control. Total usage of these herbicides in Florida during the 1999–2002 period (latest available) was 163,556 and 257,229 kg a.i. $year^{-1}$ (FDACS 2003).

Norflurazon and simazine have frequently been detected in surface water associated with South Florida agricultural

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canals at concentrations up to 3.9 and 2.5 μg L^{-1}, respectively (Miles and Pfeuffer 1997; Schuler and Rand 2008). Detectable concentrations were often associated with citrus production within the watershed (Miles and Pfeuffer 1997; Schuler and Rand 2008). Wilson et al. (2007) evaluated losses of norflurazon and simazine from citrus production beds following application. They reported maximum concentrations of 360 μg L^{-1} (norflurazon) and 490 μg L^{-1} (simazine) at the edge-of-field for flatwoods citrus production areas (Wilson et al. 2007). Furthermore, they estimated total mass losses of 4.4% (norflurazon) and 6.7% (simazine) during the first two runoff events following application. Seasonal total losses are expected to be greater with additional runoff events (Wilson et al. 2007). Losses of these herbicides are not restricted to Florida. Simazine has been reported in many freshwater and estuarine water bodies throughout the US and the world (McConnel et al. 2004; Harman-Fetcho et al. 1999; Glotfelty et al. 1984; Domagalski et al. 2008; Louchart et al. 2001). Reported basin yields have ranged from 0.06 to 1.5 g ha^{-1} (Domagalski et al. 2008; Louchart et al. 2001). Clark and Goolsby (2000) estimated that 53 t of simazine were discharged from the Mississippi River into the Gulf of Mexico in 1993. Norflurazon leaching and lateral movement has been shown in sandy coarse (Singh et al. 1985; Schroeder and Banks 1986; Ying and Williams 2000; Sharma and Singh 2001) and fine (Schroeder and Banks 1986; Hubbs and Lavy 1990; Southwick et al. 1993a) textured soils. In a monitoring study focused on Arkansas rivers, lakes, and streams, Senseman et al. (1997) detected norflurazon in several lakes and streams with median and maximum concentrations of 1.8 and 11.5 μg L^{-1}, respectively. Southwick et al. (1993a, b) reported maximum concentrations of norflurazon of 6.6 and 16.5 μg L^{-1} in surface runoff water from soybean-planted experimental plots; and total losses of 2.3% of the amount applied during their study.

Norflurazon's mode of action involves inhibition of phytoene desaturase, an enzyme responsible for carotenoid synthesis (Vencill 2002). Without carotenoids, photosynthetic pigments degrade upon exposure to light, ultimately resulting in inhibition of photosynthesis. The most common and visible symptom of norflurazon phytotoxicity is bleaching of the foliage. Wilson et al. (2006) reported bleaching no observable effects concentration (NOEC)/lowest observable effects concentration (LOEC) values of 0.04/0.06 mg L^{-1} for *Vallisneria americana* exposed for 14 days. They also reported NOEC/LOEC values of 0.08/0.1 mg L^{-1} for fresh weight gains, new leaf production, and root biomass; and 0.06/0.08 mg L^{-1} for stolon production. The algal species *Selenastrun capricornutum* is a more sensitive aquatic plant species with an EC_{50} of 9.7 μg L^{-1} (OPP 2000). The reported EC_{50} for *Lemna gibba* was 53 μg L^{-1} following 14 days exposure (OPP 2000). Simazine's mode of action involves binding to the D1 protein of the photosystem II complex in chloroplast thylakoid membranes, effectively blocking electron transport from Q_A to Q_B (Vencill 2002). Thylakoid membrane damage results from the production of free radicals formed due to the blocking of electron transport (Vencill 2002). Wilson and Wilson (2010) reported NOEC/LOEC/EC_{50} values of <0.058/0.058/0.067 mg L^{-1} for fresh weight gains (most sensitive endpoint) in *Vallisneria americana* exposed to simazine for 14 days. The EC_{50} for Lemna gibba exposed for 14 days is 140 μg L^{-1} (OPP 2000). Biochemical impacts occur at much lower concentrations relative to the abundance and mass-based endpoints for both herbicides. However, uncertainty still exists for relating many of the biochemical measurements to effects at the individual or population levels.

Given the cosmopolitan nature of these herbicides in surface water, opportunities for their removal are of interest since chronic, long-term effects to non-target organisms are not well known. This study evaluated the removal efficiency of a constructed wetland for removing norflurazon and simazine from contaminated surface water.

Materials and Methods

This study was conducted at a field site located within a citrus grove in western St. Lucie county, Florida. Originally the 1.34 ha site supported citrus production. However, analysis of crop productivity versus cost inputs indicated a net loss to the grower due to poor soil quality and drainage. As a result, the area was taken out of production and a constructed wetland was built. Originally this system was planted with Bahia grass, but had since transitioned into a wetland species dominated system due to the constant inundation. The overall footprint for the system was 120 × 118 m with a staggered flow path measuring 35 m wide by 400 m long. Water was pumped continuously into the system from an internal field ditch at a nominal rate of 740 L min^{-1}. The pump flow rate was not confirmed. At this flow rate, the hydraulic residence time for the water was approximately 64 h (2.7 days). The internal field ditches were connected to the North St. Lucie Water Control District's irrigation/drainage canal network. Water exited the system through a 0.91 m diameter vertical drop pipe, back into the canal system. Plant composition within the system was not uniform, but consisted primarily of *Panicum hemitomon*, *Panicum repens, Althernanthera plodoxeroides, and Bacopa caroliniana* (Table 1). *Distichlis spicata* was dominant in one section, and the other species consisted of unidentified filamentous algae comprising a highly visible fraction of the species. Biomass

Table 1 Percent composition of plant species at each location and total biomass (g/m^2) within the constructed wetland

Distance from inflow (m)	Percent composition					
	Panicum hemitomon	*Panicum repens*	*Alternanthera philoxeroides*	*Bacopa caroliniana*	*Distichlis spicata*	*Others*
0	–	95	–	–	–	5
26	–	60	35	–	–	5
53	–	95	3	–	–	2
79	–	85	–	10	–	5
106	–	35	60	–	–	5
133	80	10	10	–	–	–
159	–	50	48	–	–	2
186	–	28	70	–	–	2
212	–	20	10	–	70	–
239	–	30	68	–	–	2
266	–	70	20	–	–	10
292	–	10	78	10	–	2
319	–	15	75	10	–	–
345	–	–	60	30	–	10
372	–	96	–	4	–	–

The exit point for the wetland was at 400 m

ranged from 39.2 (8.1) g m^2 to 184.2 (28.5) g m^2 on a wet (dry) weight basis (data not shown).

A stock solution containing 51.1 g of each herbicide was made using formulated products. Solicam® (78.6% a.i.; Syngenta, Greenboro, NC, USA) and Simazine 4L (42.1% a.i.; Drexel, Memphis, TN, USA) were used as the norflurazon and simazine sources, respectively. The stock solution was continuously stirred using a magnetic stirrer since these concentrations exceed the water solubilities. The herbicides were injected directly into the flowing water using an eighteen channel peristaltic pump (Watson-Marlow PumpPro®, Wilmington, MA, USA) over a 2-h period. Sixteen individual delivery lines (3.2 mm i.d.) were used to deliver the stock solution across the width of the wetland, with outlets discharging directly into the flowing water at 1.9-m intervals. Assuming uniform mixing with the constant system flow (740 L min^{-1}), this dosing rate amounted to a plug of each herbicide at a concentration of approximately 0.575 mg L^{-1}. This concentration was chosen to represent worst-case edge-of-field concentration in citrus production areas (Wilson et al. 2007).

Water samples were collected upstream of the dosing location at 3 h intervals from the beginning of dosing through 360 h after dosing (HAD) using a GLI/Manning automatic surface water sampler (Hach Company, Loveland, CO, USA). Samples were collected from the exit pipe using an ISCO automatic sampler (Teledyne Isco, Inc.; Lincoln, NE, USA) at 1 h intervals from 0 to 24 HAD, 2 h intervals from 25 to 48 HAD, and 3 h intervals from 49 to 360 HAD. All samples were cooled to 4°C upon collection using wet ice or refrigeration. The herbicides were extracted from 400 to 800 mL samples using EPA method 3535 with slight modification. Briefly, each unfiltered sample was extracted using a Hyper Sep C18 (Thermo Scientific; Waltham, MA, USA) solid phase extraction (SPE) cartridge (500 mg/3 mL). The SPE cartridges were first conditioned using ~10 mL acetone followed by 10 mL of deionized water. Following extraction, the SPE cartridges were dried under vacuum for 2 h. The herbicides were eluted from the columns using 2 mL acetone, followed by addition of 1.5 g sodium sulfate to remove residual water. All solvents were pesticide grade.

Norflurazon and simazine were identified and quantified using a Varian 3800 (Varian Inc., Walnut Creek, CA, USA) gas chromatograph equipped with dual thermionic selective detectors (TSD), a Restek silanized Y-splitter, and RTX-5/RTX-50 columns (Restek Corporation, Bellefonte, PA, USA). The gc conditions included: 225°C injector temperature, 300°C detector temperature, and a column oven temperature program beginning at 80°C (2 min. hold), increasing to 180°C at 9°C min^{-1} (2 min. hold), increasing to 200°C at 2°C min^{-1} (1 min. hold), increasing to final temperature of 285°C at 7°C min^{-1} (18 min. hold). The entire run required 56.25 min. The nitrogen mobile phase flow rate was maintained at 1 mL min^{-1}. Analytical grade standards (99% purity) were obtained from Chem-Service (West Chester, PA, USA). Quality control elements included: method blanks, matrix and reagent water spikes, and matrix spike duplicates. The MDL/PQL for each herbicide was 1.24 µg L^{-1}/4.95 µg L^{-1} (norflurazon) and 0.99 μg L^{-1}/3.95 μg L^{-1} (simazine). Typical recoveries were 85% (norflurazon) and 84% (simazine).

The mass of each herbicide discharged was calculated by multiplying the concentration (μg L^{-1}) by the volume of water discharged during each sampling interval. The masses from each sampling interval were summed to estimate the total mass discharged.

Results and Discussion

Norflurazon was first detected in exit water 19 HAD at a concentration of 1.85 μg L^{-1} (Fig. 1). The concentration gradually increased to a maximum of 8.1 μg L^{-1} 75 HAD, and then gradually decreased to undetectable levels 315 HAD. The minimum, mean, and median detectable concentrations were 1.7, 3.9 ± 1.7, and 3.4 μg L^{-1}, respectively. Simazine was first detected in discharge water 23 HAD at 3.6 μg L^{-1}, increasing to a maximum concentration of 23.6 μg L^{-1} 38 HAD (Fig. 1). The minimum, mean, and median detectable concentrations for simazine were 2.0, 11.9 ± 6.8, and 12.0 μg L^{-1}, respectively. In contrast to norflurazon, simazine concentrations decreased to below the detection limit before the 84 HAD sampling period. While norflurazon concentrations were originally lower than simazine concentrations, they were present for a much longer duration (Fig. 2).

As expected from the concentration data, significant differences were observed with regard to cumulative loadings of each herbicide. All of the detectable losses of simazine occurred within a 58 h period after dosing. The total mass discharged was 26.9 g, accounting for 52.6% of the original amount injected into the system. In contrast, norflurazon discharge occurred throughout a 293 h period, with no distinct peak concentration as seen with simazine.

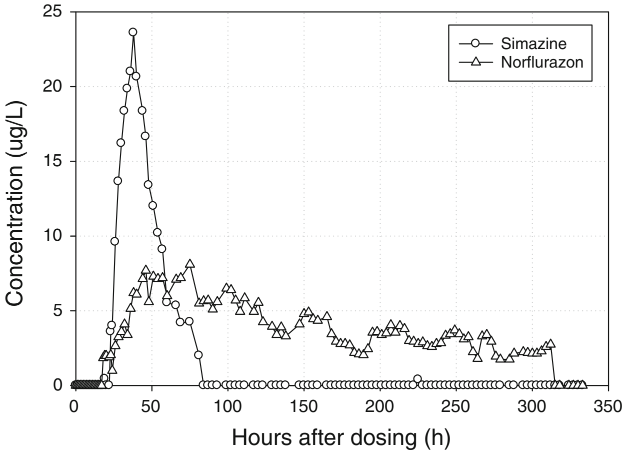

Fig. 1 Norflurazon and simazine concentrations present in water discharged from a 1.34 ha constructed wetland following injection of 51 g each over a 2 h period

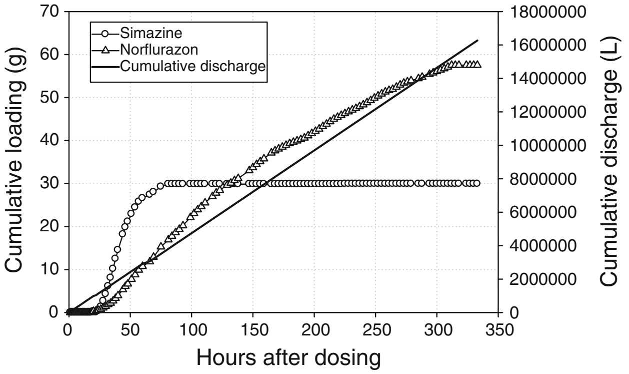

Fig. 2 Cumulative loadings of norflurazon and simazine, and cumulative volume of water discharged from a 1.34 ha constructed wetland following injection of 51 g each over a 2 h period

The total estimated discharge of norflurazon from the system was equivalent to 51.7 g, or 101% of the original amount injected into the system.

Interestingly, the constructed wetland did not retain any of the norflurazon added into the system, but did significantly delay its export as indicated by its' presence in the majority of samples collected during the monitored period. In fact, norflurazon was present in the water for a period equivalent to 4.9X the hydraulic residence time for the system. Given its' relatively high sorption coefficient (700 mL g^{-1}), it is likely that the norflurazon initially adsorbed to organic materials and plants within the system. However, once water with no detectable concentrations began flowing over these areas, the steady state equilibrium shifted resulting in slow desorption from the sediments and plant surfaces. Neither herbicide was detected in water being pumped into the system. In contrast, the sorption coefficient for simazine is lower (130 mL g^{-1}) than for norflurazon, which may have accounted for the more rapid discharge of simazine from the system, despite its' lower water solubility. During the course of the monitored period, all of the non-retained simazine was discharged within 1.3 turnover volumes of water within the system. The 47% of the original simazine retained within the system was likely removed by sorption to organic materials in the sediments, as well as to the plants within the system. The bottom of the system was fairly soft due to accretion over approximately a 5 year period. Similar simazine removal efficiencies (20–60%) were reported for a constructed wetland/urban stormwater harvesting system with a 7 days hydraulic retention time (Page et al. 2010).

Regarding the suitability for using such a system for pesticide removal from agricultural drainage water, these results indicate that it might be feasible for removal of simazine and other similar compounds. Given that 47% was removed within the 400 m length of the system, increasing the travel length could increase the removal efficiency at the same flow rate. Alternatively, reducing the flow rate through the system could also provide more opportunities for sorptive interactions between the sediments and plants. According to Kookana et al. (1992), simazine sorption is a relatively rapid process (only requiring minutes to hours). The fact that no detectable simazine concentrations were observed after 84 h indicates that the removal processes were not easily reversible, resulting in no desorption. In contrast, such a system is not suitable for removing norflurazon from surface water due to its' reversible desorption. Norflurazon is persistent in soil, but has been reported to rapidly photo-degrade (Thomas et al. 2008). Remediation systems focused on norflurazon should probably be designed to maximize exposure to sunlight. Maintenance of shallow non-vegetated areas and longer retention times could also possibly improve norflurazon removal. Additionally, removal efficiency for both herbicides (especially simazine) might be improved if a mechanism were in place to allow "drying out" of the system before use, allowing more intimate contact with the organic carbon-rich sediment pore volume.

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