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Norflurazon and Simazine Losses in Surface Runoff Water from Flatwoods Citrus Production Areas

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The Indian River Lagoon (IRL) is one of the most diverse estuaries along the east coast of the United States (Smithsonian Marine Station 2005 http://www.sms.si.edu/irlspec/index.htm.). In order to protect this biodiversity, many efforts have focused on protecting and improving water quality within this estuary. Herbicide export from flatwoods citrus production areas has been a concern in the watershed due to the high water table, large acreage planted, and the intensive drainage employed (Boman et al. 2000; Reitz and Long 1955; http://www.Indian-river.fl.us/citrus/district.html, accessed 9-14-2005). Trees are typically grown on beds separated by shallow furrows that drain into successively larger ditches and canals, which ultimately drain into the IRL. As a result of this drainage infrastructure, large volumes of surface runoff water and dissolved agrichemicals may leave grove sites in a relatively short period of time. This is especially true during the summer rainy season, typically from June through October, where large amounts of rainfall can occur within a very short period of time (Watts and Stankey 1980).

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Norflurazon[4-chloro-5-methylamino-2-(α,α,α-trifluoro-*m*-tolyl)-3(2*H*-pyridazinone)] and simazine (2-chloro-4,6-bis(ethylamino)-*s*-triazine) are two herbicides of concern within the IRL watershed. Both herbicides are used for pre- and post-emergent control of grassy and broadleaf weeds in citrus production. They are typically applied in bands underneath trees within a row. Norflurazon is a moderately water soluble (28 mg L^{-1}), non-volatile (2.66×10^{-9} kPa at 20°C) fluorinated pyridazinone (phenylpyridazinone) (Vencill 2002). Simazine belongs to the *s*-triazine family, and is moderately water soluble (6.2 mg L^{-1} at 22°C) and not volatile (vapor pressure 1.5×10^{-8} mm Hg at 25°C) (Anonymous 1995). These herbicides are of concern because of possible effects on health and reproduction of desirable submerged aquatic vegetation within freshwater and estuarine environments. Norflurazon blocks carotenoid biosynthesis by inhibiting phytoene desaturase (Vencill 2002). Wilson et al. (2006) reported that concentrations of norflurazon as low as 0.040 mg L^{-1} caused visible bleaching of *Vallisneria americana* following a 14 day exposure period. The no observable effects concentration (NOEC) and lowest observable effects concentration (LOEC) for fresh weight gains and asexual reproduction were 0.08 and 0.1 mg L^{-1}, respectively (Wilson et al. 2006). Hughes and Alexander (1991a, b) reported EC_{50}/NOEC values of 86/42.2 μg L^{-1} for *Lemna gibba*, and 13/6.23 μg L^{-1} for *Selenastrum capricornutum*. Simazine is a photosynthesis inhibitor (Vencill 2002) with reported toxicity thresholds for emergent and algal species ranging from 0.1 to 1 mg L^{-1} (Wilson et al. 1999, 2000, 2001; Oneal and Lembi 1983; Fowler 1977).

Both of these herbicides have been reported in surface water samples collected in South Florida canals. Miles and Pfeuffer (1997) reported that the spatial trends in pesticide detections followed use patterns, and that norflurazon and simazine were detected most frequently at monitoring sites near citrus groves. Through an on-going quarterly sampling program conducted by the South Florida Water Management District (SFWMD), from December 1998 through July 2004 norflurazon was detected in surface water samples in 95%, 100%, and 94% of samples collected from the Canal-44 (C-44), Canal-25 (C-25), and Ten Mile Creek, respectively, at concentrations ranging from 0.04 to 1.6 μg L^{-1} (http://www.sfwmd.gov/curre/pest/pestindex.htm). Through the same monitoring program, simazine was detected in 70%, 90%, and 94% of samples collected from the C-44, C-25, and Ten Mile Creek, respectively, at concentrations ranging from between 0.0095/0.381 (MDL/PQL) to 4.4 μg L^{-1}. While these concentrations are below the effects levels reported in the literature, much uncertainty exists regarding actual concentrations on the days between the quarterly sampling dates as illustrated by Wilson and Foos (2006) and Wilson et al. (2004). Given the frequent detections of these herbicides in the canals monitored by the SFWMD, the close association with land-use (Miles and Pfeuffer 1997), and the lack of information regarding losses of these herbicide from flatwoods citrus production areas, this study was initiated to characterize possible losses (concentrations and loads) from flatwoods citrus production areas.

Materials and Methods

This study was conducted on a flatwoods production area located in the research groves at the UF/IFAS Indian River Research and Education Center, Fort Pierce, FL, USA. This site had poorly-drained soil of the Winder series, with fine-textured materials throughout the soil profile. This area was planted on single-row beds with 'Valencia' orange on sour orange rootstock trees at a spacing of 3.7 m within-row by 9.1 m across-row. The treated area evaluated was 91.4 m in length.

Solicam® DF (a.i.: norflurazon) + Simazine 4L (a.i.: simazine) was applied as a tank-mix on 8/12/2003 using a spray boom equipped with Tee-Jet #9 nozzles and anti-drift curtains on the front and rear. The herbicides were applied at a rate of 4.4 kg ha^{-1} each, in a 1.2 m band; or at 7.7 (norflurazon) and 7.8 (simazine) kg ha^{-1} in a 2.1 m band on either side of respective water furrows. These bandwidths were chosen to maintain the weed-free zone within the tree canopy as recommended by Boman et al. (2000). The different rate/bandwidth combinations were included to provide information on possible variation associated with these common application scenarios. Three replicate water furrows were evaluated for each treatment. The treated areas were 0.0220 and 0.0384 ha for the 4.4 and 7.7 kg ha^{-1} treatments, respectively. The estimated a.i. applied to the study areas was: 96.6 and 296.1 g norflurazon for the 4.4 and 7.7 kg ha^{-1} application rates, respectively; and 98.3 and 301.2 g simazine for the 4.4 and 7.8 kg ha^{-1} rates, respectively.

Initially, these studies were designed to monitor natural surface runoff events. However, due to a lack of rainfall, an overhead irrigation system was constructed to stimulate runoff as described by Wilson et al. (2007). Briefly, impact sprinklers on 6.1 m risers were installed in portable, concrete base units and positioned throughout the study area. The sprinklers were positioned above the trees, and discharged water in a 360° pattern at a precipitation rate of approximately 0.46 cm h^{-1}. The water source for the overhead irrigation system was surface water from the Kings Highway canal.

Samples from the water supply canal were collected throughout each simulated rainfall/runoff event. Surface runoff samples were collected at the discharge end of each water furrow during each event. All samples were collected in glass jars, immediately cooled, and stored in the lab at 17°C until extraction and analysis. The water volume discharged through each water furrow was estimated by calculations based on water depth measurements taken at a 60° V-notch weir placed at the end of each furrow discharge pipe (Department of Interior 1975). Water depth measurements were taken at 10 min intervals from the time that water began flowing through the weir. The first sample in each furrow was also collected at this time. Subsequent samples were collected at 20 min intervals for the first hour, 30 min intervals for the second and third hours and at 1 h intervals thereafter. The mass of each herbicide discharged during the monitored portion of each event was estimated by multiplying the detected concentration by the volume of water that passed through the weir during each time interval.

The herbicides were extracted using a modification of EPA method 3535. Three hundred to 400 mL of sample was filtered through Whatman No. 5 qualitative filter paper and the pH was adjusted to 7.0. The sample was then passed through an activated AccuBOND II ODS-C_{18} cartridge. After air-drying the cartridges, the herbicides were eluted using 2 mL of pesticide-grade acetone. The herbicides were analyzed using either a HP 5890 Series II gas chromatograph equipped with a nitrogen-phosphorus detector, or with a Varian CP-3800 gas chromatograph equipped with thermionic selective detectors. Analytical standards (99% purity) were obtained from ChemService (West Chester, PA, USA). Both instruments were equipped with a DB-5 or DB-17 column. The column oven program included three steps; 80°C (hold 1.5 min), increase to 180°C at 9°C min^{-1} (hold 2.00 min), increase to 200°C at 2.0°C min^{-1} (hold 1.00 min), increase to 275°C at

7°C min^{-1} (hold 11.00 min). The minimum detectable levels were 3 μg L^{-1} for each herbicide, and recoveries from fortified samples were 88% and 92% for norflurazon and simazine, respectively.

Summary statistics (minimum, maximum, mean, standard deviation, and median) were calculated for herbicide concentrations on a treatment-event basis. Cumulative runoff volumes between treatments were compared for each runoff event using analysis of variance (ANOVA) with calculated least significant differences (LSD) ($P = 0.05$). Cumulative herbicide loadings between treatments were compared for each runoff event by ANOVA of the ranked data with means separation using LSD ($P = 0.05$).

Results and Discussion

Mean runoff volumes per water furrow ranged from 23,041 to 24,383 L for both events, with actual volumes ranging between 13,371–36,752 L during the first event and 15,001–31,834 L during the second event. Neither herbicide was detected in the source water used to produce each runoff event. A summary of the norflurazon and simazine concentrations from the events is shown in Table 1. Mean concentrations of both herbicides were lower in runoff water discharged from the 4.4 kg ha^{-1} treatment, relative to the 7.7/7.8 kg ha^{-1} treatment. Mean norflurazon concentrations in discharge water from the 4.4 kg ha^{-1} treatment ranged from 65.2 to 69.2 μg L^{-1} for both runoff events. Mean simazine concentrations for the same treatment ranged from 116.3 to 123.2 μg L^{-1} for both events. Mean norflurazon and simazine concentrations for the 7.7/7.8 kg ha^{-1} treatments ranged from 356.1 to 359.8 μg L^{-1} and 376.4 to 490.7 μg L^{-1}, respectively.

Mean norflurazon losses per furrow during the first event were 1,684 and 8,480 mg for the 4.4 and 7.7 kg ha^{-1} treatments, respectively (Fig. 1a). These losses represent 1.7% and 2.9% of the norflurazon applied. Mean simazine losses per water furrow during the first runoff event were 3,303 and 8,829 mg for the 4.4 and 7.8 kg ha^{-1} treatments, respectively, representing 3.4% and 2.9% of the totals applied (Fig. 1b). During the second event, norflurazon losses were 1,635 and 7,873 mg for each respective furrow, representing 1.7% and 2.7% of the total applied; while simazine losses were 2,890 and 11,487 mg for each respective treatment, representing 2.9% and 3.8% of the total applied.

These results indicate that norflurazon and simazine export from flatwoods citrus production areas can occur during runoff events following application. In both cases, concentrations and loadings in runoff water increased with increasing application rate-bandwidth. Similar results were reported for simazine losses from citrus production areas in California, where 6.1% to 6.5% of the total amount applied left the site in runoff water following two simulated runoff events (Troiano and Garretson 1998; Liu and O'Connell 2002).

Applied across the entire 80,937 ha IR region citrus producing watershed, it is evident that this land use activity can contribute these herbicides to surface water bodies through losses in runoff. It is also evident that export from production areas can be minimized (30% to 70%) by applications at the lower rate and smaller bandwidth. It should also be noted that the simulated rainfall rate used in these studies was gentle compared to rates of 5.1–

Table 1 Summary of norflurazon and simazine concentrations (μg L^{-1}) in runoff water from individual water furrows within a flatwoods citrus production site

Measure	Runoff event (kg ha^{-1})			
	8/13/2003		8/14/2003	
	4.4	7.7	4.4	7.8
No. of samples	24	24	18	18
Norflurazon				
Mean*	69.2^{A}	356.1^{B}	65.2^{A}	359.9^{B}
Standard deviation	62.1	117.4	27.0	94.7
Minimum	19.3	28.5	23.6	210.7
Maximum	324.0	532.0	120.7	548.0
Median	58.3	354.0	63.7	345.0
Simazine				
Mean*	123.2^{A}	376.4^{B}	116.3^{A}	490.7^{B}
Standard deviation	90.0	100.6	34.0	56.3
Minimum	18.0	28.0	66.0	373.3
Maximum	366.0	646.0	173.3	593.3
Median	122.7	375.7	113.3	486.7

*Different letters denote significant differences (ANOVA-LSD, $p = 0.05$) between treatments within each sampling date

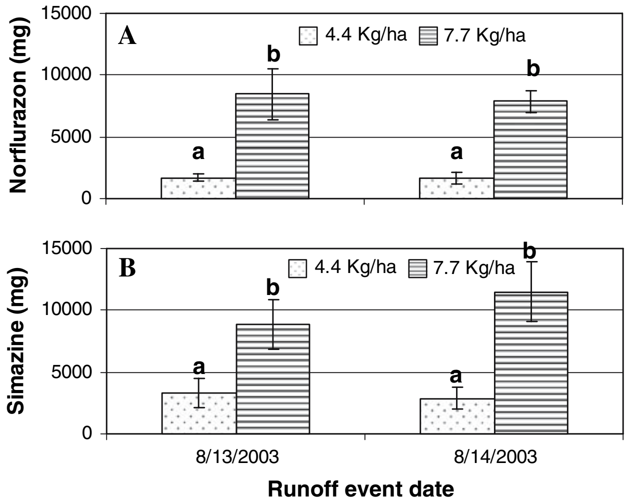

Fig. 1 Average loadings (mg) of norflurazon (**a**) and simazine (**b**) discharged in surface runoff water from individual water furrow following application at 4.4 kg ha^{-1} (1.2 m bandwidth) and 7.7 kg ha^{-1} (2.1 m bandwidth). *Bars* standard error. Different letters indicate significant differences between treatments (ANOVA of ranks, $p = 0.05$)

10.2 cm h^{-1} commonly seen during summer thunderstorms (Watts and Stankey 1980). Under those conditions, losses might be expected to be greater than those seen in these studies. Unfortunately, available grove infrastructure and equipment limited the maximum achievable rainfall simulation rates to those used in these evaluations. In addition, these studies only evaluated losses during the first several hours of the two runoff events following application. Significant amounts of each were still present during the second event, indicating that further losses were likely during subsequent events.

While combined losses for both runoff events in this study were less than or equal to 6.7% of the total active ingredient applied, concentrations within the runoff water were within the toxic range for many aquatic plant species (Wilson et al. 1999, 2000, 2001; O'Neal and Lembi 1983; Fowler 1977). These relatively high concentrations could have significant ramifications for aquatic plants and animals dependent on those plants, especially those located close to areas receiving drainage water without sufficient dilution volume to reduce concentrations. These results may also be representative of other similarly poorly drained areas and pesticides sharing common chemical and application properties. More research is needed to develop water/herbicide management practices that maintain the herbicides on-site.

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