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# Off-site transport of fungicides with runoff: A comparison of flutolanil and pentachloronitrobeneze applied to creeping bentgrass managed as a golf course fairway\*



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### ABSTRACT

Flutolanil and pentachloronitrobenzene (PCNB) are fungicides used to control or suppress foliar and soil borne diseases in turf and ornamental crops. On golf courses, sports fields, sod farms and commercial lawns these fungicides are used as preventive treatments to combat snow mold, brown patch and fairy ring. Depending on the aquatic organism, flultolanil and PCNB are considered to be moderately to highly toxic. Therefore runoff or drift from treated areas may be hazardous to organisms in adjacent aquatic sites. This research compared the transport of flutolanil and PCNB with runoff from turfgrass managed as a golf course fairway. The quantity of fungicide transported with runoff and observations reported with the chemographs followed trends in agreement with the chemical properties of the compounds. Overall, we observed the rate of transport for flutolanil was greater than PCNB, which contributed to the more than 12 times larger load ( $\mu g/m^2$ ) of flutolanil transported off-site at the conclusion of the simulated storm runoff. A better understanding of the off-site transport of pesticides with runoff is needed to make informed decisions on management practices to reduce potential adverse effects on non-target organisms, as well as maintain control of targeted pests in the area of application. In addition, data obtained with this research can be used in model simulations to predict nonpoint source pollution potentials beyond experimental conditions.

### 1. Introduction

Parks, road sides, cemeteries, athletic fields, golf courses, and residential and commercial lawns are examples of public and private spaces where managed turf is readily found. In the United States approximately 16 million hectares of land is covered by tended lawn, which includes an estimated 17,000 golf courses (Milesi et al., 2005; Saito, 2010). Worldwide there are more than 32,000 golf courses in regions including Canada, United States, Mexico, Central America and the Caribbean, South America, Europe, Africa, Asia, Australia, and Oceania/South Pacific (Saito, 2010; World Golf, 2017; World Golf Foundation, 2017). Although golf courses do not represent the largest area covered in turf, they do contain some of the most intensely managed turfgrass with putting greens (10% of an average golf course) and fairways (30% of an average golf course) receiving irrigation and application of plant protection products and fertilizer (Gross et al., 1990; Cole et al., 1997; King et al., 2006; GCSSA, 2007; Lyman et al., 2007;

Carey et al., 2012; Slavens and Petrovic, 2012; Wong and Haith, 2013; Wallace, 2016).

Terrestrial contaminants and applied plant protection products can be transported with runoff from landscapes to adjacent waters. In fact surveys throughout the world have reported contaminants in storm runoff, catchments and surface waters (Cohen et al., 1999; Hoffman et al., 2000; Soulsby et al., 2004; Gilliom et al., 2006; Nash et al., 2005; Xu et al., 2007; Bakri et al., 2008; Pärn et al., 2012; Fairbairn et al., 2016). Given that pesticides are biologically active compounds designed to interfere with processes necessary for life (e.g. metabolism, neurotransmission, respiration, hormone regulation) (Matsumura, 1985; Manahan, 1992), the detection of pesticides associated with the turf industry in surface waters of urban watersheds has led to increased concern and greater suspect of contaminant contributions from residential, urban, and recreational sources (Wotzka et al., 1994; Frick et al., 1998; Cohen et al., 1999; Hoffman et al., 2000; Gilliom et al., 2006).

Abbreviations: PCNB, Pentachloronitrobenzene; LC $_{50}$ , Lethal Concentration 50

<sup>\*</sup> Reference to specific products does not imply endorsement by U.S. Department of Agriculture or the University of Minnesota to the exclusion of other suitable products.

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Table 1
Physiochemical properties of flutolanil and pentachloronitrobenzene (PCNB).

Fungicide	CAS	Water solubility	K <sub>OC</sub> <sup>b</sup>	Log P	Half life
	Registry Number	(mg/L) at 20 °C	(ml/g)	Octanol-water	Soil - aerobic (d)
Flutolanil	66332- 96-5	8.01	(598–1570) <sup>c</sup>	(2.81–4.65) <sup>c</sup>	233
PCNB	82-68-8	0.44	(7160–10,300) <sup>d</sup>	(4.16-5.03) <sup>d</sup>	210

- a http://sitem.herts.ac.uk/aeru/iupac/index.htm.
- <sup>b</sup> Soil organic carbon partition coefficient.
- <sup>c</sup> U.S. Environmental Protection Agency (2017a).
- <sup>d</sup> U.S. Environmental Protection Agency (2017b).

We designed experiments to evaluate the off-site transport of two fungicides, differing in chemical properties, with runoff from managed fairway turf (Table 1). Pentachloronitrobenzene ((IUPAC name); quintozene (ISO name); 1,2,3,4,5-pentachloro-6-nitrobenzene (CAS name); PCNB (abbreviation used in this manuscript)), a synthetic chlorophenyl fungicide, is used on golf course turf, ornamental bulbs, cotton and potatoes (AMVAC, 2006). In turfgrass, formulated products containing PCNB are used as part of a preventive or curative program to control soil born diseases such as gray snow mold (Typhula spp.), pink snow mold (Microdochium nivale), brown patch (Rhizoctonia solani), dollar spot (Sclerotinia homeocarpa) and leaf spot (Helminthosporium spp.) on golf course fairways, greens and tees (AMVAC, 2017). Flutolanil ((ISO name); N-[3-(1-methylethoxy)phenyl]-2-(trifluoromethyl)benzamide (9CI name)) is a fungicide used to control disease on container and field grown ornamentals and on turf in golf courses, athletic fields, sod farms, and residential, commercial, institutional and municipal areas. Formulated products for turfgrass are used in preventive and curative treatments for brown patch (R. solani), fairy ring (Various Basidiomycetes), large patch (Rhizoctonia solani AG 2-2 (LP)) and gray snow mold (Typhula spp.) (Bayer Environmental Science, 2017). Repeated application of these fungicides may be required following heavy rains or repeated snow melts or during disease treatment.

### 2. Materials and methods

### 2.1. Site description

Research was conducted on plots (3 plots, plot size = 24.4 m length  $\times$  6.1 m width) consisting of Waukegan silt loam (29% sand, 55% silt, and 16% clay) with 3% organic carbon, graded to a 5  $\pm$  1% slope (running east to west) and covered with L-93 creeping bentgrass (Agrostis palustris Huds.). The turfgrass was maintained as a golf course fairway with periodic sprinkler irrigation to prevent drought stress, weekly top dressing with 1.6 mm depth of sand and mowing three times weekly at 1.25 cm height of cut. The plots were aerated with hollow tines (12  $\pm$  4 d prior to the runoff events) to control thatch and compaction. This was performed using a Ryan Greensaire II Aerator (Ryan, Barrington, IL, USA) equipped with 11.43 cm depth  $\times$  0.95 cm internal diameter tines spaced 5 cm  $\times$  5 cm apart.

### 2.2. Collection of runoff water

Runoff collection systems, based on the design of Cole et al. (1997), were constructed at the western edge of each plot. Overland flow from the turfgrass was directed by stainless steel flashing to collection gutters constructed of two 3.0-m long horizontally-split 15.2-cm schedule 40 polyvinyl chloride (PVC) pipes that were joined in the center with a PVC-T junction. From the collection gutter the water flowed into a stainless steel large 60 ° V trapezoidal flume (Plasti-Fab, Tualatin, OR, USA) equipped with sample collection and bubble tube ports (Fig. 1). A

flume shield and gutter cover prevented dilution of runoff with precipitation. Runoff water samples were collected from the flume sample collection ports using an automated runoff sampler (ISCO model 6700, Lincoln, NE, USA) equipped with a flow meter (ISCO model 4230) that delivered water samples into 24,350-ml glass bottles. Samples were collected at the initiation of runoff then every 5 min for up to 24 samples. Water samples were removed from the autosampler and stored frozen ( $-20\,^{\circ}$ C) until laboratory processing and analysis.

### 2.3. Rainfall simulator

Precipitation was delivered using a rainfall simulator modified from the design of Coody and Lawrence (1994). Details of the rainfall simulator were provided in Rice et al. (2010). Basically, the simulator base and risers were constructed of schedule 40 PVC pipe and each riser was finished with a pressure regulator (Lo-Flo, 15 psi) and nozzle (3TN Nozzle #25) containing a standard PC-S3000 spinner (Nelson Irrigation, Walla Walla, WA, USA) suspended 2.7 m above the turf (Fig. 1). Generated rainfall was targeted to represent storm intensities recorded in Minnesota, USA, with recurrence interval of 25 years (Hershfield, 1961) and to be delivered with a droplet size spectrum and impact velocity similar to natural rainfall. The rainfall simulator was designed to distribute precipitation to two plots simultaneously (plots 1 and 2, 3 and 4, or 5 and 6). For this research we are reporting data from three of the six plots (plots 2, 4 and 5) as the remaining three plots (1, 3 and 6) were part of a separate study and managed in a different way. Therefore, in this study, each rainfall simulation provided data from one plot.

### 2.4. Fungicide application

Commercially available fungicide products (flutolanil: Prostar 70 WG, Bayer Environmental Science; pentachloronitrobenzen: PCNB 75 W, AMVAC) were tank mixed and applied at label rates, perpendicular to runoff flow, using a 4.6 m spray boom fitted with TeeJet XR8004 nozzles (TeeJet Technologies) spaced 50.8 cm apart (sprayer pressure: 138 kPa, speed: 3.2 kmph). The measured active ingredients were flutolanil and pentachloronitrobenzene (PCNB). The physiochemical properties of flutolanil and PCNB are described in Table 1. Runoff collected prior to fungicide application was free of fungicide residues. No irrigation or natural precipitation occurred between completion of the fungicide application and initiation of simulated precipitation.

### 2.5. Precipitation event timeline

Rainfall simulations were performed in triplicate during two separate events, occurring over 8 weeks apart, for a total of 6 rainfall simulations (Event-1 Simulations 1-3, Event-2 Simulations 4-6) (Table 2). Two days prior to initiation of each simulation event, the plots were pre-wet beyond soil saturation to ensure uniform water distribution and allow for collection of background runoff samples. The following day, the turf was mowed to the standard height-of-cut (1.25 cm) and the runoff collection systems were cleaned. The mornings of the rainfall event automated samplers were programmed and runoff collection gutters were covered with plastic sheeting to prevent contamination during fungicide application. In addition, Petri dishes (glass, 14-cm) were distributed diagonally across each plot to capture spray residues and verify fungicide application rates. After fungicide application the plastic sheeting and Petri dishes were removed and 12-cm rain gauges (Taylor Precision Products, Las Cruces, NM) were distributed in a grid pattern across each plot to quantify precipitation. Rainfall simulations were initiated 13  $\pm$  3 h (Event-1 Simulations 1–3) and 21 ± 10 h (Event-2 Simulations 4-6) after fungicide application and terminated 90 min after the onset of runoff. This time interval was selected to represent a worst case scenario and to provide fungicide transport field data that did not include dissipation by degradation.

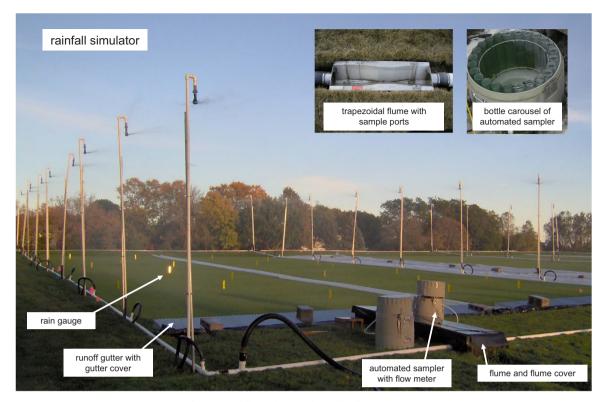


Fig. 1. Rainfall simulator and runoff collection system.

**Table 2** Initiation of fungicide application and start of similated precipitation.

Fungicide application <sup>a</sup> (Julian Day, Time (hh: mm))	Simulated precipitation <sup>b</sup> (Julian Day, Time (hh: mm))
223, 10:30	223, 20:55
223, 10:30	223, 23:40
223, 10:30	224, 02:56
281, 9:48	281, 20:12
281, 9:48	282, 10:51
281, 9:48	282, 14:01
	(Julian Day, Time (hh: mm))  223, 10:30 223, 10:30 223, 10:30 281, 9:48 281, 9:48

<sup>&</sup>lt;sup>a</sup> Fungicides were applied in a tank mix across all plots, perpendicular to runoff flow.

Within 3 h of each rainfall simulation soil moistures were measured (n=9 per plot) using a time domain reflectometry meter (Field Scout TDR 300, Spectrum Technologies, Plainfield, IL). Simulated rainfall was initiated once measured on-site wind speeds (Davis Instruments, Hayward, CA, USA) dropped below 2 m/s to prevent precipitation drift. For the present study, data was collected from one plot during each simulation.

### 2.6. Fungicide analysis

Runoff water and application rate samples were processed in groups of 10 with a positive control sample (laboratory-grade organic-free water sample fortified with the target analytes) and a blank sample (untreated laboratory-grade organic-free water) processed with each filtration batch. Irrigation source water and background runoff water (runoff collected from turf plots prior to the application of fungicides) served as matrix samples. Petri dishes, containing fungicide residues for confirmation of actual application rates, were rinsed with methanol and the rinsate was filtered through a  $0.45~\mu m$  nylon filter then diluted with

laboratory-grade organic-free water to 14% methanol. Collected runoff water samples (3 ml) were filtered through a 0.45 µm nylon syringe filter (Whatman) followed by methanol (0.5 ml) to rinse the filter, resulting in a 14% methanol solution equivalent to the processed application rate samples. Fungicide concentrations were measured by direct injection of 500 µl of each processed sample onto a high performance liquid chromatograph with a photodiode array detector set at 230 nm (Waters 1525 HPLC System composed of a Waters 717 Plus Autosampler, a Waters 1525 Binary Pump and a Waters 2996 photodiode array detector). Analytes were eluted from a 150 mm long, 4.6 mm diameter C-18 column with 5 µm packing (Agilent) at a rate of 1 ml/min using two solvents [solvent A: laboratory-grade organic-free water (0.17% trifluoroacetic acid); solvent B: 82:18 methanol:acetonitrile]. Initial conditions, 60% B, were held for 2 min followed by a gradient ramped from 60% to 95% B in 23 min, a 3 min hold, then back to 60% B in 10 min with a 5 min hold. Analytes were quantified by direct comparison with seven-point external standard calibration curves of the analytical standards (flutolanil CAS# 66332-96-5, PCNB CAS# 82-68-8; correlation of the external standard curves: flutolanil r<sup>2</sup>  $= 0.9999 \pm 0.0002$ , PCNB  $r^2 = 0.9987 \pm 0.0024$ ). Method detection limits and limits of quantification were 41  $\mu$ g/L and 94  $\mu$ g/L for flutolanil and 5 µg/L and 10 µg/L for PCNB. Method recoveries were 94.8  $\pm$  9.3% for flutolanil and 101.3  $\pm$  7.5% for PCNB.

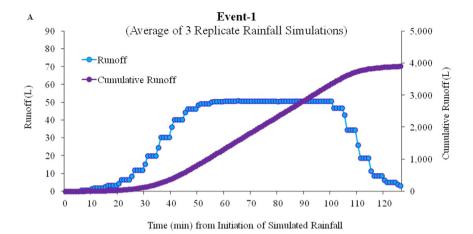
### 2.7. Calculation of fungicide loads

Fungicide loads ( $F_L,\ \mu g/m^2)$  from edge-of-plot runoff were calculated by

$$F_{L} = \frac{\sum (F_{C} \cdot R \cdot T)}{A}$$

where  $F_C$  is the measured fungicide concentration (µg/L) in the runoff sample (n=24 bottles per plot per runoff event), R is the runoff flow rate (L/min) at the time of sampling, T denotes the time (min) between sample collection (automated sampling every 5 min), and A is the area ( $m^2$ ) of the fairway turf plots.

<sup>&</sup>lt;sup>b</sup> Simulated precipitation was delivered to one of three plots during each simulation.



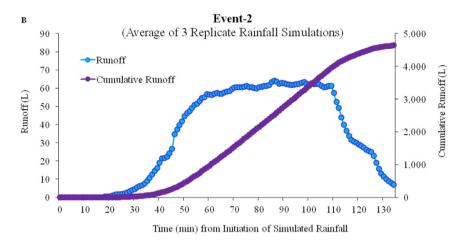


Fig. 2. Runoff hydrographs and cumulative runoff volumes for Event-1 (A) and Event-2 (B). Each graph represents the average of three replicated rainfall simulations (Event-1, Simulations 1–3; Event-2, Simulations 4–6).

### 2.8. Statistical analysis

Completely randomized analysis of variance was completed comparing the percentage of rainfall measured as runoff and the percent of applied fungicides measured in runoff. Least significant difference (LSD, 0.05 = error degrees of freedom and 0.05 probability to determine two-tailed t values) identified statistical significance between means. Coefficients of determination ( $r^2$ ) were calculated to evaluate the relationship of runoff volume (L) and fungicide concentration ( $\mu g/L$ ) to fungicide load ( $\mu g/m^2$ ) (Steel et al., 1997).

### 3. Results and discussion

## $3.1. \ Simulated \ rainfall \ and \ runoff$

The runoff hydrographs (Fig. 2) revealed the interception of precipitation by the turfgrass and its infiltration into the soil continued for  $8\pm 6$  min (Event-1) and  $15\pm 3$  min (Event-2), after which time the rate and quantity of rainfall (Event-1:  $7\pm 4$  mm, Event-2:  $9\pm 1$  mm) exceeded the infiltration capacity and overland flow began. Runoff flow was greater than 37.91/min from  $42\pm 8$  min to  $105\pm 5$  min (Event-1) and  $40\pm 1$  min to  $109\pm 6$  min (Event-2), which readily diminished following termination of the simulated precipitation (Event-1:  $111\pm 5$  min; Event-2:  $107\pm 5$  min).

The type of vegetation and its growth stage will influence the amount of precipitation lost to interception storage, which typically varies between 1 mm and 4 mm of rainfall. Dense grass cover has a greater storage capacity than cereal crops. In addition, dense vegetative

cover also protects the soil from raindrop impact, which minimizes soil crusting and reduces runoff volume compared to bare soil (Critchley et al., 1991).

The infiltration capacity of fairway turf can be influenced by the soil texture, management practices (e.g. hollow tine core cultivation, sand top dressing) and antecedent soil moisture content prior to the rain event. The reduced antecedent soil moisture prior to Event-2 explained the delay to first runoff compared to Event-1, as the soil texture and management practices were similar and precipitation depth and rate were slightly greater for Event-2 (Table 3). Overall the storm events resulted in statistically comparable results with 3894  $\pm$  976 L of runoff (Fig. 2A, Event-1) and 4637  $\pm$  277 L of runoff (Fig. 2B, Event-2) representing 40  $\pm$  13% and 45  $\pm$  1% of the applied rainfall, respectively. This is similar to results reported by Shuman (2002) who likewise simulated precipitation 2d following irrigation to field capacity

**Table 3**Average soil moisture and simulated rainfall duration, depth and rate.

Study	Soil moisture (%) <sup>a,b</sup>	Precipitation		
rachineation		Duration (min) <sup>a</sup>	Depth (mm) <sup>a</sup>	Rate (mm/ h) <sup>a</sup>
Event-1 Event-2	39 ± 3 35 ± 2	111 ± 5 107 ± 5	68 ± 9 70 ± 3	36 ± 4 39 ± 1

<sup>&</sup>lt;sup>a</sup> Data presented as the mean  $\pm$  standard deviation (soil moisture n=27, precipitation n=24).

b Percentage water holding capacity 3 h prior to simulated precipitation.

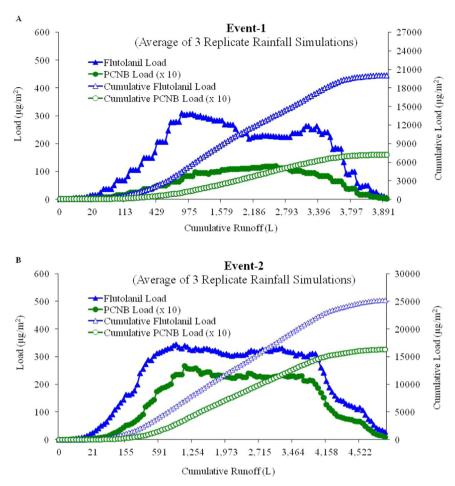


Fig. 3. Flutolanil and pentachloronitrobenzene (PCNB) chemographs and cumulative loads with runoff. Each graph represents the average of three replicated rainfall simulations performed during each experimental event (A: Event-1, B: Event-2).

and measured 37–44% of applied rainfall as runoff from Tifway bermudagrass (Cynodon dactylon (L.) Pers.).

### 3.2. Fungicide transport with runoff

Flutolanil and PCNB were not detected in the source water used for maintenance irrigation or simulated precipitation. Runoff subsamples collected at the start of runoff and throughout the runoff events confirmed detection of both fungicides in all runoff samples. Similar quantities of PCNB (528  $\pm$  200 mg/m<sup>2</sup>, n = 24) and flutolanil  $(519 \pm 60 \,\mathrm{mg/m^2}, \, n = 24)$  were applied to the turf plots. However, evaluation of the cumulative chemical loads showed greater quantities of flutolanil were transported in runoff than PCNB (Fig. 3A and B - note PCNB is graphed at ten times the measured rate for visual clarity. Event-1: flutolanil 20,017  $\pm$  4589 µg/m<sup>2</sup>, PCNB 717  $\pm$  122 µg/m<sup>2</sup>; Event-2: flutolanil 25,279  $\pm$  3377 µg/m<sup>2</sup>, PCNB 1631  $\pm$  100 µg/m<sup>2</sup>). Looking at the chemographs, the maximum loads of flutolanil (Event-1: 308 µg/ m<sup>2</sup>, Event-2: 345 µg/m<sup>2</sup>) occurred at 827 L and 912 L of runoff, which is before the maximum loads of PCNB (Event-1: 11.8 μg/m<sup>2</sup>, Event-2: 26.7 μg/m<sup>2</sup>) measured at 2590 L and 1082 L of runoff for Event-1 and Event-2, respectively. A comparison of chemograph slopes from 20 L of runoff to the point of maximum loading showed mass transport rates of flutolanil were 4.5 times (Fig. 3A, Event-1) and 1.4 times (Fig. 3B, Event-2) greater than the mass transport of PCNB under the same environmental conditions. Therefore a rainstorm of similar intensity but of a shorter duration would still result in a greater cumulative total for the off-site transport of flutolanil than PCNB. For example in a 30 min storm with a 1 year return period (40.6-40.8 mm/h, 3020-3776 L rainfall) (Hershfield, 1961) we would anticipate 15,689–19,451 μg/m<sup>2</sup>

and 17,353–21,141  $\mu$ g/m² flutolanil and 561–697  $\mu$ g/m² and 1108 to 1380  $\mu$ g/m² PCNB according to the chemographs of Event-1 and Event-2, respectively. Correlation analysis of chemical loads with runoff volumes and fungicide concentrations revealed the mass of fungicides transported off-site with runoff were more associated with runoff volumes than the concentration of fungicides in the runoff (flutolanil: volume  $r^2=0.94$ , concentration  $r^2=0.23$  (Event-1)) and volume  $r^2=0.97$ , concentration  $r^2=0.13$  (Event-2); PCNB: volume  $r^2=0.91$ , concentration  $r^2=0.44$  (Event-1) and volume  $r^2=0.91$ , concentration  $r^2=0.44$  (Event-2). Similar findings have been observed for other plant protection products in runoff from turf (Rice et al., 2010) and for plant protection products loads in runoff from agricultural crops (Rice et al., 2007).

The percentage of applied fungicide transported off-site with runoff was 3.89  $\pm$  0.88% (Event-1) and 4.87  $\pm$  0.65% (Event-2) for flutolanil and 0.14  $\pm$  0.02% (Event-1) and 0.31  $\pm$  0.02% (Event-2) for PCNB, with no statistical difference observed between Event-1 and Event-2 for comparisons within the same active ingredient. In contrast, comparison across active ingredients such as percentage of applied flutolanil with PCNB within Event-1, within Event-2, or between Events 1 and 2 were statistically significant (p = 0.01). Our findings of < 5%of applied active ingredient transported with runoff from managed turfgrass is analogous to the research of others evaluating pesticides with a water solubility less than 600 mg/L. For example, Armbrust and Peeler (2002) measured less than 2% of applied imidacloprid in runoff from Tifway Bermuda grass that received simulated rainfall 24 h after application. Likewise Wauchope et al. (1990) found less than 3% cyanazine and sulfometruon-methyl in runoff. In contrast, active ingredients with water solubility's above 800 mg/L have been reported

with 9–37% of the applied chemistry transported with runoff. Examples include runoff of mecoprop, dicamba and 2,4-D from fairway plots planted in bermudagrass (Ma et al., 1999) and creeping bentgrass (Rice et al., 2010). Considering the soil organic carbon partition coefficient ( $K_{\rm OC}$ ) of flutolanil and PCNB (Table 1) and soil mobility classes reported by Swann et al. (1983), flutolanil ( $K_{\rm OC}$  = 1090) is expected to have low mobility ( $K_{\rm OC}$  = 500–2000) and PCNB ( $K_{\rm OC}$  = 4498) is close to immobile ( $K_{\rm OC}$  > 5000), which parallels observations we observed in a previous study with chlorpyrifos (water solubility 1.05 mg/L,  $K_{\rm OC}$  = 8151) showing less than 1–2% of applied transported with runoff from creeping bentgrass turf (Rice et al., 2010). Classification of leaching potential using  $K_{\rm OC}$  and soil degradation rates (DT<sub>50</sub>) to calculate a Groundwater Ubiquity Score (GUS) categorizes PCNB (GUS = 0.81) as unlikely to leach (GUS < 1.8) and flutolanil (GUS = 2.68) with a marginal leaching potential (GUS 1.8 – 2.8).

Although mobility and leaching indices suggest minimal transport of these fungicides with water and we measured less than 5% of the active ingredient in runoff in the present study, the reported toxicity of PCNB to sensitive aquatic organisms still necessitates precaution with its use. For example on the basis of an acute exposure PCNB is classified as highly toxic to freshwater fish, with formulated end-use products containing PCNB classified as moderately to highly toxic (U.S. EPA, 2012). We measured 3–310 µg/L PCNB in runoff from our turf plots with an average runoff concentration of 64  $\pm$  48 µg/L. This average concentration is below 96-h LC50 for freshwater fish (Rainbow Trout (*Oncorhynchus mykiss*) 310 µg/L, Bluegill (*Lepomis macrochirus*) 240 µg/L) but above concentrations shown to reduce hatching of Japanese medaka fish (*Oryzias latipes*) ( $\geq$  9 µg a.i./L) (U.S. EPA, 2012).

Acute toxicity classifications for aquatic organisms rank flutolanil as moderately toxic to freshwater fish and freshwater invertebrates (U.S. EPA, 2014). We measured 37–1413 µg/L flultolanil in runoff from our turf plots with an average runoff concentration of 798  $\pm$  84 µg/L. This average runoff concentration was seven times less than the 96-h LC50 of Rainbow Trout (O. mykiss) 5400 µg/L and Bluegill (L. macrochirus) > 5400 µg/L, prior to dilution in surface water (U.S. EPA, 1992). In Minnesota, USA, flutolanil is considered to be a chemical of high concern with development cited as the health endpoint of interest (Minnesota Department of Health, 2016).

Direct exposure of aquatic organisms to runoff concentrations is highly unlikely as dilution would occur in the surface waters receiving the runoff. However, pesticide persistence, bioavailability, and length of an organism's exposure to the surface water concentrations would have to be considered in order to accurately estimate risk. Exposure during sensitive life stages, potential for endocrine disruption and potential synergistic effects with contaminant mixtures should also be considered as this could lower concentrations of concern.

### 4. Conclusions

We evaluated the off-site transport of fungicides (flutolanil, PCNB) with runoff from turfgrass (creeping bentgrass on Waukegan silt loam, managed as a golf course fairway) using simulated rainfall in a worst case scenario. Flutolanil and PCNB were measured in all runoff samples from first runoff through completion of the evaluated runoff events. Greater quantities of flutolanil were transported in runoff than PCNB, which was in agreement with the differences in their water solubility and soil sorption coefficients. In addition to the total percentage of applied fungicide transported with the evaluated storm event, the rate of transport for flutolanil was greater than PCNB therefore rain events of shorter duration are still anticipated to result in greater cumulative off-site transport of flutolanil with runoff. The mass of fungicides transported off-site with runoff were more associated with runoff volumes than the concentration of fungicides in the runoff thus mitigation strategies that reduce runoff should be targeted. Greater understanding of the transport of these fungicides with runoff will support informed decisions for environmental stewardship with their use, optimizing

retention of fungicides at their site of application to maintain efficacy and reduce potential environmental impacts.

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