

# Urban Pesticides Risk Assessment and Management

# PESTICIDE TRANSPORT WITH RUNOFF FROM CREEPING BENTGRASS TURF: RELATIONSHIP OF PESTICIDE PROPERTIES TO MASS TRANSPORT

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Abstract—The off-site transport of pesticides with runoff is both an agronomic and environmental concern, resulting from reduced control of target pests in the area of application and contamination of surrounding ecosystems. Experiments were designed to measure the quantity of pesticides in runoff from creeping bentgrass (*Agrostis palustris*) turf managed as golf course fairway to gain a better understanding of factors that influence chemical availability and mass transport. Less than 1 to 23% of applied chloropyrifos, flutolanil, mecoprop-p (MCPP), dimethylamine salt of 2,4-dichlorophenoxyacetic acid (2,4-D), or dicamba was measured in edge-of-plot runoff when commercially available pesticide formulations were applied at label rates  $23 \pm 9$  h prior to simulated precipitation ( $62 \pm 13$  mm). Time differential between hollow tine core cultivation and runoff did not significantly influence runoff volumes or the percentage of applied chemicals transported in the runoff. With the exception of chloropyrifos, all chemicals of interest were detected in the initial runoff samples and throughout the runoff events. Chemographs of the five pesticides followed trends in agreement with mobility classifications associated with their soil organic carbon partition coefficient ( $K_{\rm OC}$ ). Data collected from the present study provides information on the transport of chemicals with runoff from turf, which can be used in model simulations to predict nonpoint source pollution potentials and estimate ecological risks. Environ. Toxicol. Chem. 2010;29:1209–1214. © 2010 SETAC

Keywords—Bentgrass Partition coefficient Pesticide Runoff Golf course fairway turf

#### INTRODUCTION

An estimated 25% of pesticide use in the United States results from nonagricultural pest control, including applications on golf courses, in lawns and gardens, for protection of structures, control of roadsides and right of ways, and to repel and control nuisance and disease-carrying pests for humans and animals [1]. Highly managed systems, such as golf course turf, often require multiple applications of pesticides at rates that exceed those typically found in agricultural or home environments [2.3]. Surface waters of urban watersheds have been found to contain pesticides associated with the turfgrass industry ([4,5]; http://pubs.usgs.gov/circ/2005/1291), which have been measured in 85% of storm runoff events (dicamba, mecoprop, and dimethylamine salt of 2,4-dichlorophenoxyacetic acid [2,4-D]) [6] detected in surface waters throughout the year (chlorpyrifos, diazinon, and 2,4-D) [7], and have been reported at levels that exceeded criteria for the protection of aquatic life during spring and summer months (carbaryl and diazinon) [8].

The mobility and persistence of pesticides in the environment are governed by abiotic and biotic processes, which are influenced by the physical and chemical properties of the compound and its interaction with surrounding matrices [9]. The extent to which organic chemicals distribute between environmental compartments (e.g., soil, water, air, biota) is described by physical partitioning processes, which are used to predict the fate and transport of potentially hazardous chemicals [10]. One example includes the soil–organic–carbon partition coefficient ( $K_{\rm OC}$ ) that has been used to estimate the affinity of pesticides for the solid phase or solution phase of soil, to predict

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if a pesticide is immobile in soil or transported in leachate or runoff, and the tendency of pesticides to favor water or sediment in aquatic systems [11]. The distribution of chemicals between the water and air can be described by the water-air ratio [12] or the Henry's Law constant [9,13]. The partitioning of organic chemicals between n-octanol, a lipophilic liquid, and water  $(K_{\rm OW})$  has been used to measure a chemical's hydrophobicity [14] and tendency to transfer from water to lipids, representing their ability to cross cell membranes [15]. This partition coefficient has been associated with the bioconcentration factor: the ratio of chemical concentration in an organism to the concentration in the surrounding water [16]. A number of researchers have reported a relationship between the water solubility of chemicals and their  $K_{OC}$ ,  $K_{OW}$ , and bioconcentration factor, as well as a relationship between partition coefficients (e.g.,  $K_{\rm OC}$ and  $K_{OW}$ ) [14,17–19].

The goal of this investigation was to improve the current understanding of pesticide transport with runoff from creeping bentgrass turf managed as golf course fairway. Specific objectives were to measure runoff volume and quantify pesticide concentrations in runoff from turf, calculate pesticide mass transport with overland flow, and compare the percent of applied pesticides measured in runoff with published partition coefficients ( $K_{\rm OC}$ ,  $K_{\rm OW}$ ) and water solubility to determine how well these parameters describe the measured chemical transport.

## MATERIALS AND METHODS

Site description

The 976-m<sup>2</sup> study site is located in Saint Paul, Minnesota, USA, at the University of Minnesota Turfgrass Research, Outreach, and Education Center. The soil was characterized as Waukegan silt loam (fine-silty over sandy or sandy-skeletal,

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mixed superactive, mesic Typic Hapludolls) with 3% organic carbon, 29% sand, 55% silt, and 16% clay. A natural slope running east to west was graded to 4% with less than 1% slope from north to south and planted with L-93 creeping bentgrass sod a minimum of 14 months prior to initiation of the reported runoff studies. The study site was divided into six plots  $(24.4\,\mathrm{m}\times6.1\,\mathrm{m},\ \mathrm{length}\times\mathrm{width})$  prepared in an east-to-west direction, with runoff collection systems at the western edge of each plot [20].

## Runoff collection system

Stainless steel flashing guided the runoff from the turf into 6.1-m gutters, constructed of 15.2-cm schedule 40 polyvinyl chloride (PVC) pipe that was cut in half lengthwise. Polyester landscape cloth covered the soil under the metal flashing to maintain soil structure. Large nails held the flashings in place, and paraffin wax provided a watertight seal between the turf edge and flashing. At the central point of the gutter, a PVC-T  $(15.2 \, \text{cm} \times 15.2 \, \text{cm} \times 15.2 \, \text{cm})$  lead runoff to a stainless steel large 60° V trapezoidal flume (Plasti-Fab, Tualatin) equipped with a bubble-tube port and two sample-collection ports. The gutter system and trapezoidal flume were embedded in sandfilled trenches to provide support and maintain appropriate conditions for accurate measurement of runoff volume and flow rates. The alignment and integrity of the runoff collection systems were assessed each spring and prior to simulated precipitation events. Gutter covers and flume shields prevented precipitation from entering the runoff collection apparatus.

## Management practices

Creeping bentgrass turf was managed as a fairway with 1.25-cm height of cut (three times weekly, clippings removed), top-dressed with sand (weekly, 1.6-mm depth) and irrigated to prevent drought stress. The quantity of water applied with the maintenance irrigation was not enough to produce surface runoff. Plots were aerated twice during each season (June 21, 2005 and September 27, 2005; August 4, 2006 and September 19, 2006). Three of the six plots were aerated with hollow tines ([HT]: 0.95-cm internal diameter × 11.43-cm depth with 5-cm × 5-cm spacing) (Ryan Greensaire II Aerator, Ryan), whereas the remaining plots were aerated using solid tines (2005) or vertical mowing (2006). Cores removed with the HT were allowed to dry, broken into smaller pieces, and worked back into the turf. A backpack blower and leaf rake removed the turf and thatch from the plot surface. Sand topdressing was not performed immediately after core cultivation or within a week of simulated precipitation and generation of runoff. Data used in this manuscript are limited to plots managed with hollow tine core cultivation. A comparison of pesticide transport with runoff as influenced by management practices is reported elsewhere [21].

## Pesticide application

Commercially available pesticide formulations including ProStar® 70WP fungicide (Chipco® Professional Products, Aventis CropScience) containing 70% flutolanil (*N*-[3-(1-methylethoxy) phenyl]-2-(trifluoromethyl) benzamide), Dursban® 50W insecticide (Dow AgroSciences LLC) containing 50% chlorpyrifos (*O*, *O*-diethyl *O*-[3,5,6-trichloro-2-pyridinyl] phosphorothioate), and Trimec® Bentgrass Formula herbicide (PBI Gordon) containing 9.92% Mecoprop-p (dimethylamine salt of [+]-[R]-2-[2-methyl-4-chlorophenoxy] propionic acid) (MCPP), 6.12% 2,4-D (dimethylamine salt of 2,4-dichlorophenoxyacetic acid), and 2.53% dicamba (dimethylamine salt of

3,6-dichloro-o-anisic acid) were applied to all plots perpendicular to runoff flow, at a speed of 3.2 kmph. Pesticide formulations were applied at label rates using a 4.6-m spray boom fitted with TeeJet XR8004 nozzles (TeeJet Technologies) spaced 50.8 cm apart with a sprayer pressure of 138 kPa. The average measured application rates for the active ingredients, considering all plots for the four events, were  $24.8 \pm 3.9 \, \text{mg/m}^2$  dicamba,  $9.8 \pm 1.8 \, \text{mg/m}^2$  2,4-D,  $17.5 \pm 3.5 \, \text{mg/m}^2$  MCPP,  $393.7 \pm 33.5 \, \text{mg/m}^2$  flutolanil, and  $48.1 \pm 10.9 \, \text{mg/m}^2$  chlorpyrifos. Application was completed  $23 \pm 9 \, \text{h}$  prior to initiation of each rainfall simulation. No irrigation or natural precipitation occurred between completion of the pesticide application and initiation of simulated precipitation. Runoff collected prior to pesticide application did not contain the compounds of interest.

## Simulated precipitation

A rainfall simulator was built following the design of Coody and Lawrence (U.S. patent 5,279,151) [22], which delivered precipitation at a rate of  $33\pm 6$  mm/h to two 24.4-m  $\times$  6.1-m plots simultaneously. The base of the simulator was constructed of 5-cm schedule 40 PVC pipe that guided water to 18 2.54-cm schedule 40 PVC risers, each fitted with a pressure regulator (Lo-Flo, 15 psi) and a nozzle (no. 25) containing a standard PC-S3000 spinner (Nelson Irrigation). Risers were spaced 3.7 m apart with nozzles and spinners suspended 2.7 m above the turf to produce precipitation with droplet size spectrum, impact velocity, and spatial uniformity characteristic of natural rainfall.

All plots were prewet beyond the soil saturation (volumetric water content:  $68 \pm 3\%$ ) approximately 48 h prior to initiation of simulated precipitation, which ensured uniform water distribution throughout the plots and allow for collection of background samples. The following day the turf was mowed (1.25-cm height, clippings removed), flumes and runoff collection gutters were cleaned, and gutters were covered with plastic sheeting to prevent contamination during chemical application. Petri dishes (glass, 14 cm) were distributed across the plots prior to pesticide application to verify chemical delivery and quantify actual application rates. Plastic sheeting and Petri dishes were removed following chemical application and plots were hydrologically isolated from each other with removable berms consisting of inverted horizontally split 10.2-cm schedule 40 PVC pipe. Twelve-centimeter rain gauges (Taylor Precision Products) were distributed throughout each plot to quantify simulated precipitation. Soil moisture was measured to a depth of 12 cm using a soil moisture meter (Field Scout TDR 300; Spectrum Technologies) recording measurements along a grid pattern (1.5, 3.1, and 4.6 m north to south by 3.1, 12.2, and 21.3 m west to east, n = 9) prior to and following simulated precipitation. Simulated precipitation was initiated once wind speeds dropped below 2 m/s (average wind speed during simulation =  $0.8 \pm 0.7$  m/s) (Davis Instruments) and continued until 90 min of runoff had been generated from each plot. Observations during runoff events showed no water movement under the PVC berms.

#### Runoff collection and analysis

Automated runoff samplers (ISCO model 6700) equipped with flow meters (Isco model 730; Lincoln) recorded runoff flow rates every minute, calculated total runoff volumes, and collected time-paced (5 min) runoff samples into glass bottles. Water samples were removed from the samplers and stored at  $-20^{\circ}$ C until laboratory analysis. Irrigation source water, background runoff water, and background runoff spiked with known quantities of pesticides served as blank and positive control

samples. Water samples were processed by filtering 3 ml through a 0.45-µm nylon syringe filter (Whatman) followed by methanol (0.5 ml) to rinse the filter. Each runoff sample was analyzed for pesticides. No samples were combined. Methanol rinsates of Petri dishes, containing pesticide residues for determination of actual application rates, were diluted with laboratory-grade organic-free water to 14% methanol to mimic the methanol and water content of the filtered runoff samples. Concentrations of each pesticide were measured by direct injection (500 µl) onto a high-performance liquid chromatograph (Waters model 717 plus autosampler and model 1525 binary pump) with a photodiode array detector (Waters model 2996) set at 230 nm. Analytes were eluted from an Agilent C-18 column (150 mm long, 4.6 mm diameter, 5-µm packing) using two solvents (solvent A: laboratory-grade organic-free water [0.17% trifluoroacetic acid]; solvent B: 82:18 methanol:acetonitrile) at a rate of 1 ml/min. 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. Recoveries were: chlorpyrifos  $74 \pm 23\%$ , dicamba  $102 \pm 6\%$ , flutolanil  $91 \pm 8\%$ , MCPP  $104 \pm 7\%$ , and 2,4-D  $105 \pm 11\%$ . Method detection limits ranged from 2.5 to  $3.7 \,\mu g \, L^{-1}$ . Limits of quantification for the target analytes were chlorpyrifos  $5.3 \pm 0.9 \,\mu\text{g/L}$ , dicamba  $5.1 \pm 0.6 \,\mu\text{g/L}$ , flutolanil  $4.5 \pm 0.8 \,\mu\text{g/L}$ , MCPP  $5.3 \pm 0.9 \,\mu\text{g/L}$ , and 2,4-D  $4.5 \pm 0.8 \,\mu g/L$ .

#### Statistical analysis

Completely randomized analysis of variance was performed comparing the percent of applied precipitation resulting as runoff and the percent of applied chemicals transported in runoff for all runoff events. A significant F (at 0.01 or 0.05) implied a significant difference among means. Coefficients of determination were calculated to evaluate the association of runoff volume and chemical concentration with chemical load, and  $K_{\rm OW}$ ,  $K_{\rm OC}$ , and water solubility with percentage of applied pesticides transported with runoff [23].

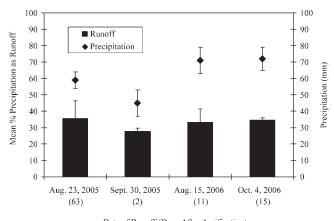
## RESULTS AND DISCUSSION

## Simulated precipitation

Simulated precipitation was initiated  $22\pm10\,h$  (mean  $\pm$  standard deviation) following pesticide application and 63, 2, 11, and 15 d following HT core cultivation. Precipitation was terminated 90 min after the onset of runoff totaling  $59\pm5$  mm,  $45\pm8$  mm,  $71\pm8$  mm, and  $75\pm7$  mm of precipitation, respectively (Fig. 1). Rain gauges distributed throughout the plots measured rainfall rates of  $24\pm4$  mm/h to  $37\pm2$  mm/h. Variations in generated rainfall rates were most likely the result of changes in pressure at the water source during the time of simulated precipitation. Measured coefficient of uniformity for the rainfall simulator was 82 to 84%.

## Runoff

Volumetric soil moistures measured less than 2 h prior to initiation of precipitation (48 h postsaturation) were  $44 \pm 4\%$  with postsimulation (<3 h) moisture measurements of  $67 \pm 6\%$ . Runoff was first observed  $22 \pm 3$  min following the initiation of precipitation. Steady-state runoff rates were measured for  $54 \pm 9$  min beginning approximately 64 min after the initiation of precipitation with average flow rates of  $27 \pm 8$  L/min and maximum flow rates of  $43 \pm 10$  L/min. Cumulative runoff volumes reported for each event are as follows: August 23,  $2005 = 3,149 \pm 932$  L, September 30,  $2005 = 1,856 \pm 139$  L,



Date of Runoff (Days After Aerification)

Fig. 1. Precipitation (mm) and percentage of precipitation resulting as runoff from creeping bentgrass turf managed as a golf course fairway. Error bars represent standard deviation of the means.

August 15,  $2006 = 3,964 \pm 168 \,\text{L}$ , and October 4, 2006 = $3,843 \pm 130 \,L$ ; representing  $36 \pm 11\%$ ,  $28 \pm 2\%$ ,  $33 \pm 8\%$ , and  $35 \pm 1\%$  of the water applied as precipitation, respectively (Fig. 1). Although the time differential between aeration and runoff varied (63, 2, 11, and 15 d), the mean percentage of applied precipitation resulting as runoff was statistically similar. This implies overland flow volumes are not significantly impacted by the turf recovery rate and filling of holes with soil and plant biomass following HT core cultivation. Similar findings were observed by Kauffman and Watschke [24], where 25 min of simulated rainfall (152 mm/h) applied to creeping bentgrass plots 2, 9, and 16 d following HT cultivation resulted in statistically similar quantities of runoff despite the elapsed time from aeration to runoff. We observed an increased time to runoff and larger percentage of precipitation as runoff relative to the Kauffman and Watschke study. The delay in time to runoff is most likely the result of a more gradual plot slope (4% rather than 9-11%), lesser precipitation rates (24-37 mm/h rather than 152 mm/h), and removal of deeper and more closely spaced cores (depth  $\times$  spacing  $\times$  diameter: 11.43 cm  $\times$  5 cm  $\times$  $0.95 \,\mathrm{cm}$  rather than  $3.8 \,\mathrm{cm} \times 6.4 \,\mathrm{cm} \times 1.6 \,\mathrm{cm}$ ). We speculate the increased runoff (28 to 36% vs 3.7 to 10% of applied precipitation) is the result of greater presimulation soil moistures as the precipitation depth (average: 62.5 mm vs 63.3 mm) and plot area  $(6.1 \text{ m} \times 24.4 \text{ m vs } 6.4 \text{ m} \times 18.9 \text{ m})$  are similar. Shuman [25] reported a direct relationship between runoff volume and soil moisture at the time of the precipitation, as well as runoff volumes that more closely resemble our observations. In that study, 37 to 44% of applied water was measured as runoff from fairways of Tifway bermudagrass (Cynodon dactylon [L.] Pers.) that received 50 mm of simulated precipitation 2 d following irrigation to field capacity, although core cultivation was not reported.

# Pesticide concentrations in runoff

Analysis of the source water applied as simulated precipitation and maintenance irrigation contained no residues of dicamba, 2,4-D, MCPP, flutolanil, or chlorpyrifos. With the exception of chlorpyrifos, the chemicals of interest were detected in the initial runoff samples. Average concentrations measured in the edge of turf plot runoff for the four evaluated events were as follows: dicamba =  $281.2 \pm 76.9 \,\mu\text{g/L}$ ; 2,4-D =  $106.8 \pm 32.0 \,\mu\text{g/L}$ ; MCPP =  $164.1 \pm 84.5 \,\mu\text{g/L}$ ; flutolanil =  $1,099.7 \pm 177.7 \,\mu\text{g/L}$ ; chlorpyrifos =  $17.8 \pm 13.7 \,\mu\text{g/L}$ .

Mass of applied pesticides transported with runoff

When overland flow volumes and plot size were considered, the average mass of chemicals transported with runoff for all events was  $5.978 \pm 2.529 \, \mu \text{g/m}^2$  dicamba;  $2.031 \pm 752 \, \mu \text{g/m}^2$  2,4-D;  $2.717 \pm 991 \, \mu \text{g/m}^2$  MCPP;  $25.560 \pm 6.369 \, \mu \text{g/m}^2$  flutolanil; and  $378 \pm 336 \, \mu \text{g/m}^2$  chlorpyrifos. Statistical analysis of chemical loads with runoff volumes and chemical concentrations revealed loads were more associated with runoff volume than chemical concentrations (dicamba, volume  $r^2 = 0.81$ , concentration  $r^2 = 0.07$ ; 2,4-D, volume  $r^2 = 0.68$ , concentration  $r^2 = 0.12$ ; MCPP, volume  $r^2 = 0.60$ , concentration  $r^2 = 0.14$ ; flutolanil, volume  $r^2 = 0.98$ , concentration  $r^2 = 0.21$ ; chlorpyrifos, volume  $r^2 = 0.76$ , concentration  $r^2 = 0.21$ ; Similar findings have been observed for pesticide loads in runoff from agricultural crops [26].

The percentage of applied pesticides transported in runoff with each event is presented in Figure 2. For all runoff events the turf was actively growing (mean air temperatures: August 2005 (21.7°C, 71°F), September 2005 (19.4°C, 67°F), August 2006 (22.2°C, 72°F), September 2006 (15.6°C, 60°F), October 4, 2006 (12.2°C, 54°F). Statistical analysis revealed the mean percentage of applied dicamba (Fig. 2A), 2,4-D (Fig. 2B), MCPP (Fig. 2C), flutolanil (Fig. 2D), or chlorpyrifos (Fig. 2E) transported with each runoff event was statistically similar regardless of the time differential between HT core cultivation and runoff (63, 2, 11, or 15 d) or the date the runoff was collection (2005 or 2006, mid-August to early October). The mean total percentage of applied pesticides transported in runoff for all events was  $22.8 \pm 9.2\%$  for dicamba;  $21.1 \pm 6.3\%$ for 2,4-D;  $16.2 \pm 5.3\%$  for MCPP;  $5.8 \pm 1.6\%$  for flutolanil, and  $0.9 \pm 0.6\%$  for chlorpyrifos. Wauchope et al. [27] found less than 3% sulfometruon-methyl and cyanazine in runoff from small plots. Armbrust and Peeler [28] reported less than 2% of imidacloprid and less than 3% of 2,4-D was found in runoff from Tifway Bermuda grass that received simulated precipitation 24 h after application. Ma et al. [29] observed runoff from bermudagrass plots managed as a fairway contained 9, 10, and 15% of applied 2,4-D, mecoprop, and dicamba, respectively. This concurs with the findings of Cole et al. [20], who measured less than 3 to 15% of applied 2,4-D, mecoprop and dicamba in runoff from bermudagrass turf. The 16 to 22% of applied dicamba, MCPP and 2,4-D measured in our runoff is most likely related to the greater soil moisture prior to pesticide application. Increased transport of pesticides with runoff from turf has been noted with greater preapplication soil moistures [20].

## Chemographs and partition coefficients

The mobility and transport of the evaluated pesticides with runoff is depicted in Figure 3. Based on their soil organic carbon partition coefficient ( $K_{OC}$ ) (Table 1) and the six soil mobility classes reported by Swann et al. [12], the herbicides dicamba, 2,4-D, and MCPP are considered highly mobile ( $K_{OC} < 150$ ), the fungicide flutolanil ( $K_{OC} = 735$ ) is considered to have a low mobility ( $K_{\rm OC} = 500-2,000$ ) and the insecticide chlorpyrifos  $(K_{\rm OC} = 8151)$  is considered to be immobile  $(K_{\rm OC} > 5,000)$ . Chemographs of dicamba, 2,4-D and MCPP closely resembled the runoff hydrograph during the first 50 min of precipitation while the chemographs of the less mobile flutolanil and chlorpyrifos quickly diverged from the hydrograph. The percentage of applied precipitation and active ingredient associated with the runoff at 50 min were as follows: runoff (4.5%), dicamba (4.4%), 2,4-D (4.3%), MCPP (3.6%), flutolanil (1.0%), and chlorpyrifos (0.1%) (Fig. 3). The greatest quantity of dicamba,

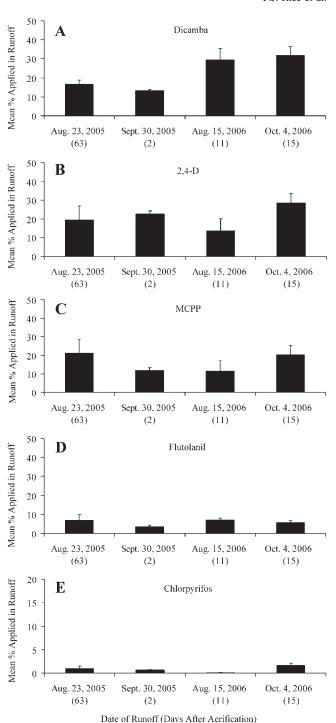


Fig. 2. Mean percentage of applied dicamba (A), dimethylamine salt of 2,4-dichlorophenoxyacetic acid (2,4-D) (B), Mecoprop-p (MCPP) (C), flutolanil (D), and chlorpyrifos (E) measured in runoff from creeping bentgrass turf managed as a golf course fairway. Error bars represent standard deviation of the means.

2,4-D, MCPP, flulolanil, and chlorpyrifos measured in the runoff occurred at 59, 65, 65, 80, and 67 min, respectively. Analysis of percentage of applied pesticides recovered in the runoff (dicamba [22.8%], 2,4-D [21.1%], MCPP [16.2%], flutolanil [5.8%], chlorpyrifos [0.9%]) with the water solubility,  $K_{\rm OC}$ , and  $K_{\rm OW}$  of the active ingredients (Table 1) suggests  $K_{\rm OC}$  ( $r^2=0.60$ ),  $K_{\rm OW}$  ( $r^2=0.55$ ), and water solubility ( $r^2=0.37$ ) describe only a portion of the difference in the observed chemical transport, with  $K_{\rm OC}$  and  $K_{\rm OW}$  somewhat better pre-

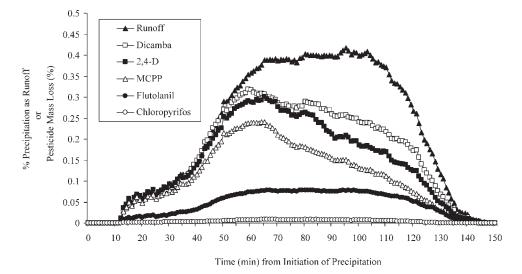


Fig. 3. Runoff hydrograph and pesticide (dicamba, dimethylamine salt of 2,4-dichlorophenoxyacetic acid [2,4-D], Mecoprop-p [MCPP], flutolanil, and chlorpyrifos) chemographs representing the average of all replicates from the four runoff events (August 23, 2005; September 30, 2005; August 15, 2006; October 4, 2006). Runoff quantities are reported as a mean percentage of total simulated precipitation. Pesticide mass loss in runoff is reported as the mean percentage of applied active ingredient.

dictors of chemical availability than water solubility for the experimental conditions of the present study.

In established turf, pesticides are applied directly to the plant material or deposited in the thatch when not intercepted by the plants [30]. This differs from most agricultural crop production in which pesticides are applied to the targeted plant (crop or weed) and residues may be washed off onto soil or pesticides are applied directly to the soil [31,32]. Researchers have reported the availability of a sizeable percentage of pesticide residues from plant foliage. As much as 91% of applied trifloxysulfuron was measured in foliar wash off from cotton 72 h after application [32]. This agrees with the observations of Wauchope et al. [31], who found ethalfiuralin, chlorothalonil, and metolachlor were dislodged from peanut foliage within minutes of rainfall, and the majority of the pesticide residues was washed off the plant foliage when precipitation occurred within days of pesticide application. Aerial parts of plants, including leaves and most stems, are coated with a waxy cuticle that is secreted from the epidermis to help prevent desiccation [33]. The greater coefficient of determination associated with  $K_{OW}$  compared to water solubility may result from the more accurate representation of pesticide availability with partitioning between cuticle waxes and precipitation using *n*-octanol, a lipophilic liquid used as a surrogate to represent fatty tissue [15]. In our experiments, plots were saturated 48 h prior to generation of simulated precipitation and no irrigation or rainfall occurred between

Table 1. Pesticide properties<sup>a</sup>

Pesticide	Water solubility (20°C) (mg/L)	$K_{\rm OC}^{b}$ (ml/g)	$K_{\rm OW}^{\rm c}$ (pH 7, 20°C)
Dicamba	250,000	12	0.01
$2,4-D^d$	23,180	56	0.15
MCPP <sup>e</sup>	860	31	1.05
Flutolanil	8.01	735	1,479
Chlorpyrifos	1.05	8,151	50,119

a http://sitem.herts.ac.uk/aeru/footprint/en/index.htm

pesticide application and initiation of simulated precipitation and runoff. Therefore, the pesticides were primarily on the leaf tissues rather than in the underlying thatch or soil at the onset of precipitation. Others have shown that pesticide residues can be found in thatch where they may be sorbed [34–36], resulting in reduced mobility to underlying soil [37,38]. It is important to point out that numerous environmental and management factors contribute to the availability of pesticides for movement with overland flow. For example, storm intensity and frequency following pesticide application, soil moistures at the time of precipitation, and thatch thickness will influence pesticide infiltration, runoff volume, and the availability of pesticides for transport with runoff. Simulation models that consider environmental and management factors in addition to chemical properties can extend predictions of pesticide availability and transport beyond evaluated experimental constraints [29,39,40].

## CONCLUSIONS

The detection of pesticides in surface waters of urban and suburban areas has led to greater suspect of contaminant contributions from residential and recreational sources. In the present study we measured the concentration and mass transport of an insecticide (chlorpyrifos), a fungicide (flultolanil), and three herbicides (dicamba, MCPP, and 2,4-D) in edge-of-plot runoff from creeping bentgrass turf managed as a golf course fairway. We observed that time differential between HT core cultivation and runoff (2, 11, 15, or 63 d) did not significantly influence the quantity of pesticides transported in the runoff. With the exception of chlorpyrifos, all chemicals of interest were detected in the initial runoff samples and throughout the runoff events. Calculation of coefficients of determination revealed the overall mass of pesticides transported in the runoff were attributed more to runoff volumes ( $r^2 = 0.60$  to 0.98) than to the concentration of the pesticides in the runoff ( $r^2 = 0.07$  to 0.22). Chemographs of the five pesticides followed trends in agreement with mobility classifications related to their soil organic carbon partition coefficient  $(K_{OC})$ ; however,  $K_{OC}$  $(r^2 = 0.60)$ ,  $K_{OW}$   $(r^2 = 0.55)$ , and water solubility  $(r^2 = 0.37)$ can only describe a portion of the observed differences in

<sup>&</sup>lt;sup>b</sup>Soil organic carbon partition coefficient.

<sup>&</sup>lt;sup>c</sup>Octanol-water partition coefficient.

<sup>&</sup>lt;sup>d</sup> 2,4-Dichlorophenoxyacetic acid.

<sup>&</sup>lt;sup>e</sup> Mecoprop-p.

chemical transport. Data from the present study contribute to the understanding of pesticide transport with runoff from managed turf and can be used in simulation models to predict pesticide transport beyond experimental conditions and to estimate ecological risks.

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