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Chemical application strategies to protect water quality☆

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ABSTRACT

Management of turfgrass on golf courses and athletic fields often involves application of plant protection products to maintain or enhance turfgrass health and performance. However, the transport of fertilizer and pesticides with runoff to adjacent surface waters can enhance algal blooms, promote eutrophication and may have negative impacts on sensitive aquatic organisms and ecosystems. Thus, we evaluated the effectiveness of chemical application setbacks to reduce the off-site transport of chemicals with storm runoff. Experiments with water soluble tracer compounds confirmed an increase in application setback distance resulted in a significant increase in the volume of runoff measured before first off-site chemical detection, as well as a significant reduction in the total percentage of applied chemical transported with the storm runoff. For example, implementation of a 6.1 m application setback reduced the total percentage of an applied water soluble tracer by 43%, from 18.5% of applied to 10.5% of applied. Evaluation of chemographs revealed the efficacy of application setbacks could be observed with storms resulting in lesser (e.g. 100 L) and greater (e.g. > 300 L) quantities of runoff. Application setbacks offer turfgrass managers a mitigation approach that requires no additional resources or time inputs and may serve as an alternative practice when buffers are less appropriate for land management objectives or site conditions. Characterizing potential contamination of surface waters and developing strategies to safeguard water quality will help protect the environment and improve water resource security. This information is useful to grounds superintendents for designing chemical application strategies to maximize environmental stewardship. The data will also be useful to scientists and regulators working with chemical transport and risk models.

1. Introduction

Tended lawns are commonly found around buildings (residential, commericial, instituational and municipal), along roadsides, in cemetaries, and associated with recreational spaces such as parks, athletic fields and golf cources. More than 32,000 golf courses are located throughout the world with an estimated 17,000 golf courses in the United States (Saito, 2010; World Golf, 2017; World Golf Foundation, 2017). Maintained turfgrass represents on average 67% of an 18-hole golf course (GCSSA, 2007). Some of the most highly managed turfgrass is found on golf courses greens and fairways where irrigation can be more frequent and application rates of fertilizer and pesticides can exceed those found in agricultural settings and home environments (Barbash and Resek, 1996; Gianessi and Anderson, 1996; Smith and Bridges, 1996). Plant protection products offer benefits to the turfgrass systems in which they are applied. Conversely, their potential off-site transport into nearby surface waters incites concern for aquatic biota as excess nutrients may result in eutrophication and harmful algal blooms and pesticides are biologically active compounds designed to interfere with metabolic processes (Matsumura, 1985; U.S. Environmental Protection Agency, 1999; Cohen et al., 1999; Hoffman et al., 2000; Gilliom et al., 2006; Ansari et al., 2011). Therefore it is important to identify management practices that will reduce the off-site transport of plant protection products in order to lessen potential adverse impact to surrounding areas and ecosystems.

Plant protection products can be transported from their point of application to adjacent areas with overland flow. This has been documented with concentrations measured directly in storm runoff and in runoff catchments, as well as supported by detection of land-applied chemicals in surface waters throughout the world (Cohen et al., 1999; Hoffman et al., 2000; Soulsby et al., 2004; Rice et al., 2011; Gilliom et al., 2006; Nash et al., 2005; Xu et al., 2007; Bakri et al., 2008; Pärn

Abbreviations: DFBA, 2,6-difluorobenzoic acid; PFBA, pentafluorobenzoic acid; KBr, potassium bromide; TFMBA, *o*-(trifluoromethyl)benzoic acid

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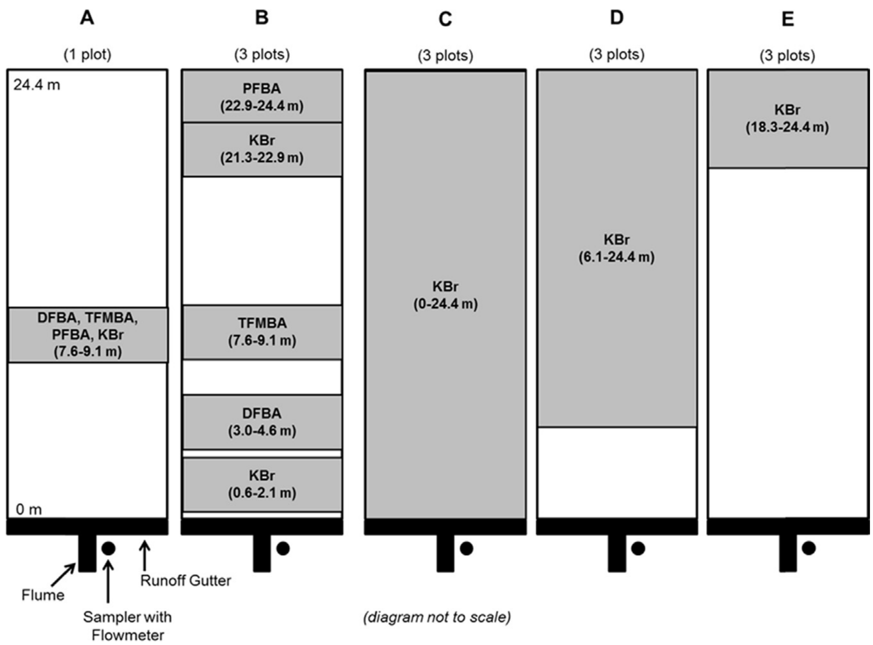


Fig. 1. Diagram of turfgrass plot experiments to evaluate the influence of application setback distances. The initial study (A and B) utilized multiple analytically-distinct tracer compounds to (A) compare the mobility of the four tracer compounds with runoff, and (B) evaluate use of these multiple tracer compounds to simultaneously evaluate application setback distances. Subsequent studies (C-E) evaluated the influence of application setback distances using a single tracer compound and one application setback distance each year during a three year study. Evaluation A was observed on a single plot. Experiments B-E were replicated on three plots. DFBA = 2,6-Difluorobenzoic acid; TFMBA = *o*-(Trifluoromethyl)benzoic acid; PFBA = Pentafluorobenzoic acid; KBr = potassium bromide.

et al., 2012; Fairbairn et al., 2016). Management practices have been shown to reduce runoff and quantity of nutrients and pesticides transported with runoff from agricultural crops (Hansen et al., 2001; Rice et al., 2007; Potter et al., 2015) and managed turfgrass (Cole et al., 1997; Rice et al., 2010b; Rice and Horgan, 2011). Vegetative filter strips or buffers, vegetative areas adjacent to surface waters designed to intercept stormwater runoff, are an example of a mitigation approach to reduce contaminant transport from developed property and land in production of agricultural crops (SULIS, 2017; Lerch et al., 2017; Franco and Matamoros, 2016; Carluer et al., 2017). In July 2015 the Minnesota Buffer Law was established requiring landowners in Minnesota, USA, to implement perennial vegetation buffers on public waters; up to 15.2 m (50 ft) along lakes, rivers and streams and 5.0 m (16.5 ft) along ditches (https://mn.gov/portal/natural-resources/buffer-law). Flexibility for alternative practices may be considered when buffers are less appropriate for land management objectives or site conditions; however, the alternative practice must provide water quality benefits comparable to that provided by a buffer (https://mn.gov/portal/natural-resources/buffer-law/practices). In suburban/urban environments open land is less prevelant and the installation of mixed-vegetation perennial-buffers may be less asethetically desired. In addition, research has shown that densely uniform manicured lawns have reduced frequency and total volume of runoff and less nutrient loss with runoff than low maintenance lawns and residential forested landscapes (Spence et al., 2012). For this reason our goal was to investigate application setbacks as an alternative practice to mitigate the off-site transport of applied chemicals with runoff from turf managed as a golf course fairway.

Golf courses can be found adjacent to natural surface waters (e.g. rivers, lakes, oceans) as well as contain surface waters within the course. In fact golf course designs often include water features in the form of ponds or creeks surrounded by fairways, turfgrass maintained between 1.27 cm and 3.18 cm height-of-cut depending on the grass species (Kains, 2017; Kelly, 2017). These surface waters act as a hazard to increase the challenge of play as well as improve golf course aesthetics, enhance drainage and water storage for irrigation, and provide habitat for wildlife. For this research we evaluated creeping bentgrass, the most commonly used turfgrass for fairways, putting greens and tees in cool and humid climates (Riggs, 2008). Experiments were performed with highly water soluble tracer compounds that would represent transport of inorganic fertilizer or a worst-case scenario for highly water soluble and minimally adsorbed pesticides. If proven effective, application setback distances could offer turfgrass managers an alternative practice to enhance environmental stewardship through mitigation of nonpoint source contamination of surrounding surface waters.

2. Materials and methods

2.1. Turf plots equipped with runoff collection systems

Runoff experiments were conducted on plots (24.4 m length x 6.1 m width, graded to a 5 ± 1% slope running east to west) sodded with *Agrostis palustris* Huds. (L-93 creeping bentgrass) at the University of Minnesota Turfgrass Research and Outreach Center (Saint Paul, MN, USA). The bentgrass was managed as a golf course fairway with 1.27 cm height of cut (3 times weekly), top-dressed with 1.6 mm depth of sand (weekly), periodically irrigated to prevent drought stress, and aerated (11 ± 4 d prior to the runoff events) with hollow tines measuring 11.43 cm depth x 0.95 cm internal diameter, spaced 5 cm × 5 cm (Ryan Greensaire II Aerator, Ryan, Barrington, IL, USA). The soil below the turfgrass was characterizes as Waukegan silt loam (fine-silty over sandy or sandy-skeletal, mixed superactive, mesic Typic Hapludolls; 55% silt, 29% sand, 16% clay) with 3% organic carbon and bulk density of 1.37 ± 0.24 g cm^{-3} for 0–7.62 cm depth.

Runoff collection systems were constructed at the down-slope (western) edge of each plot, modified from the design of Cole et al. (1997) (Fig. 1). Stainless-steel flashing directed runoff from the turf into 6.1-m gutters (horizontally-split 15.2-cm schedule 40 polyvinyl chloride (PVC) pipe that were joined in the center with a PVC-T (15.2 cm × 15.2 cm × 15.2 cm)). Water flowed from the gutter into a stainless steel large 60° V trapezoidal flume (Plasti-Fab) equipped with a bubble tube port and two sample collection ports. The gutter system and trapezoidal flume were supported in sand-filled trenches to maintain appropriate conditions for accurate measurement of runoff volume and flow rates. Gutter covers and flume shields prevented dilution of runoff with precipitation. Runoff water samples were collected using an automated sampler (Teledyne ISCO model 6700) equipped with a flow meter (Teledyne ISCO model 730) that recorded water level in the flume, reported flow rates, calculated total runoff volume and triggered collected of 24 time-paced (5 min) samples for each plot. Samples were stored at 4 °C until analysis.

2.2. Rainfall simulator

A rainfall simulator adapted from the original design of Coody and Lawrence (1994) provided reproducible precipitation for the runoff studies. Specific details of the rainfall simulator are described elsewhere (Rice et al., 2010a). Briefly, 5-cm schedule 40 PVC pipe functioned as the base of the simulator guiding water to 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, Walla Walla, WA, USA) suspended 2.7 m above the turf. We targeted simulated precipitation that represented storm events in Minnesota from April through October, which also includes a 2-h storm with recurrence interval of 25 years (Hershfield, 1961).

2.3. Application of tracer compounds

We selected potassium bromide (KBr), a conservative tracer previously used in agricultural studies (Tyner et al., 2003, 2007), and three fluorobenzoic acid compounds (2,6-difluorobenzoic acid (DFBA), *o*-(trifluoromethyl)benzoic acid (TFMBA) and pentafluorobenzoic acid (PFBA)), which fit a criteria of being highly water soluble and similar to each other in chemical structure yet distinguishable from one another during chemical analysis (Fig. 2). Potassium bromide was applied at a higher concentration to surpass anticipated natural background levels and accommodate an analytical methodology with a greater limit of quantification.

For the initial experiments DFBA, TFMBA, PFBA and KBr were dissolved in water and applied in bands 1.5 m (flow length) by 6.1 m (width of plot) using a backpack sprayer (targeted application rates: DFBA, TFMBA and PFBA each at 32 g/m^2; KBr at 55 g/m^2). All four tracer compounds were applied to a single location in order to compare their mobility (Fig. 1**A**). In contrast, for the experiments evaluating the influence of application setback distance each of the four tracer compounds were applied in a band of the same size (1.5 m (flow length) x 6.1 m (width of plot)) but at a different location within the plot (Fig. 1**B**). For the subsequent studies using only KBr and performed in multiple years (Fig. 1**C-E**), KBr was dissolved in water and applied from the application setback distance (0 m, 6.1 m, or 18.3 m from the runoff collection gutter) to the top of the plot (24.4 m from the runoff collection gutter) 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. Measured application rates of the KBr were 1.5 ± 0.3 g/m^2 (224.7 ± 37.1 g applied) for 0–24.4 m (Fig. 1**C**, 0 m setback), 1.7 ± 0.2 g/m^2 (188.4 ± 20.8 g applied) for 6.1–24.4 m (Fig. 1**D,** 6.1 m setback) and 2.5 ± 0.2 g/m^2 (92.1 ± 7.5 g applied) for 18.3–24.4 m (Fig. 1**E,** 18.3 m setback).

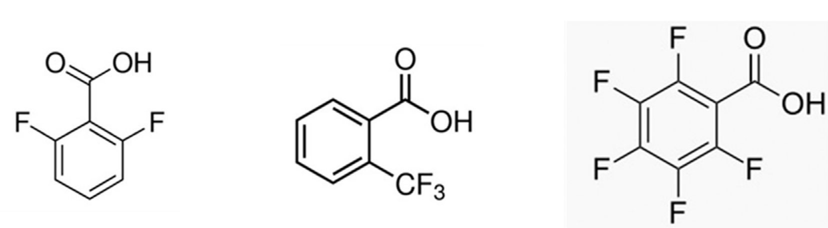
2.4. Field preparation and data collection prior to simulated precipitation

Forty-eight hours prior to initiation of simulated precipitation, samples of irrigation source water were collected and the plots were pre-wet beyond soil saturation to allow for collection of background runoff samples and to ensure uniform water distribution across all plots. Twenty-four hours later the turf was mowed (1.25 cm height, clippings removed) and runoff collection gutters and flumes were cleaned and covered with plastic sheeting to eliminate any potential contamination from application spray drift. Prior to application of the tracer, Petri dishes (glass, 14-cm) were distributed across the plots to verify delivery and application rates. Following chemical 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. Less than 3 h prior to initiation of simulated rainfall the soil moisture was measured (Field Scout TDR 300, Spectrum Technologies, Plainfield, IL). On-site wind speeds were measured using a hand-held meter (Davis Instruments, Hayward, CA, USA) and simulated precipitation began once wind speeds dropped below 2 m/s to avoid precipitation drift. Exceptions: tracer application rates, precipitation measurements and soil moisture measurements were not performed during the initial studies with the fluorobenzoic acid tracers.

2.5. Chemical analysis

The three fluorobenzoic acid compounds were analyzed using liquid chromatography-mass spectrometry. Chromatographic separation was performed on a Waters Alliance 2695 Separation Module (Waters, Milford, MA, USA)) equipped with a 2.1 × 15 mm Zorbax SB-Phenylhexyl column (Agilent). All solvents were HPLC grade and separation of the fluorobenzoic acid compounds was achieved under isocratic conditions using methanol and diluted acetic acid (0.2%, v/v, in water) at 85% MeOH 15% water. The injection volume was 50 µl and the flow rate was 0.2 ml/min with a column temperature of 30 °C. The mass spectrometer was a Micro Mass ZMD (Micromass, Manchester, UK) operated in electrospray ionization negative mode. The ion source and desolvation temperatures were 90 °C and 220 °C, respectively. The flow rate for the nitrogen desolvation gas was ~300 L/h. Capillary and cone voltage were 3.25 kV and 20 V, respectively. Ions monitored in Select Ion Monitoring mode were 157, 189, 211. Analysis of source water used for the simulated precipitation confirmed no residues of the selected fluorobenzoic acid compounds.

Runoff water samples were analyzed for total solubilized bromide using a bromide ion-selective electrode (Orion 9435) with a double-junction reference electrode (Orion 9002) following U.S. Environmental Protection Agency Method 9211 (U.S. Environmental Protection Agency, 1996). In brief, 50-ml of runoff water was combined with 1-ml of 5 M $NaNO_3$ as an ion strength adjustment solution and concentrations were determined using a 5-point standard curve. Reagent blanks, matrix spikes, initial calibration verification standards, and continuing calibration verification standards were used to confirm quality control. Trace levels of bromide ion were detected in the source



2,6-Difluorobenzoic acid (CAS RN 385-00-2) | 2-(Trifluoromethyl)benzoic acid (CAS RN 433-97-6) | Pentafluorobenzoic acid (CAS RN 602-94-8)

Fig. 2. Structures and CAS registry numbers for the three fluorobenzoic acid compounds applied as tracers to the turfgrass plots. Abbreviations used in this manuscript are as follows: DFBA = 2,6-difluorobenzoic acid, TFMBA = *o*-(trifluoromethyl)benzoic acid and PFBA = pentafluorobenzoic acid.

water used for simulated precipitation, which was subtracted from measured concentration data for the runoff water samples prior to calculation of chemical loads and percentage of applied KBr transported with runoff.

2.6. Statistical analysis

Significance in the percentage of applied tracer compound transported off-site with the runoff was assessed by analyses of variance with application setback distance as the single criteria of classification. Coefficients of determination were calculated to evaluate the relationship of percentage of applied tracer compound recovered in the runoff with application setback distance, soil moisture prior to rainfall, quantity and rate of precipitation, and volume and rate of runoff (Steel et al., 1997).

3. Results and discussion

3.1. Comparison of tracer mobility

In the initial evaluation the goal was to compare the mobility of the four tracer compounds (DFBA, TFMBA, PFBA and KBr). This was accomplished by applying all four tracers to the same location (7.6–9.1 m from the edge of plot, Fig. 1**A**) and observing their off-site transport with runoff. Transport of the four tracer compounds with surface flow was similar, exhibiting comparable chemographs with the initial detection of the four tracers observed at 308 ± 51 L (average ± standard deviation) of runoff (Fig. 3). Distinct elevations in the chemographs were observed at similar locations, which also corresponded to elevations in the runoff hydrograph. Based on theoretical application rates 2.1 ± 0.4% of the applied tracers were recovered with the runoff. The quantity of runoff observed to contain 25%, 50% and 75% of the 2% recovered tracer compounds were measured at 788 ± 152 L, 1192 ± 190 L, and 1688 ± 148 L, respectively. Overall, sufficient similarity was reported in the mobility of the four tracer compounds to validate their use in a differential application study.

3.2. Differential application of multiple tracers

The influence of application setback distance on the quantity of chemical residues transported with runoff was evaluated with the application of four tracer compounds to different locations within a single plot, and replicated on three plots (Fig. 1**B**). Under these experimental conditions, the KBr tracer, applied at 0.6–2.1 m from the runoff collection gutter, was first detected at 11 ± 2 L of runoff (Fig. 4). Increasing the application setback to 3.0 m (2,6-DFBA) further protected adjacent areas by requiring 153 ± 24 L of runoff before the chemical was first transported off-site. Likewise increasing the setback distance to 7.6 m (TFMBA) pushed the initial detection of chemical residue back to 447 ± 48 L of runoff. The delay in chemical residue detection with distance in application setback was statistically significant (p = 0.05). We recovered in the runoff 2.6 ± 0.6% of the applied (theoretical) tracer compounds placed at 0.6–2.1 m, 3.0–4.6 m, and 7.6–9.1 m from the runoff gutter. This is similar to the observations of the initial evaluation where all four tracer compounds were applied to the same location, 7.6–9.1 m from the runoff collection gutter. Average ± standard deviation (minimum–maximum) concentrations of the tracers measured in the surface runoff were 68.3 ± 9.5 mg/L (0.0–531.0 mg/L) for KBr, 35.3 ± 19.4 mg/L (0.0–105.0 mg/L) for 2,6-DFBA and 27.1 ± 26.3 mg/L (0.0–73.1 mg/L) for TFMBA. There was no evidence of chemical residue in the runoff from the KBr tracer applied at 21.3–22.9 m or PFBA applied at 22.9–24.4 m. A linear (r^2 = 0.99) relationship was observed between the application setback distance and the volume of runoff in which chemical residues were initially detected for the tracers applied at 0.6 m, 3.0 m and 7.6 m from the runoff collection gutter. Therefore we would anticipate detection of the tracers applied at 21.3–22.9 m (KBr) and 22.9–24.4 m (PFBA) with runoff from 1302 to 1397 L and 1397 to 1492 L, respectively. Calculation of the expected runoff concentrations (assuming recovery of 2% of applied) for these two tracer zones show they would have been 7 mg/L for KBr and 4 mg/L for PFBA, 36 and 3 times greater than the concentrations of our lowest standards in the analytical standard curves (0.2 mg/L for KBr, 1.5 mg/L for PFBA). Additional calculations assuming dilution in the total cumulative runoff volume (3082 ± 267 L) would have resulted in 3 mg/L for KBr and 2 mg/L for PFBA, both concentrations within the analytical standard curve. Therefore the absence of their detection was not the result of dilution below quantifiable concentrations.

The initial occurrence data provided by this experiment demonstrates the usefulness of application setbacks to delay contamination of adjacent ecosystems; however, the fluorobenzoic acid tracers browned the turfgrass, which delayed further investigations in order to allow the turfgrass to recover. In addition, the cost of these compounds limited their application to a 1.5 m (flow length) by 6.1 m (plot width) band, an unrealistic application scenario. Consequently modifications were made to the research experiment for the subsequent field seasons.

3.3. Potassium bromide tracer applied multiple years

Unlike the previous experiment that utilized analytically distinct compounds with similar transport behavior to simultaneously evaluate application setback distances, this experiment was performed with a

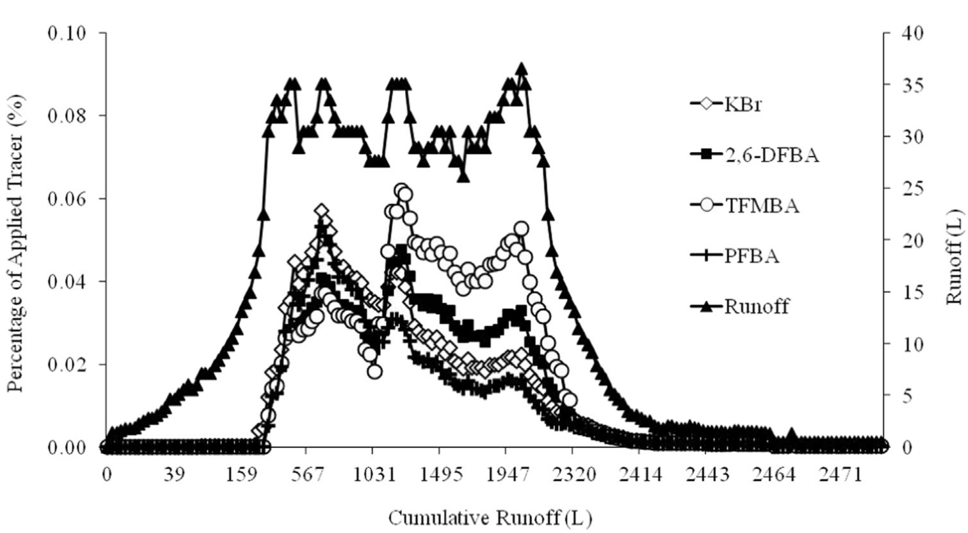


Fig. 3. Comparing mobility between tracer compounds: Runoff hydrograph and chemographs of the four tracer compounds (KBr = potassium bromide; 2,6-DFBA = 2,6-difluorobenzoate; TFMA = *o*-(trifluoromethyl) benzoate; PFBA = pentafluorobenzoate) that were applied the width of the turf plot (6.1 m) and 7.6–9.1 m from the edge of plot where the runoff was collected. The area of application represented 9.2 m^2. The KBr data has been divided by 100 to accommodate the display of all tracers on a single graph.

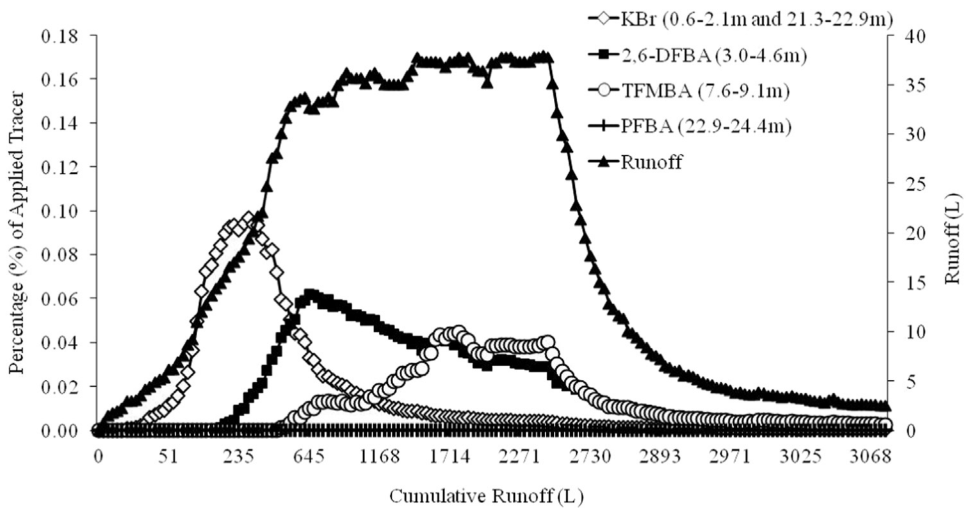


Fig. 4. Comparing tracer mobility as influenced by application setback distance: Runoff hydrograph and chemographs of the four tracer compounds (KBr = potassium bromide; 2,6-DFBA = 2,6-difluorobenzoate; TFMA = *o*-(trifluoromethyl) benzoate; PFBA = pentafluorobenzoate) applied at different distances from the edge-of-plot where the runoff was collected. The tracer compounds were applied in 1.5-m strips extending the width of the plot (24.4 m). The area of application for each tracer is provided in the legend and reported as the distance from the edge-of-plot (e.g. KBr: 0.6–2.1 m represents potassium bromide applied from 0.6 m from the edge-of-plot to 2.1 m from the edge of plot, resulting in a 1.5 m by 24.4 m (plot width) area of application).

single tracer compound, KBr, evaluating a single application setback distance on three replicate plots each year (Fig. 1**C-E**). Advantages to the modified study included application of the tracer compound from the setback distance to the top of the 24.4 m plot, providing a more realistic application scenario over the banded multi-tracer study (Fig. 1).

3.4. Precipitation and runoff

Additional data was collected for the modified KBr experiments, including pre-simulation soil moistures, measured tracer application rates, and the quantity of simulated rainfall delivered to each plot (Table 1). Simulated rainfall (n = 9 simulations) was initiated 20 ± 10 h following KBr application and terminated 90 min after the onset of runoff, resulting in precipitation lasting 110 ± 8 min. Runoff was first recorded at 17 ± 6 min, 17 ± 11 min, and 16 ± 6 min following initiation of the rainfall simulation and represented 44.8 ± 14.3%, 36.9 ± 3.8% and 30.1 ± 6.1% of the precipitation delivered to the plots with KBr applied at 0–24.4 m (0–80 ft), 6.1–24.4 m (20–80 ft), and 18.3–24.4 m (60–80 ft), respectively. Calculation of coefficients of determination revealed the percentage of applied precipitation that resulted in runoff was attributed to pre-simulation soil moisture ($r^2 = 0.87$), precipitation rate ($r^2 = 0.90$), and precipitation depth ($r^2 = 0.97$). A runoff hydrograph representing the average runoff of the nine rainfall simulations is provided as the top line in Fig. 5**A**.

Table 1
Soil moistures, precipitation rates and precipitation depths measured for the runoff events.

Runoff event identification			Precipitation	
Application[a]	Study Year	Soil Moisture (%)[b,c]	Rate (mm/h)[b]	Depth (mm)[b]
0–24.4 m	Year-1, 3 Plots	48 ± 1	34 ± 5	60 ± 7
6.1–24.4 m	Year-2, 3 Plots	41 ± 3	37 ± 3	74 ± 10
18.3–24.4 m	Year-3, 3 Plots	40 ± 2[d]	46 ± 4	80 ± 9

[a] Distance (m) from runoff gutter (application start - application finish). Plot width (6.1 m).
[b] Data presented as the mean ± standard deviation (soil moisture *n* = 27, precipitation *n* = 24).
[c] Percentage water holding capacity 3 h prior to simulated precipitation.
[d] Percentage water holding capacity < 3 h after simulated precipitation was 55 ± 5% (*n* = 18).

3.5. Chemical transport with runoff

The average ± standard deviation (minimum–maximum) concentrations of KBr measured in the runoff of the replicate plots were as follows: no setback [0–24.4 m area of application] = 10.5 ± 1.1 mg/L (5.7–14.6 mg/L), 6.1 m setback [6.1–24.4 m area of application] = 4.3 ± 1.2 mg/L (0.1–8.7 mg/L), and 18.3 m setback [18.3–24.4 m area of application] = 0.9 ± 0.1 mg/L (0.3–2.1 mg/L).

Fig. 5**A** presents the percentage of applied KBr transported with runoff as the average of the three replicate plots. For the first year of this study KBr was applied to the entire length of the plots (0–24.4 m) providing the percentage of applied KBr transported off-site with runoff when no application setback was utilized (Table 1**,** Fig. 1**C,** Fig. 5**A**). In contrast, the second and third years of this study evaluated off-site transport of KBr with runoff when a 6.1 m and a 18.3 m application setback was established (Table 1**,** Figs. 1**D &** 2**E,** Fig. 5**A**). Quantifiable concentrations of KBr exceeding the natural background level were first reported at 6 ± 2 L of runoff when no application setback was practiced. Introducing an application setback of 6.1 m delayed initial detection of KBr to 66 ± 42 L of runoff, while a larger application setback of 18.3 m further protected adjacent areas by requiring 316 ± 222 L of runoff before chemical residues were first transported off-site. In this study, the volume of runoff at which the tracer was first measured was less than that observed with the banded application study using the fluorobenzoic acid tracers. We speculate the delay in detection in the banded study was the result of dilution with runoff from the untreated area immediately upslope. Further investigation is required to confirm or disprove our speculation.

At the completion of the runoff events (3796 ± 721 L, n = 9 simulations) 18.5 ± 8.2% of the applied KBr was transported off-site from the plots with no application setback (0–24.4 m), while 10.5 ± 1.6% and 3.7 ± 0.8% were transported off-site from plots with a 6.1 m setback (applied from 6.1 to 24.4 m) and 18.3 m setback (applied from 18.3 to 24.4 m), respectively (Fig. 5**B**). Therefore implementation of a 6.1 m and 18.3 m application setback reduced the off-site transport of applied water soluble tracer by 43% and 80%. This association between increased application setback distance with reduced total percentage of applied chemical residue transported with storm runoff was statistically significant ($p = 0.05$) and described by an exponential relationship ($y = 18.20e^{-.087\times}$, $r^2 = 0.99$) better than linear relationship ($y = -0.77 \times + 17.16$, $r^2 = 0.94$). Lerch et al. (2017) observed reduction of herbicide loads in runoff with vegetative buffer strips on eroded claypan soil was a function of buffer flow length and described by first-order decay models. Others have reported linear correlations for nutrient and pesticide removal with riparian buffer zones (Mander et al., 1997; Aguiar et al., 2015). Correlation analysis

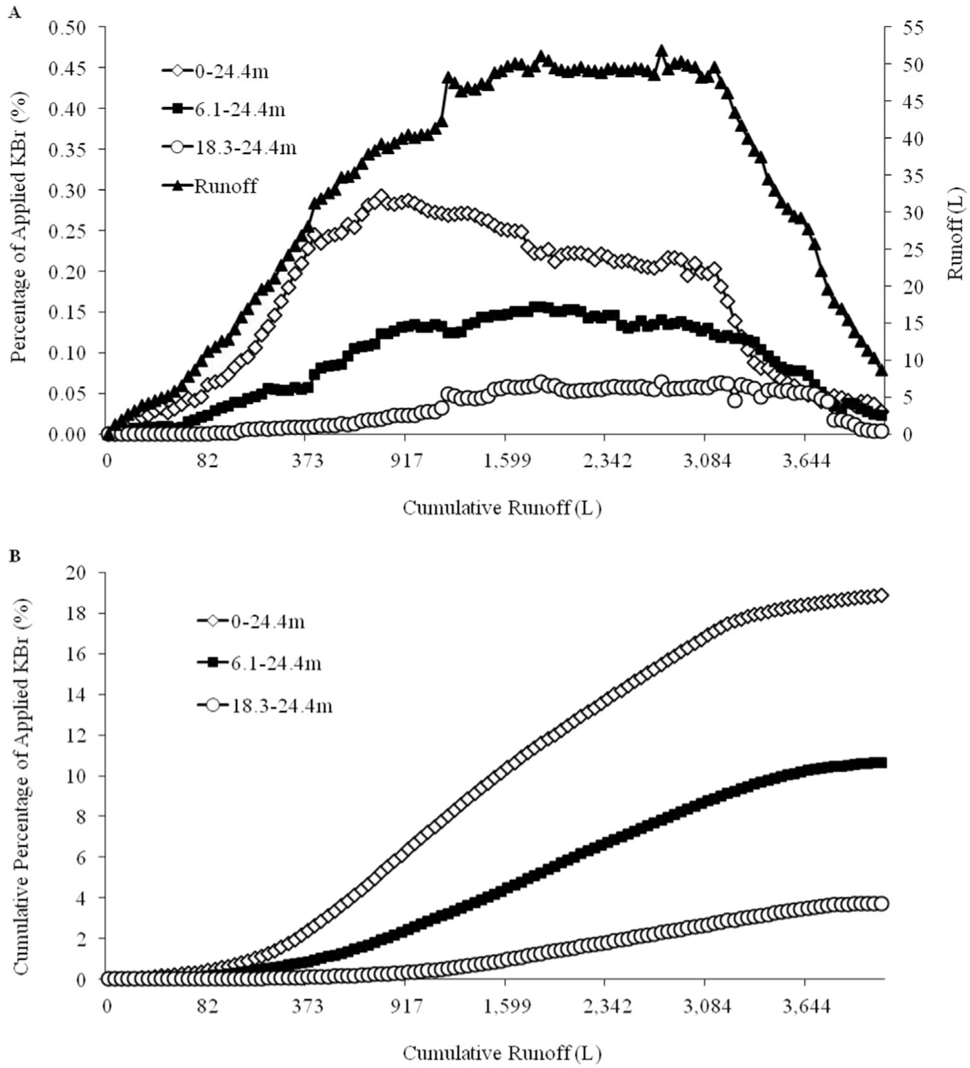


Fig. 5. (A) Runoff hydrograph showing the average runoff volumes (L) of 9 rainfall simulations and three potassium bromide (KBr) chemographs, each representing the average from three rainfall simulations. Area of KBr application is provided in the legend and percentage of applied KBr in the runoff shown on the Y-axis. Application setbacks evaluated were no setback (0–24.4 m area of application), 6.1 m setback (6.1–24.4 m area of application) and 18.3 m setback (18.3–24.4 m area of application). (B) Cumulative percentage of applied KBr measured in the runoff relative to the cumulative runoff volume. This is a cumulative summary of the chemographs provided in (A).

with our 9 simulated rainfall-runoff experiments showed the percentage of applied KBr transported off-site with runoff was influenced by soil moisture (r^2 = 0.50) more than precipitation quantity (r^2 = 0.25) or precipitation rate (r^2 = 0.25).

Evaluating the chemographs (Fig. 5**A**), the maximum single-point percentage of applied KBr transported with runoff (0–24.4 m = 0.29%, 6.1–24.4 m = 0.15%, 18.3–24.4 m = 0.06%) occurred at 758 L, 1798 L, and 2738 L for the plots with 0 m, 6.1 m and 18.3 m application setbacks. A comparison of chemograph slopes from start of runoff to these maximum values showed with application setbacks of 6.1 m and 18.3 m the transport rates of KBr were 3 and 9 times less than from the plots with KBr applied to the entire plot under the same environmental conditions (Fig. 5**A**). This highlights the efficacy of application setbacks even with storms delivering less precipitation than the simulated rainstorm evaluated with this research. Looking at precipitation data recorded for this location in the summer of 2017 we observed storm events of less and greater magnitude than our experimental simulation (2-h storm with recurrence interval of 25 years (31.8–38.1 mm/h) or 50 years (38.1–44.5 mm/h)) (Hershfield, 1961). Extrapolation of our experimental data to these rainfall events illustrates the estimated mitigation potentials of this management strategy depending on the application setback distance and the storm characteristics (Fig. 6).

Dissipation of compounds applied to the turf can result from volatilization, adsorption (to vegetation and soil), plant uptake, degradation, or transport with water by infiltration (leaching) and overland flow (runoff) (Haith et al., 2002; Raturi et al., 2003; Magri and Haith, 2009; Rice et al., 2010a; Potter et al., 2015). For this investigation we used highly water soluble compounds with low volatility, and simulated precipitation that generated runoff less than 30 h from chemical application. Therefore transport of the applied compounds by means of water flow was anticipated to be the primary route of dissipation with minimal contributions from the other pathways. Measurement of 45% or less of the applied precipitation as runoff points to infiltration as a key mechanism for off-site chemical load reductions with runoff. The water holding capacity of the soil at the time of a storm event will influence infiltration and the quantity and duration of precipitation required to reach soil saturation, resulting in overland flow. In order to control thatch and maintain the quality of the playing surface, golf course fairways and greens are managed with aerification practices (e.g. hollow tine core cultivation, verticutting) and sand top dressing, which increases infiltration (Barton et al., 2009; Stier and Hollman, 2003). The infiltration and drainage capacity of our managed fairway turf was measured by the rapid recovery from saturated to 55 ± 5% soil moisture < 3 h from termination of the simulated precipitation

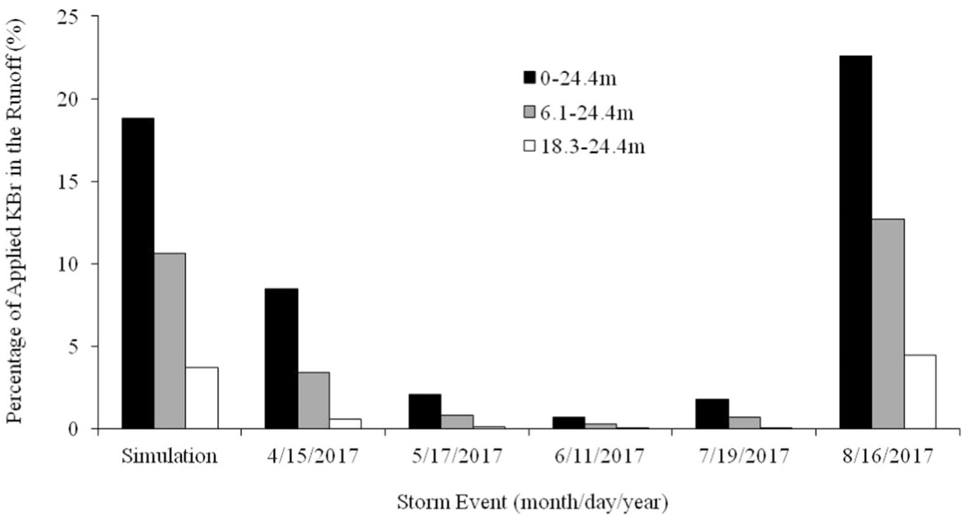


Fig. 6. Percentage of applied potassium bromide (KBr) measured in the runoff from the simulated rainfall experiments (shown as the average of 9 simulations) and anticipated in runoff when the experimental data was extrapolated to recorded natural storm events in April–August 2017. Application setbacks include no setback (0–24.4 m area of application), 6.1 m setback (6.1–24.4 m area of application) and 18.3 m setback (18.3–24.4 m area of application).

(Table 1, footnote). In previous work we have found the quantity of runoff was more important to the off-site mass transport (loading) of plant protection products from fairway turf than the concentration of the plant protection product measured in the runoff, highlighting the importance of infiltration and water holding capacity on the prevention of contamination of adjacent surface waters (Rice et al., 2010a). In this study we have shown that application setbacks can significantly delay the occurrence of applied chemistries in the runoff, resulting in up to an 80% reduction of these chemistries reaching adjacent areas. However we must highlight the effectiveness of application setbacks is anticipated to be reduced for soils with insufficient water holding capacity.

Overall application setbacks can reduce the percentage of applied chemicals transported off-site with runoff from turfgrass, offering a mitigation strategy to reduce non-point source contamination of adjacent surface waters and enhanced environmental stewardship. Depending on the condition of the turfgrass, managers may choose to use plant protection products to the edge of managed turf; however, planning to implement application setbacks as often as possible, particularly during times of greater storms, will reduce nonpoint source pollutant contributions from managed turf. Climatology data shows larger storm events are becoming more frequent (Matonse and Frei, 2013; Cid et al., 2016), which points to a greater necessity for mitigation planning.

It is important to note that this experiment was performed with conservative tracers that are water soluble and more closely represent plant protection products such as inorganic fertilizer or pesticides with high water solubility and minimal adsorption. Physical chemical properties of the applied plant protection product will influence its persistence and mobility with overland flow and should be considered when selecting application setback distance and designing mitigation strategies (Rice et al., 2010a; Ulrich et al., 2013; Bonmatin et al., 2015; Yang et al., 2016). For instance application setbacks with a shorter flow distance may be sufficient for mitigating off-site transport of plant protection products that are less water soluble and have greater soil sorption. Studies on vegetative buffer strips with various grass treatments have shown reduction of herbicide transport with runoff was influence by adsorption and infiltration (Lerch et al., 2017). The toxicity of the plant protection product and the potential duration and timing of exposures to non-target organisms should also be considered. A greater setback distance may be required to protect adjacent ecosystems if the active ingredient is moderately to highly toxic to aquatic organisms or could be transported off-site into surface waters during sensitive lifecycle stages (Key et al., 2003; Miko et al., 2017; Zubrod et al., 2017).

In conclusion, a direct benefit of this research is the confirmation that application setbacks can be an effective strategy to reduce the off-site transport of applied plant protection products with runoff from managed turf. Application setbacks offer managers a mitigation approach that requires no additional resources or time inputs and provides options in situations where traditional vegetative filter strips are not realistic or aesthetically desired. Indirect benefits of this research include valuable data for refining simulation models to more accurately predict the transport of plant protection products with runoff from managed turf. Use of this data in modeling efforts can help conserve resources by extrapolation to scenarios outside of the experimental parameters and may provide information towards decision making for product development, use or regulation.

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References

Aguiar, T.R., Jr, Bortolozo, F.R., Ferreira, M.T., 2015. Riparian buffer zones as pesticide filters of no-till crops. Environ. Sci. Pollut. Res. 22, 10618–10626.
Ansari, A.A., Gill, S.S., Khan, F.A., 2011. Eutrophication: threat to aquatic ecosystems. In: Ansari, A.A., Gill, S.S., Lanaza, G.R., Rast, W. (Eds.), Eutrophication: Causes, Consequences and Control, pp. 143–170. http://dx.doi.org/10.1007/978-90-481-9625-8_7.
Bakri, D.A., Rahman, S., Bowling, L., 2008. Sources and management of urban stormwater pollution in rural catchments, Australia. J. Hydrol. 356, 299–311.
Barbash, J.E., Resek, E.A., 1996. Pesticides in Groundwater: Distribution, Trends, and Governing Factors. Lewis, Boca Raton, FL.
Barton, I., Wan, G.C.Y., Buck, R.P., Colmer, T.D., 2009. Effectiveness of cultural thatch-mat controls for young and mature Kikuyu turfgrass. Agron. J. 101, 67–74.
Bonmatin, J.M., Giorio, C., Girolami, V., Goulson, D., Kreutzweiser, D.P., Krupke, C., Liess, M., Long, E., Marzaro, M., Mitchell, E., Noome, D.A., Simon-Delso, N., Tapparo, A., 2015. Environmental fate and exposure; neonicotinoids and fipronil. Environ. Sci. Pollut. Res. 22, 35–67.
Carluer, N., Lauvernet, C., Noll, D., Munoz-Carpena, R., 2017. Defining context-specific scenarios to design vegetated buffer zones that limit pestiscide transfer via surface runoff. Sci. Total Environ. 575, 701–712.
Cid, A., Menéndez, M., Castanedo, S., Abascal, A.J., Méndez, F.J., Medina, R., 2016. Long-term changes in the frequency, intensity and duration of extreme storm surge events in southern Europe. Clim. Dyn. 46, 1503–1516.
Cohen, S., Svrjcek, A., Durborow, T., Barnes, N.L., 1999. Water quality impacts by golf courses. J. Environ. Qual. 28, 798–809.
Cole, J.T., Baird, J.H., Basta, N.T., Huhnke, R.L., Storm, D.E., Johnson, G.V., Payton, M.E., Smolen, M.D., Martin, D.L., Cole, J.C., 1997. Influence of buffers on pesticide and nutrient runoff from bermudagrass turf. J. Environ. Qual. 26, 1589–1598.
Coody, P.N., Lawrence, L.J., 1994. Method and system for conducting meso-scale rainfall simulations and collecting runoff US Patent 5,279, 151 US Patent Office, Washington D.C.

Fairbairn, D.J., Karpuzcu, E.M., Arnold, W.A., Barber, B.L., Kaufenberg, E.F., Koskinen, W.G., Novak, P.J., Rice, P.J., Swackhamer, D.L., 2016. Sources and transport of contaminants of emerging concern: a two-year study of occurrence and spatio-temporal variation in a mixed land use watershed. Sci. Total Environ. 551–552, 605–613.

Franco, J., Matamoros, V., 2016. Mitigation of polar pesticides across a vegetative filter strip. A mesocosm study. Environ. Sci. Pollut. Res. 23, 25402–25411. http://dx.doi.org/10.1007/s11356-016-7516-1.

GCSSA, 2007. Golf course environmental profile; Property profile and environmental stewardship of golf courses, Volume 1 Summary, 4p. 〈https://www.gcsaa.org/Uploadedfiles/Environment/Environmental-Profile/Property-Profile/Golf-Course-Environmental-Profile–Property-Summary.pdf〉. (Accessed 5 August 2017).

Gianessi, L.P., Anderson, J.E., 1996. Pesticide Use in U. S. Crop Production. National Data Report. National Data Report. National Center for Food and Agricultural Policy, Washington, D.C, USA.

Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., Wolock, D.M., 2006. The Quality of Our Nation's Waters: Pesticides in the Nation's Streams and Ground Water, 1992-2001 15 U.S. Geological Survey, Reston, VA. 〈http://pubs.usgs.gov/circ/2005/1291〉.

Haith, D.A., Lee, P.C., Clark, J.M., Roy, G.R., Imboden, M.J., Walden, R.R., 2002. Modeling pesticide volatilization from turf. J. Environ. Qual. 31, 724–729.

Hansen, N.C., Moncrief, J.F., Gupta, S.C., Capel, P.D., Olness, A.E., 2001. Herbicide banding and tillage system interactions on runoff losses of alachlor and cyanazine. J. Environ. Qual. 30, 2120–2126.

Hershfield, D.M., 1961. Rainfall frequency atlas of the Unitied States for durations from 30 minutes to 24 hours and return periods from 1 to 100 years. Technical Paper No. 40. Department of Commerce. Washington, D.C., 61p.

Hoffman, R.S., Capel, P.D., Larson, S.J., 2000. Comparison of pesticides in eight U.S. urban streams. Environ. Toxicol. Chem. 19, 2249–2258.

Kains, R., 2017. Robert Kains Golf Course Design. 〈https://www.kainsgolfdesign.com/golf-course-water-feature-design.html〉, (last accessed 9 January 2018).

Kelly, B., 2017. What is the fairway on a golf hole? 〈https://www.thoughtco.com/fairway-golf-definition-1560842?Print〉 (last accessed 9 January 2018).

Key, P.G., Meyer, S.L., Chung, K.W., 2003. Lethal ad sub-lethal effects fo the fungicide chlorothalonil on three life stages of the grass shrimp, Paldemonetes pugio. J. Environ. Sci. Health Part B-Pestic. Food Contam. Agric. Wastes 38, 539–549. http://dx.doi.org/10.1081/PFC-120023512.

Lerch, R.N., Lin, C.H., Goyne, K.W., Kremer, R.J., Anderson, S.H., 2017. Vegetative buffer strips for reducing herbicide transport in runoff: effects of bufer width, vegetation and season. J. Am. Water Resour. Assoc. 53, 667–683.

Magri, A., Haith, D.A., 2009. Pesticide decay in turf: a review of processes and experimental data. J. Environ. Qual. 38, 4–12.

Mander, U., Kuusemets, V., Lõhmus, K., Mauring, T., 1997. Effciency and dimensioning of riparian buffer zones in agricultural catchments. Ecol. Eng. 8, 299–324.

Matsumura, F., 1985. Toxicology of Insecticides. Plenum Press, New York.

Matonse, A.H., Frei, A., 2013. A seasonal shift in the frequency of extreme hydrological events in southern New York State. J. Clim. 26, 9577–9593.

Miko, Z., Ujszegi, J., Hettyey, A., 2017. Age-dependent changes in sensitivity to a pesticide in tadpoles of the common toad (Bufo bufo). Aquat. Toxicol. 187, 48–54.

Nash, D., Clemow, L., Hannah, M., Barlow, K., Gangaiya, P., 2005. Modeling phosphorus exports from rain-fed and irrigated pastures in southern Australia. Aust. J. Soil Res. 43, 745–755.

Potter, T.L., Bosch, D.D., Strickland, T.C., 2015. Tillage impact on herbicide loss by surface runoff and lateral subsurface flow. Sci. Total Environ. 530, 357–366.

Pärn, J., Pinay, G., Mander, Ü., 2012. Indicators of nutrient transport from agricultural catchments under temperate climate: a review. Ecol. Indic. 22, 4–15.

Raturi, S., Carroll, M.J., Hill, R.L., 2003. Turfgrass thatch effects on pesticide leaching: a laboratory and modeling study. J. Environ. Qual. 32, 215–223.

Rice, P.J., Harman-Fetcho, J.A., Sadeghi, A.M., McConnell, L.L., Coffman, C.B., Teasdale, J.R., Abdul-Baki, A.A., Starr, J.L., McCarty, G.W., Herbert, R.R., Hapeman, C.J., 2007. Reducing insecticide and fungicide loads in runoff from plastic mulch with vegetative-covered furrows. J. Agric. Food Chem. 55, 1377–1384.

Rice, P.J., Horgan, B.P., Rittenhouse, J.L., 2010a. Pesticide transport with runoff from creeping bentgrass turf: relationship of pesticide properties to mass transport. Environ. Toxicol. Chem. 29, 1209–1214.

Rice, P.J., Horgan, B.P., Rittenhouse, J.L., 2010b. Evaluation of core cultivation practices to reduce ecological risk of pesticides in runoff from Agrostis palustris. Environ. Toxicol. Chem. 29, 1215–1223.

Rice, P.J., Horgan, B.P., 2011. Nutrient loss with runoff from fairway turf: an evaluation of core cultivation practices and their environmental impact. Environ. Toxicol. Chem. 30, 2473–2480.

Riggs, N. 2008. Newer bentrass cultivars. 〈https://www.turfmagazine.com/maintenance/newer-bentgrass-cultivars/〉. (last accessed 9 January 2018).

Saito, O., 2010. Measuring the lifecycle carbon footprint of a golf course and greening the golf industry in Japan. 〈http://www.thesustainabilitysociety.org.nz/conference/2010/papers/Saito.pdf〉. (Accessed 10 August 2017).

Smith, A.E., Bridges, D.C., 1996. Movement of certain herbicides following application to simulated golf course greens and fairways. Crop Sci. 36, 1439–1445.

Soulsby, C., Rodgers, P.J., Petry, J., Hannah, D.M., Malcolm, I.A., Dunn, S.M., 2004. Using tracers to upscale flow path understanding in mesoscale mountainous catchments: two examples from Scotland. J. Hydrol. 291, 174–196.

Spence, P.L., Osmond, D.L., Childres, W., Heitman, J.L., Robarge, W.P., 2012. Effects of lawn maintenance on nutrient losses via overland flow during natural rainfall events. J. Wmer. Water Resour. Assoc. 48, 909–924.

Steel, R.G.D., Torrie, J.H., Dickey, D.A., 1997. Principles and Procedures of Statistics: A Biometrical Approach, 3rd ed. McGraw-Hill, New York, NY.

Stier, J.C., Hollman, A.B., 2003. Cultivation and topdressing requirements for thatch management in A and G bentgrass and creeping bluegrass. Hortic. Sci. 38, 1227–1231.

SULISSustainable Urban Landscape Information Series. Vegetative Buffer Zones. 〈http://www.extension.umn.edu/garden/landscaping/design/water2.html〉 (Accessed 11 May 2017).

Tyner, J.S., Wright, W.C., Yoder, R.E., 2003. Bi-modal subsurface transport of atrazine and bromide at the field scale. Total Maximum Daily Load (TMBL): Environmental Regulations II, Proceedings pp. 307–316.

Tyner, J.S., Wright, W.C., Yoder, R.E., 2007. Identifying long-term preferential and matrix flow recharge at the field scale. Trans. ASABE 50, 2001–2006.

Ulrich, U., Dietrich, A., Fohrer, N., 2013. Herbicide transport via surface runoff during ntermittent artificial rainfall: a laboratory plot scale study. Catena 101, 38–49.

U.S. Environmental Protection Agency, 1996. Method 9211, Potentiometric determination of bromide in aqueous samples with ion-selective electrode. 8pp. 〈https://www.epa.gov/sites/production/files/2015-12/documents/9211.pdf〉 (Accessed 2 December 2015).

U.S. Environmental Protection Agency, 1999. National recommended water quality criteria; EPA 822-Z-99-001: Washington, D.C.

World Golf. Golf courses of the world. 〈http://www.worldgolf.com/courses〉 (last accessed 14 September 2017).

World Golf Foundation. Golf and the environment. 〈http://www.worldgolffoundation.org/industry-initiatives/golf-the-environment〉 (last accessed 14 September 2017).

Xu, L., Zhang, Q., Li, H., Viney, N.R., Xu, J., Liu, J., 2007. Modeling of surface runoff in Xitiaoxi catchment, China. Water Resour. Manag. 21, 1313–1323.

Yang, X.M., Van Der Zee, S., Gai, L.T., Wesseling, J.G., Ritsema, C.J., Geissen, V., 2016. Integration of transport concepts for risk assessment of pesticide erosion. Sci. Total Environ. 551, 563–570.

Zubrod, J.P., Englert, D., Luderwald, S., Poganiuch, S., Schulz, R., Bundschuh, M., 2017. History matters: pre-exposure to wastewater enhances pesticide toxicity in invertebrates. Environ. Sci. Technol. 51, 9280–9287.