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ABSTRACT

A repeated measures analysis was conducted on a set of data from a multi-year study to assess the effect of vegetative buffers on the surface runoff of selected herbicides and nutrients. Multiplicative models describing the observed behavior of runoff concentration over time for buffered and non-buffered plots were fitted on a log-transformed scale using linear mixed models with PROC MIXED in PC SAS version 6.11. A spatial power covariance structure was used. Additional models for contaminant mass flow rates were fitted to evaluate the effect of buffers on total runoff mass.

1. INTRODUCTION

The extent and effect of runoff of herbicides and nutrients from turf, especially golf course fairways, has become a subject of increased interest and concern in recent years. While not more than one-third of a golf course is comprised of treated fairway grass, this area is typically bounded by a variety of water features such as ponds, lakes, and streams (Watson et al., 1992). Such areas can receive contaminated runoff from treated fairways as a result of an intense rain event during which the infiltration rate of the soil is exceeded by the precipitation rate. This allows the herbicides and nutrients to escape through overland flow as dissolved, suspended, or sediment-bound particles (Balogh and Anderson, 1992; Walker and Branham, 1992).

The current project represents part of a multi-year study sponsored by the United States Golf Association and the Oklahoma Agricultural Experiment Station to investigate the effect of using untreated bermudagrass buffer strips, placed downslope from treated fairways, on the surface loss of contaminants. In theory, such buffer strips should help to reduce runoff by 1) increasing infiltration potential, 2) reducing surface flow velocity, thereby lessening the erosive power and sediment carrying capacity of runoff water, 3) providing filtering of sediment or chemicals in solution and 4) diluting applied chemicals (Muscutt et al., 1993).

Contaminants of interest included the herbicides 2,4-D and mecoprop and the nutrient phosphorus. These contaminants were selected because of their widespread use by turf managers and potential for surface runoff based on their physicochemical properties. Phosphorus is necessary for the establishment, growth, and color of turfgrass, while 2,4-D and mecoprop are commonly applied either together or separately to control broadleaf weed species. Although the runoff characteristics of each of these contaminants has been investigated in agricultural and urban settings (White et al., 1976; Dillaha et al., 1989; Watschke and Mumma, 1989), prior to the current research, their behavior with respect to bermudagrass buffers had not been examined.

In previous phases of the study, effects of buffer strip height (1.3 cm, 3.8 cm, 7.6 cm) and length (no buffer, 1.2 m, 2.4 m, 4.9 m) were determined based on estimates of contaminant concentrations in total runoff from individually treated plots (Cole et al., 1997). Estimated concentrations of each contaminant were determined using runoff-volume-weighted composites of samples taken throughout the course of a simulated rain event from each plot. The focus of the current investigation was the manner in which these buffer strips affected contaminant transport over the course of the simulation. For this purpose, each sample taken from the no-buffer and 4.9-m buffer plots was individually analyzed for herbicide and nutrient content. The resulting concentration data were subjected to a repeated measures analysis of the effect of continuous time on each contaminant in order to establish and compare runoff profiles for the selected buffer treatments.

2. MATERIALS AND METHODS

Data for the overall study were collected during July and August of 1995 and 1996 on a 1.2-ha sloped field of common bermudagrass at the Oklahoma State University Agronomy Farm in Stillwater, Oklahoma. A portable rainfall simulator was used to apply precipitation simultaneously to four parallel 1.8-m wide x 9.8-m long plots on each of eight simulator setups. Simulated rain events were conducted on two setups per day. Treatment combinations of buffer length and buffer height were applied to individual plots according to a randomized incomplete block design, with setups as blocks.

A central 3-m-wide alley located in the center of each setup accommodated the simulator boom, which rotated at approximately 7 revolutions/min from 2.7 m above ground, delivering 63.5 mm/h for a duration of 75 min. The boom extended at least 1.5 m beyond all corners of each setup to ensure uniform coverage. The average slope of the plots was 6% ($\pm 0.6\%$) toward troughs designed to channel water from individual plots toward 1-m wide x 1-m deep collection pits. Excess water, not collected at the trough mouths for analysis, was pumped from the pits. Plot borders were sealed using flexible plastic hose filled with masonry sand.

Data for this repeated measures analysis were collected in July 1996 from a total of four setups which each contained plots with the no-buffer and 4.9-m buffer treatments. Plot surfaces receiving herbicide and nutrient application were mowed at 1.3 cm to represent a golf course fairway. To create the buffer treatment, this applied area was separated from its collection trough by a 4.9-m strip mowed at 3.8 cm to represent the standard height of bermudagrass rough in Oklahoma. This strip was taken to represent an untreated rough located between the treated fairway and surface water.

Phosphorus was applied at a rate of 49 kg/ha to each treatable surface, which was then irrigated with 5 mm of water over 6 min using the rainfall simulator. After the turf had dried, herbicides were applied at 1.1 kg ae/ha for 2,4-D and at 0.6 kg ae/ha for mecoprop using a CO_2-powered sprayer. Simulated rainfall was initiated within 24 h of this application.

The sampling strategy for the overall study required that water samples be taken at approximately 2.5-min intervals during the first 30 min of the rain event and at 5-min intervals thereafter. Longer intervals were considered acceptable after the first 30 min because contaminant content of the samples was expected to stabilize. Collection of the first sample from an individual plot began when a continuous trickle of water was observed at the trough mouth. Samples were collected in 0.45-L, 1.0-L, or 5.0-L containers, depending on the perceived runoff rate at the time of collection. Estimated runoff rates were obtained from the time required to fill the selected containers and were used to determine a single volume-weighted estimate of concentration of total runoff for each plot. For the repeated measures analysis, individual water samples were examined for the presence (in µg/L) of 2,4-D and mecoprop and for phosphorus content (in mg/L).

3. MODELING STRATEGY

Of interest was the behavior of contaminant concentration in runoff water over time for buffered versus non-buffered plots, as well as the aggregate effect of the buffer on the total mass of contaminants in runoff water at the conclusion of the rain event. The experimental setting suggested that concentration be analyzed using time as a repeated measure, with plots as main units. Main-unit treatments corresponded either to no buffer or a 4.9-m buffer, with main units organized into four simulator setups (blocks). Observed concentration levels were most appropriately associated with the midpoints of their respective sampling intervals, requiring that time be treated as a continuous variable. Within this framework, a multiplicative model incorporating a gamma structure for the effect of time on concentration was fitted but required a log transformation so that a linear mixed model could be used. In particular, the model

$$y_{ijt} = \mu \exp(\beta_i + \tau_j + (\beta\tau)_{ij})\ t^{\alpha+\gamma_j} \exp((\delta + \theta_j)t) \exp(\varepsilon_{ijt})$$

was fitted as

$$\log y_{ijt} = \mu^* + \beta_i + \tau_j + (\beta\tau)_{ij} + (\alpha + \gamma_j)\log t + (\delta + \theta_j)t + \varepsilon_{ijt},$$

where $\mu^* = \log \mu$ is the overall mean,
β_i is the random effect of the i^{th} setup ($i = 1, 2, 3, 4$),
τ_j is the fixed effect of the j^{th} buffer ($j = 1, 2$),
$(\beta\tau)_{ij}$ describes the random interaction between the i^{th} setup and j^{th} buffer,
α, δ are the fixed slope effects of log t and t, respectively,
γ_j, θ_j are the fixed effects of the j^{th} buffer on the slope effects of log t and t, respectively,
ε_{ijt} is the residual error,

and where it was assumed that $\beta_i \sim \text{iid } N(0, \sigma_\beta^2)$, $(\beta\tau)_{ij} \sim \text{iid } N(0, \sigma_{\beta\tau}^2)$. In recognition of the unequally spaced repeated measure of time, a spatial power covariance structure was employed wherein it was assumed that $\text{cov}(\varepsilon_{ijt1}, \varepsilon_{ijt2}) = \sigma_\varepsilon^2 \rho^{|t1 - t2|}$. Residual errors for different plots were assumed to be normally distributed and uncorrelated. This model was found to be appropriate for both 2,4-D and mecoprop when predicted values were compared to the log-transformed data. For phosphorus, a fourth-order polynomial was substituted for the gamma component on the log scale and was found graphically to perform better than the gamma model (see Table 1 for parameter estimates for all models).

An analysis of the effect of the 4.9-m buffer strip on the total mass of contaminants in surface runoff also was desired but could not be obtained practically from the total runoff of individual plots, so that an alternative approach was required. For each water sample, the observed concentrations of individual contaminants were multiplied by the estimated runoff rate associated with the sample to obtain estimated contaminant mass flow rates, which were subsequently associated with the midpoint of the sampling interval. If the true mass flow rate equations for individual plots could have been determined, these could have been integrated to obtain the total mass of each contaminant in surface runoff from each plot. By fitting models with spatial power covariance structures to individual plots using PROC MIXED, both sampling variability and autocorrelation of observed mass rates were accommodated when estimating these equations. In most cases, multiplicative polynomial models (up to fourth order) were fitted by taking the log transformation of the observed rates. For a few contaminant-plot combinations, graphs of predicted values versus the original data suggested that additive polynomial models were more appropriate. Once estimated contaminant totals were available for each plot, these values were analyzed using a paired t-test for each contaminant to assess whether significant differences in average estimated runoff mass between buffer and no-buffer treatments were present.

4. RESULTS

To assess the buffer effect on runoff concentration, estimated ratios of treatment means in the original scale were obtained from the antilogs of estimated treatment contrasts built using the fitted models (Steel and Torrie, 1980, p. 235; Steel et al., 1997, pp. 242-245). Observed times until start of runoff in the experiment ranged from 12.5 min to 24 min for the buffered plots and from 9 min to 23 min for non-buffered plots. Lognormal-adjusted predicted treatment means and estimated ratios in the original scale were calculated for each 5-min interval beginning 15 min after the start of rainfall (Steel et al., pp. 242-245). Each ratio was tested at the 5% level for a significant difference from one using an estimated contrast in the log scale.

Estimated ratios for 2,4-D ranged from 54.1 times higher for non-buffered plots at 15 min to 2.6 times larger at 60 min (see Table 2). All were significant at the 5% level. Overall, the buffer was found to reduce and delay the onset of 2,4-D concentration in runoff, with a peak contamination of 41.0 μg/L occurring approximately 46 min after the start of rainfall, according to the fitted model.

Similar results were found for mecoprop (see Table 3). Significant ratios were determined at each 5-min interval throughout the rainfall event, ranging from 23.9 times more concentration for the no-buffer treatment at 15 min to 2.3 times higher at 55 min. Like 2,4-D, peak concentration for buffered plots was delayed from the onset of runoff until approximately 40 min, at which time a predicted level of 17.4 μg/L occurred, still less than the lowest predicted concentration of 22.1 μg/L for non-buffered plots.

Observed buffer effects were less extensive for phosphorus (see Table 4). Unlike 2,4-D and mecoprop, significantly higher ratios were found for non-buffered plots only during the first 65 min of the experiment, ranging from 59.3 times larger at 15 min to 1.9 times larger at 40 min. According to the fitted polynomial model, peaks in runoff concentration of 2.6 mg/L and 1.7 mg/L for the buffered plots were observed approximately 33 min and 68 min, respectively, after the onset of rainfall.

Analyses of differences in average estimated runoff mass of each contaminant showed no significant effect of the buffer, although the data suggested that the buffer strip was, in fact, effective in reducing total contaminant runoff (see Table 5). Experimental results suggest that the lack of significance of each test can be attributed in part to the small number of setups used.

5. SUMMARY AND CONCLUSIONS

Results suggest that bermudagrass buffer strips are effective in reducing and delaying the onset of contaminant concentration in runoff water. With the exception of phosphorus, predicted concentrations were significantly lower throughout the rain event for buffered plots compared to non-buffered plots, suggesting that the buffer takes an important role in reducing contaminant transport even after extensive rainfall has occurred. Analyses of estimated total runoff mass were not conclusive but likewise suggested an effect of the buffer on runoff water quality.

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Table 1. Parameter Estimates for 2,4-D and Mecoprop Concentration Models

Contaminant	μ*	τ_1	α	γ_1	δ	θ_1	ρ	σ_ε^2
2,4-D	8.30	-16.04	-0.0039	-0.084	-0.92	4.91	0.80	0.28
Std. Error				(0.039)		(1.65)	(0.057)	
P-value				(0.034)		(0.004)	(<0.001)	
mecoprop	6.72	-12.70	-0.011	-0.069	-0.69	3.90	0.52	0.24
Std. Error				(0.032)		(1.35)	(0.18)	
P-value				(0.033)		(0.005)	(0.004)	

(Note: τ_1, γ_1, and θ_1 correspond to buffer treatment. PROC MIXED parameterization gives $\tau_2 = \gamma_2 = \theta_2 = 0$ for no-buffer treatment. P-values for γ_1 and θ_1 based on approximate F-test. P-value for ρ based on large-sample z test. Block variance estimates were $\sigma_\beta^2 = 0.00$, $\sigma_{\beta\tau}^2 = 0.14$ for 2,4-D and $\sigma_\beta^2 = 0.00$, $\sigma_{\beta\tau}^2 = 0.13$ for mecoprop.)

(Note: Model for phosphorus concentration gave $\ln y = -13.20 + 1.23t - 0.038t^2 + 0.00050t^3 - 0.0000024t^4$ for buffer treatment and $\ln y = 2.95 - 0.036t - 0.0010t^2 + 0.000033t^3 - 0.00000024t^4$ for no-buffer treatment ($p = 0.007$ for treatment x t^4 interaction). Block variance estimates were $\sigma_\beta^2 = 0.00$, $\sigma_{\beta\tau}^2 = 0.071$. Autocorrelation term $\rho = 0.84$ (std. err. = 0.043, $p < 0.001$). Residual variance $\sigma_\varepsilon^2 = 0.088$.)

Table 2. Predicted Concentration of 2,4-D by Treatment for Five-Minute Intervals and Associated P-values for Significance of Ratio Comparisons

Time* (min)	Buffer (μg/L)	No Buffer (μg/L)	Ratio	P-value
15	7.06	381.55	54.07	<0.001
20	14.36	286.73	19.97	<0.001
25	22.59	228.72	10.13	<0.001
30	30.20	189.48	6.27	<0.001
35	36.07	161.12	4.47	<0.001
40	39.69	139.63	3.52	<0.001
45	41.01	122.79	2.99	0.001
45.6	41.02 (peak)	121.01	2.95	0.002
50	40.33	109.22	2.71	0.003
55	38.10	98.07	2.57	0.004
60	34.81	88.73	2.55	0.005
65	30.95	80.79	2.61	0.005
70	26.87	73.97	2.75	0.007
75	22.85	68.06	2.98	0.009

* From start of simulated rainfall event

Table 3. Predicted Concentration of Mecoprop by Treatment for Five-Minute Intervals and Associated P-values for Significance of Ratio Comparisons

Time* (min)	Buffer (µg/L)	No Buffer (µg/L)	Ratio	P-value
15	5.47	130.84	23.90	<0.001
20	9.25	101.49	10.97	<0.001
25	12.72	82.31	6.47	<0.001
30	15.34	68.66	4.48	<0.001
35	16.89	58.40	3.46	<0.001
40	17.40	50.38	2.90	0.001
40.3	17.40 (peak)	49.95	2.87	0.001
45	17.07	43.94	2.57	0.002
50	16.09	38.66	2.40	0.004
55	14.67	34.24	2.33	0.005
60	13.02	30.50	2.34	0.005
65	11.31	27.31	2.41	0.004
70	9.64	24.55	2.55	0.005
75	8.07	22.14	2.74	0.006

* From start of simulated rainfall event

Table 4. Predicted Concentration of Phosphorus by Treatment for Five-Minute Intervals and Associated P-values for Significance of Ratio Comparisons

Time* (min)	Buffer (mg/L)	No Buffer (mg/L)	Ratio	P-value
15	0.18	10.61	59.25	<0.001
20	0.81	8.41	10.41	<0.001
25	1.82	6.79	3.74	<0.001
30	2.52	5.63	2.23	0.001
33.1	2.64 (peak)	5.07	1.92	0.007
35	2.61	4.83	1.85	0.011
40	2.31	4.28	1.85	0.013
45	1.96	3.92	1.99	0.007
50	1.72	3.67	2.14	0.003
55	1.61	3.51	2.17	0.003
60	1.62	3.36	2.07	0.007
65	1.69	3.16	1.87	0.032
68.3	1.72 (peak)	3.00	1.74	0.070
70	1.71	2.89	1.69	0.096
75	1.51	2.49	1.65	0.224

* From start of simulated rainfall event

Table 5. Average Predicted Total Masses of Contaminant Runoff by Treatment and P-values for Significance of Treatment Differences

Contaminant	Buffer	No Buffer	P-value
2,4-D (μg)	13831.03	21949.79	0.220
mecoprop (μg)	5239.67	7414.46	0.309
phosphorus (mg)	733.16	868.07	0.691