Research Article

The Influence of Form and Rate on the Efficacy of Matrix-Based Fertilizers to Reduce Nutrient Leaching

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We tested the efficacy of matrix-based fertilizers (MBFs) to reduce NO_3, NH_4, and total phosphorus (TP) leaching compared to Osmocote 14-14-14, a commercial slow release fertilizer (SRF) in greenhouse column studies. The MBFs covered a range of inorganic N and P in compounds that are relatively loosely bound (MBF4) and more tightly bound compounds (MBF5) with $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ and with high ionic exchange compounds starch, chitosan, and lignin. When N and P are released, the chemicals containing these nutrients in the MBF bind N and P to an $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ starch- chitosan- lignin matrix. SRF leachate contained a greater amount of NO_3, NH_4, DRP, and TP than leachate from MBF4 and MBF5 regardless of whether fertilizers were pellets, banded or broadcast, or fertilizer rate. St Augustine grass growing in soils receiving MBF4 and MBF5 had decreased shoot biomass by 49% to 56% and decreased total biomass by 33% to 46% respectively as grass receiving SRF. Although further greenhouse and field testing are necessary, results of this initial investigation are promising and with further development, testing, and rate calibration should be competitive with commercial fertilizers in environmentally sensitive markets.

1. Introduction

Transport of N and P from agricultural soils to surface waters has been linked to eutrophication in fresh water and estuaries [1–3]. Eutrophication is widespread and rapidly expanding in fresh surface waters and coastal seas of the developed world. Eutrophication accounts for about 50% of the impaired lake area and 60% of the impaired rivers in the United States. It is also the most widespread pollution problem in estuaries [4]. In most lakes, streams, and coastal ecosystems, N is the element most limiting to production of plant material such as algae. Algal blooms cloud the water and block sunlight, causing native underwater flora to die contributing to a wide range of aquatic problems including summer fish kills, foul odors, and unpalatable tastes in drinking water [5]. Native underwater flora provide food, shelter, and spawning and nursery habitat for aquatic fauna. When algae die and decompose, oxygen is depleted, suffocating aquatic fauna. Phosphorus is also an essential

element that contributes to both freshwater and coastal eutrophication. The incidence of harmful algal blooms in lakes, streams, and coastal oceans has dramatically increased in recent years [4]. This increase is linked to eutrophication and other factors, such as changes in aquatic food webs that may increase decomposition and nutrient recycling or reduce populations of algae-grazing fish. Increasing conversion of native lands to agriculture or development has increased the land area receiving fertilizer and contributes to N and P pollution of surface waters.

Fertilizer regimens could greatly benefit from more effective time release technologies that help managers better protect surface and ground water. We developed matrix-based fertilizers (MBFs) that may reduce NH_4, NO_3, dissolved reactive phosphate (DRP), and total P (TP) leaching. The MBFs (patent pending) cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF4) to more tightly bound compounds (MBF5) mixed with $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ and with
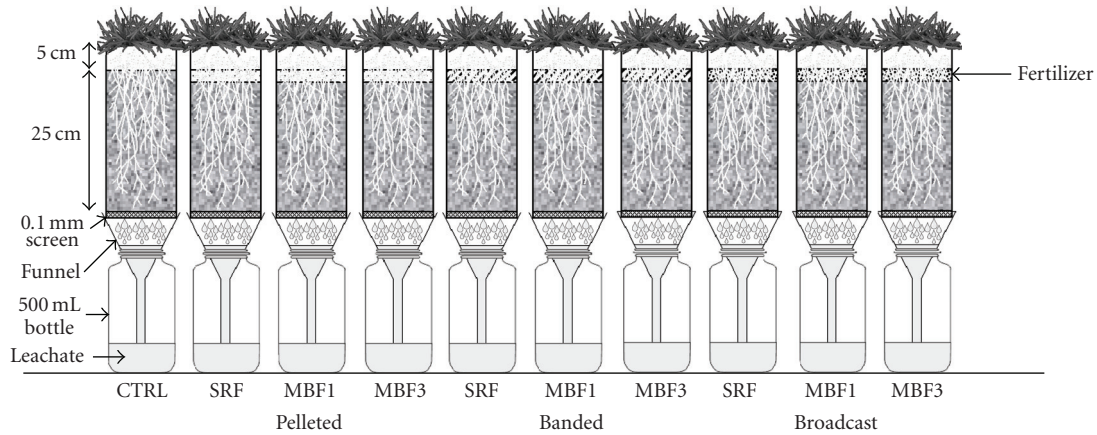
Figure 1: Diagram of column apparatus for fertilizer form.

the high ionic exchange compounds, starch, chitosan, and lignin. Starch, chitosan, and lignin were chosen because of their high concentration of ionic exchange sites and their decomposition characteristics. The organic components in the matrix degrade starch>chitosan>lignin in the order of more to less rapid. The matrix-based formulations can be made to bind inorganic nutrients relatively loosely (MBF4) to more tightly (MBF5) by increasing the concentration of $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ and by varying the amounts of starch, chitosan, and lignin in the matrix. When the matrix is applied to soil, microorganisms degrade the starch in the matrix comparatively rapidly while chitosan degrades less rapidly. Lignin degrades the slowest and should retain most of its ionic exchange sites for a longer time in most soil environments. Nutrients bound to the $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$-starch-chitosan-lignin matrix also become slowly available to plants as the organic components in the matrix degrade. The MBFs also cover a range of N and P concentration MBFs 1 and 4 contain a higher N and a high P concentration, MBF2 contains a more moderate N and a higher P concentration, and MBFs 3 and 5 contain a low N and a high P concentration [6, 7].

In previous experiments, Osmocote 14-14-14, a slow release fertilizer (SRF), combined with $Al_2(SO_4)_3 \cdot 18H_2O$ and $Fe_2(SO_4)_3 \cdot 3H_2O$ leached 78%–84% more NH_4, 58–78% more TP, 20–30% more TRP, and 61%–77% more DRP than MBF formulations [6]. The SRF treatment leached 34% less NO_3 than MBF formulations. Total plant weight did not differ among fertilizer treatments. Arbuscular mycorrhizal infection did not differ among plants receiving SRF and MBF formulations. Entry and Sojka [7] found that in three soil textures the SRF leachate contained a higher amount of NH_4, NO_3, and TP than leachate from MBF formulations. However, wheat plants growing in soils receiving SRF had greater shoot, root, and total biomass than all MBF formulations. Arbuscular mycorrhizal infection in plant roots did not differ among plants growing in soil receiving SRF, MBFs, and non amended control treatments. In this study our objectives were to determine the influence of (1) MBF application method of pellet, banded, or broadcast on plant growth and

N and P leaching and (2) MBF4 and MBF5 and the slow release fertilizer (SRF) Osmocote 14-14-14 at low, moderate, or high fertilizer application rates on plant growth and N and P leaching in two separates soil types.

2. Materials and Methods

2.1. Fertilizer Treatments

2.1.1. Experiment 1: Fertilizer Form. Treatment 1 was a control and no fertilizer was applied (Figure 1). Treatments 2, 5, and 8 were 5.0 g of the Osmocote (14-14-14) slow release fertilizer (SRF) which was equal to 0.210 m N, 0.200 g P, and 0.180 g K per column, and was equal to 267 kg N ha^{-1}, 255 kg P ha^{-1}, and 159 kg K ha^{-1} (Table 1). Treatments 3, 6, and 9 were MBF4 which received 0.191 g N and 0.206 P per column and was equal to 243 kg N ha^{-1} and 262 kg P ha^{-1}. Treatments 4, 7, and 10 were MBF5 which received 0.86 g N and 0.185 g P per column and was equal to 121 kg N ha^{-1} and 287 kg P ha^{-1}. Fertilizer treatments 2, 3, and 4 were applied as 1 cm diameter pellets equally distributed in the top 4 cm of each column. Fertilizers in treatments 4, 5, and 6 were banded and were applied as 2 cm diameter bands 4 cm long in the top 4 cm in each column. Fertilizers in treatments 8, 9, and 10 were broadcast and mixed with soils in the top 4 cm in each column. We then added 8000 spores of *Glomus interadicies* in 1.00 mL of reverse osmosis water to all MBF treatments (per column) to increase plant nutrient uptake.

2.1.2. Experiment 2: Fertilizer Rate. Treatment 1 was a control; no fertilizer was applied to the columns (Figure 2). Fertilizer treatments 2, 3, and 4 were applied at a low rate and broadcast applied as described above in the fertilizer form experiment and mixed with the top 4 cm of soil. Treatment 5 was 10.0 g of Osmocote (14-14-14) slow release fertilizer (SRF) which was equal to 0.420 g N and 0.400 g P per column, which was equal to 534 kg N ha^{-1} and 510 kg P ha^{-1} (Table 2). Treatment 6 was MBF4 which received 0.382 g N and 0.412 g P per column and was equal to 486 kg N ha^{-1} and 510 kg P ha^{-1}. Treatment 7 was MBF5
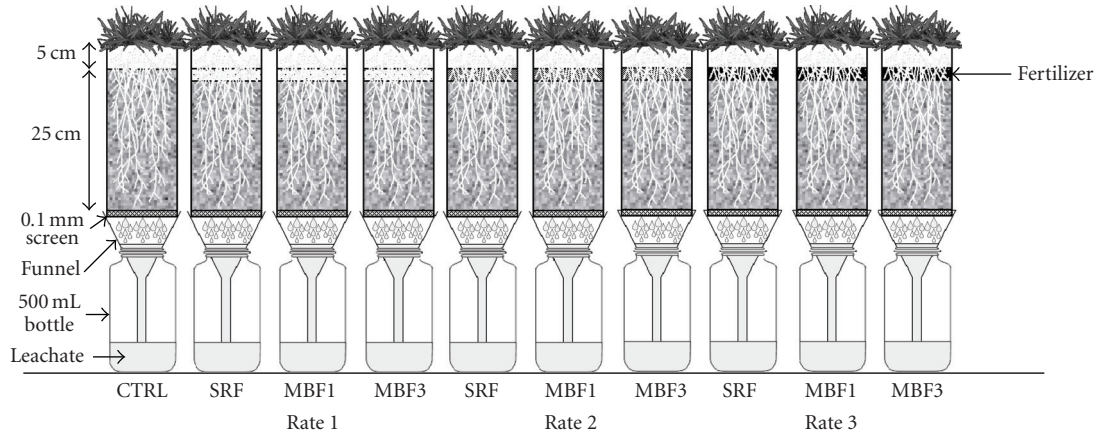
FIGURE 2: Diagram of column apparatus for fertilizer rate.

TABLE 1: Chemical compounds used to comprise three different matrix-based fertilizers in experiment 1 fertilizer form[a].

Treatment	1	2	3	4	5	6	7	8	9	10
Compound	CONT	SRF	MBF4	MBF5	SRF	MBF4	MBF5	SRF	MBF4	MBF5
Fertilizer Form			Banded			Broadcast			Pellet	
g compound in each column										
NH_4NO_3	0.000	0.210	0.000	0.000	0.126	0.000	0.000	0.126	0.000	0.000
P_2O_5	0.000	0.200	0.000	0.000	0.120	0.000	0.000	0.120	0.000	0.000
K_2O	0.000	0.180	0.180	0.180	0.108	0.180	0.180	0.108	0.180	0.180
$Ca(NO_3)_2\,4H_2O$	0.000	0.000	0.472	0.236	0.000	0.472	0.236	0.000	0.472	0.236
$Al(NO_3)_3\,9H_2O$	0.000	0.000	0.750	0.000	0.000	0.750	0.000	0.000	0.750	0.000
$NH_4(H_2PO_4)$	0.000	0.000	0.230	0.115	0.000	0.230	0.115	0.000	0.230	0.115
$Ca(H_2PO_4)_2$	0.000	0.000	0.468	0.234	0.000	0.468	0.234	0.000	0.468	0.234
$Fe(P_2O_7)$	0.000	0.000	0.334	0.750	0.000	0.334	0.750	0.000	0.334	0.750
$Al_2(PO_4)_3$	0.000	0.000	0.360	0.000	0.000	0.360	0.000	0.000	0.360	0.000
$Al_2(SO_4)_3\,18H_2O$	0.000	0.000	0.366	0.000	0.000	0.366	0.000	0.000	0.366	0.000
$Fe_2(SO_4)_3\,3H_2O$	0.000	0.000	0.800	1.600	0.000	0.800	1.600	0.000	0.800	1.600
Starch	0.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000
Chitosan	0.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000
Lignin	0.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000

[a]MBF4 is matrix-based fertilizer formulation 1 = 243 kg N ha^{-1} and 262 kg P ha^{-1}; MBF5 is matrix-based fertilizer formulation 3 = 121 kg N ha^{-1} and 236 kg P ha^{-1}. SRF is the slow release fertilizer 5.0 g of Osmocote (14-14-14) = 267 kg N ha^{-1}, 255 kg P ha^{-1}, and 159 kg K ha^{-1}.

which received 0.172 g N and 0.370 g P per column and was equal to 242 kg N ha^{-1} and 472 kg P ha^{-1}. Treatment 8 was 15.0 g of Osmocote (14-14-14) slow release fertilizer (SRF) which was equal to 0.630 g N and 0.600 g P per column and 801 kg N ha^{-1} and 765 kg P ha^{-1}. Treatment 9 was MBF4 which received 0.573 g N and 0.618 g P per column and was equal to 729 kg N ha^{-1} and 786 kg P ha^{-1}. Treatment 10 was MBF5 which received 0.258 g N and 555 g P per column and was equal to 258 kg N ha^{-1} and 708 kg P ha^{-1}. Fertilizers in all treatments were broadcast and mixed with soils in the top 4 cm in each column.

2.2. Column Description.

A 2.0 mm wire screen was cut into squares (125 × 125 mm) and secured to the bottom of each 10.0 cm diameter × 30 cm long polyvinyl chloride cylinder. A 14 cm diameter funnel was placed below each column in the rack and secured. Three kilograms of soil were placed in each column (columns were filled to 25 cm) leaving a 5 cm space at the top of each column. Soil in columns was loosely packed and then repeatedly washed with reverse osmosis water to flush nutrients that could be loosely held to soil particles. Columns were allowed to drain for 1 hour prior to the start of leachate collection as described below.

2.3. Soil Descriptions.

Two different textured soils were used to determine the effectiveness of the fertilizers to reduce leaching. The Simco soil was a coarse-loamy sand and classified as a mixed nonacidic, mesic Xeric Torriorthent. The Kuna soil was a sandy loam and classified as a mixed, mesic lithic Xerollic Camborthid [8]. Soil physical and

TABLE 2: Chemical compounds used to comprise three different matrix-based fertilizers in experiment 2: fertilizer rate[a].

Treatment	1	2	3	4	5	6	7	8	9	10
Compound	CONT	SRF	MBF4	MBF5	SRF	MBF4	MBF5	SRF	MBF4	MBF5
			Low Rate			Moderate Rate			High Rate	
					g compound in each column					
NH_4NO_3	0.000	0.210	0.000	0.000	0.420	0.000	0.000	0.630	0.000	0.000
P_2O_5	0.000	0.200	0.000	0.000	0.400	0.000	0.000	0.600	0.000	0.000
K_2O	0.000	0.180	0.180	0.180	0.360	0.360	0.360	0.540	0.540	0.540
$Ca(NO_3)_2\, 4H_2O$	0.000	0.000	0.472	0.236	0.000	0.944	0.472	0.000	1.888	0.944
$Al(NO_3)_3\, 9H_2O$	0.000	0.000	0.750	0.000	0.000	1.500	0.000	0.000	3.000	0.000
$NH_4(H_2PO_4)$	0.000	0.000	0.230	0.115	0.000	0.460	0.230	0.000	0.920	0.460
$Ca(H_2PO_4)_2$	0.000	0.000	0.468	0.234	0.000	0.936	0.468	0.000	1.872	0.936
$Fe(P_2O_7)$	0.000	0.000	0.334	1.490	0.000	0.668	2.980	0.000	1.336	5.960
$Al_2(PO_4)_3$	0.000	0.000	0.360	0.000	0.000	0.720	0.000	0.000	1.440	0.000
$Al_2(SO_4)_3\, 18H_2O$	0.000	0.000	0.366	0.000	0.000	0.732	0.000	0.000	1.464	0.000
$Fe_2(SO_4)_3\, 3H_2O$	0.000	0.000	0.800	1.600	0.000	1.600	3.200	0.000	3.200	6.400
Starch	0.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000
Chitosan	0.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000
Lignin	0.000	0.000	1.000	1.000	0.000	1.000	1.000	0.000	1.000	1.000

[a] At the low rate: MBF4 = 243 kg N ha^{-1} and 262 kg P ha^{-1}; MBF5 = 121 kg N ha^{-1} and 236 kg P ha^{-1}; SRF is the slow release fertilizer 5.0 g of Osmocote (14-14-14) = 267 kg N ha^{-1} and 255 kg P ha^{-1} and 159 kg K ha^{-1}. At the moderate rate: MBF4 = 486 kg N ha^{-1} and 524 kg P ha^{-1}; MBF5 is 242 kg N ha^{-1} and 472 kg P ha^{-1}; SRF is the slow release fertilizer 10.0 g of Osmocote (14-14-14) = 534 kg N ha^{-1} and 510 kg P ha^{-1}. At the high rate: MBF4 = 729 kg N ha^{-1} and 786 kg P ha^{-1}; MBF5 = 363 kg N ha^{-1} and 708 kg P ha^{-1}; SRF is the slow release fertilizer 15 g of Osmocote (14-14-14) = 801 kg N ha^{-1}, 765 kg P ha^{-1}, and 477 kg K ha^{-1}.

microbiological properties are presented in (Sojka et al., [9] and Entry et al., [10]).

2.4. Experimental Design. The fertilizer form experiment was arranged in a completely randomized design with 3 fertilizer treatments (SRF, MBF4, and MBF5) × 3 forms of fertilizer application (pellet, banded, and broadcast) × 2 soil textures (loam and loamy sand) × 3 replications × 4 leachate measurements at 21, 42, 63, and 84 days. There were a total of 54 columns and 216 leachate measurements. The fertilizer rate experiment was also arranged in a completely randomized design with 3 fertilizer treatments (SRF, MBF4, and MBF5) × 3 fertilizer rate treatments (low, moderate, and high) × 2 soil textures (loam and loamy sand) × 3 replications × 6 leachate measurements at 21, 42, 63, 84, 105, and 126 days. There were a total of 54 columns and 354 leachate measurements.

2.5. Fertilizer Placement and Growing Conditions. In experiments 1 and 2 we placed a 2 cm × 2 cm starter patch (approximately 10 g) of St Augustine grass (*Stenotaphrum secundatum* (Walt.) Kuntze) in the top 10 cm of each column. Plants were watered with 100 mL of water daily to maintain field capacity of the soil. Leachate did not flow through columns when 100 mL reverse osmosis water was applied. We collected leachate on the above stated days after fertilizer placement (start of the experiment) by giving Plants 500 mL reverse osmosis water on the above stated days in lieu of the 100 mL daily reverse osmosis water. On each sampling day approximately 200 mL leachate was collected

from each column and prepared for analysis. Subsamples were analyzed for NO_3 and NH_4, DRP, and TP as described below. Throughout the experiment plants were exposed to light having a photosynthetic active radiation of 400–700 : mol m^{-2} S^{-1} and a 14–16-hour photoperiod.

2.6. Harvesting and Arbuscular Mycorrhizae Assessment. Plants were harvested after 84 days in experiment 1 and 126 days in experiment 2. At harvest plants were removed from the columns and separated into roots and shoots. Roots were washed in reverse osmosis water until all visible soil particles were removed. Three grams of roots were randomly selected from each plant and placed in a solution of 2.5% (w/v) KOH for 24 hours. The roots in the KOH solution were then placed in an autoclave for 5 minutes and then rinsed in 2% HCl for 24 hours. Roots were then placed in 0.05% (w/v) trypan blue in acidic glycerol for 24 hours [11]. Roots were observed for hyphal colonization under a 200x microscope by the cross hair intersection method [12]. Approximately 100 intersections were scored and used to determine percent of root length infected. Root tissue excluding roots examined for mycorrhizal infection and shoot tissue was dried at 80EC for 48 hours and weighed for shoot and root biomass.

2.7. Chemical Analysis. Nitrate and NH_4 were determined using a Lachat Automated Ion Analyzer (Quickchem 8000 Systems, Milwaukee, WI) using the method described by APHA [13]. Total P and DRP in leachate were determined by digesting 25 mL aliquots in an autoclave at 103.5 kPa and 121EC for 60 minutes with 4.0 mL acidified ammonium

TABLE 3: Total amount of NH$_4$, NO$_3$, total phosphorus (TP), and dissolved reactive phosphorus (DRP) leached from sandy loam and loam soils and shoot and root dry weight arbuscular mycorrhizal infection of St. Augustine grass receiving pellet, banded, or broadcast.

Fertilizer	DRP	TP	NO$_3$	NH$_4$	Shoot Weight	Root Weight	Total weight	Mycorrhizal infection[d]
		mg element L^{-1} water				g		%
Fertilizer not applied (Control)	3.33[b]	5.47[b]	9.94[c]	0.10[c]	2.69[d]	0.98[d]	3.67[d]	44[a]
Matrix Based Fertilizer 1 (MBF4)	4.68[b]	5.00[b]	12.57[b]	0.45[b]	14.21[b]	3.34[b]	17.58[b]	48[a]
Matrix Based Fertilizer 3 (MBF5)	3.29[b]	3.89[b]	4.39[d]	0.28[b]	7.38[c]	1.88[c]	9.26[c]	39[a]
Osmocote 14-14-14 (SRF)	10.78[a]	8.33[a]	108.29[a]	3.17[a]	30.68[a]	3.49[a]	36.24[a]	37[a]

[a] In each column, values followed by the same letter are not significantly different as determined by the least square means test ($P \leq .05$; $n = 36$).
[b] Statistical comparisons of parameters in water are presented with regard to fertilizer because interactions of and soil × fertilizer × fertilizer form × week sampled, soil × fertilizer × fertilizer form, soil × fertilizer × week sampled were not significant in the GLM model ($P \leq .05$; $n = 18$).
[c] Fertilizer rates were MBF4 = 243 kg N ha^{-1} and 262 kg P ha^{-1}; MBF5 = 121 kg N ha^{-1} and 236 kg P ha^{-1}; SRF = 267 kg N ha^{-1}, 255 kg P ha^{-1}.
[d] Percent (%) of fine roots infected with arbuscular mycorrhizae.

persulfate [13]. Samples were dried at 65°C for 72 hours and passed through a 2 mm sieve. Total N was determined using standard microkjeldahl procedures modified for NO$_3$ [14]. A 2 g subsample of soil was extracted 10 mL 1 N ammonium acetate [15] and analyzed for Mn, Fe, Al, Si, S, and Zn being determined using inductively coupled plasma emission spectrometry (ICP; Perkin-Elmer, Boston, MA). At harvest, plant root and shoot material were weighed then ground to pass a 1 mm mesh. A 0.50 g subsample was analyzed for total N with a LECO CHN-600 nitrogen analyzer (St. Joseph, Michigan). A 0.25 g subsample was ashed at 500EC, dissolved in 25 mL of 1.0 M HCl, brought to 50 mL volume with reverse osmosis water, and analyzed for P, K, Ca, Mg, Mn, Fe, Cu, B, and Zn using an ICP.

2.8. Statistical Analysis. All data sets were tested for normal distribution with Statistical Analysis Systems [16] and then analyzed using general linear models (GLMs) procedures for a completely random design. In all analyses, residuals were equally distributed with constant variances. Differences reported throughout are significant at $P \leq .05$, as determined by the Least Squares Means test. Correlations were determined using DRP, TP, NH$_4$, and NO$_3$ as the independent (x) variable and days since fertilizers were applied as dependant (y) variables using SAS programs. Regression slopes and y intercepts among fertilizers were compared using t ratios [16]. Regression slopes and y intercepts among fertilizers were also compared using confidence limits. Assume that a variance ratio of 1 and confidence limits of the slope and each intercept were calculated at $P \leq .05$. Confidence limits of the y intercepts were estimated by confidence limits of the slope and mean values of the x and y variables. If the confidence interval region includes the matched pairs mean difference of 0 on the y-axis, then the results obtained by each method are not significantly different at $P \leq .05$ [17, 18].

3. Results

3.1. Fertilizer Form. The GLM models of leached nutrients for fertilizer type × fertilizer form × soil type × sample day, fertilizer × fertilizer form, soil type × fertilizers form, soil type × fertilizers, and soil type × sample day

were not significant. Therefore, statistical comparisons of NO$_3$, NH$_4$, DRP, TP, shoot, root, and total plant weight and shoot and root nutrient concentrations are presented for fertilizer treatments because GLM models showed that these interactions were significant at $P \leq .05$ [17, 18]. plants growing in soils receiving SRF had greater shoot, root, and total biomass than all fertilizer formulations; MBF4 and MBF5 decreased shoot biomass by 53% and 76%, decreased root biomass by 4% and 46% and total plant biomass by 51% and 74% compared to the SRF (Table 3). Arbuscular mycorrhazal infection in plant roots did not consistently differ among plants growing in soil receiving SRF and all MBF formulations and plants growing in soils receiving no fertilizer (control). We found that at from 45% to 58% of the NH$_4$, 40% to 85% of the NO$_3$, 49 to 86% of the DRP and 33 to 83% of the TP was leached from soil columns in the first 63 days after Osmocote (14-14-14) SRF was applied (data not shown). After 84 days, SRF leachate contained a greater amount of NO$_3$, NH$_4$, DRP, and TP than leachate from MBF4 and MBF5 regardless of fertilizer application form (Table 3). MBF4 and MBF5 reduced DRP in leachate by 57% and 70%, respectively, compared to the SRF. MBF4 and MBF5 reduced TP in leachate by 40% and 53%, respectively, compared to the SRF. MBF4 and MBF5 reduced NO$_3$ in leachate by 86% and 91% respectively, compared to the SRF. MBF4 and MBF5 reduced NH$_4$ in leachate by 88% and 96%, respectively, compared to the SRF. The concentration of N, P, K, Mg, Mn, Fe, Zn, Al, and Na shoot tissue did not differ among fertilizer or form of application treatments (data not shown). Nitrogen concentration was higher in root tissue of plants receiving the SRF than MBF5, regardless of the form of fertilizer application (data not shown). The concentration of Fe was higher in root tissue of plants receiving the control and MBF5 than SRF or MBF4.

3.2. Fertilizer Rate. The GLM models of leached nutrients for fertilizer type × fertilizer rate × soil type × sample day, soil type × fertilizers rate, soil type × fertilizers, and soil type × sample day were not significant. Therefore, statistical comparisons of DRP, TP NO$_3$, NH$_4$, shoot, root, and total plant weight and shoot and root nutrient concentrations are presented for fertilizer × fertilizer rate

TABLE 4: Total amount of NH_4, NO_3, total phosphorus (TP), and dissolved reactive* phosphorus (DRP) leached from sandy loam and loam soils and shoot and root dry weight and arbuscular mycorrhizal infection of St. Augustine grass receiving low, moderate, and high rate of matrix-based fertilizer 1 (MBF4), matrix-based fertilizer 3 (MBF5), and the slow release fertilizer Osmocote (14-14-14) (SRF) over 126 days.

Fertilizer	Rate	Nitrogen Applied	Phosphorus Applied	DRP	TP	NO_3	NH_4	Shoot Weight	Root Weight	Total Weight	Myc
		kg ha^{-1}			mg element L^{-1} water				g		%
Fertilizer not applied (Control)		0	0	3.86[e]	7.16[d]	8.45[f]	0.83[e]	21.82[d]	16.35[b]	38.18[e]	70[a]
Matrix Based Fertilizer 1 (MBF4)	Low	243	262	3.75[e]	6.60[d]	12.77[f]	0.39[e]	25.10[c]	16.69[b]	41.78[d]	80[a]
Matrix Based Fertilizer 3 (MBF5)	Low	121	235	3.44[e]	6.07[d]	5.73[f]	0.17[e]	28.27[c]	16.41[b]	44.69[d]	75[a]
Osmocote 14-14-14 (SRF)	Low	267	255	12.98[c]	11.90[bc]	173.77[c]	4.53[c]	50.23[b]	16.74[b]	66.97[bc]	60[a]
Matrix Based Fertilizer 1 (MBF4)	Moderate	486	524	3.91[e]	6.30[d]	30.44[e]	0.91[e]	30.16[c]	17.28[b]	47.44[d]	63[a]
Matrix Based Fertilizer 3 (MBF5)	Moderate	242	470	3.24[e]	5.42[d]	7.40[f]	0.24[e]	33.11[c]	17.01[b]	50.12[d]	73[a]
Osmocote 14-14-14 (SRF)	Moderate	534	510	20.91[b]	17.47[b]	258.16[b]	51.75[b]	54.68[b]	16.88[b]	71.56[b]	79[a]
Matrix Based Fertilizer 1 (MBF4)	High	729	786	7.05[d]	8.20[cd]	72.81[d]	3.61[d]	38.99[c]	17.29[b]	56.28[cd]	75[a]
Matrix Based Fertilizer 3 (MBF5)	High	363	705	7.16[d]	5.38[d]	11.07[f]	0.86[e]	30.33[c]	16.81[b]	47.15[d]	74[a]
Osmocote 14-14-14 (SRF)	High	801	765	27.29[a]	23.28[a]	402.68[a]	114.70[a]	69.73[a]	18.65[a]	88.02[a]	82[a]

[a] In each column, values followed by the same letter are not significantly different as determined by the least square means test ($P \leq .05$; $n = 6$). [b] Statistical comparisons of parameters in water are presented with regard to fertilizer × rate because interactions of fertilizer × rate × soil × week sampled, fertilizer × rate × soil, and fertilizer × rate × week sampled were not significant in the GLM model ($P \leq .05$; $n = 6$). [c] Percent (%) of fine roots infected with arbuscular mycorrhizae.

treatments because GLM models showed these interactions were significant at $P \leq .05$ [17, 18]. Plants given the SRF fertilizer had greater shoot, root and total biomass than plants given the MBF4 and MBF5 fertilizers (Table 4). When fertilizers were applied at the high rate, plants receiving MBF4 had decreased shoot and total biomass by 44% and 36%, respectively, compared to plants receiving SRF. Plants receiving MBF5 had decreased shoot biomass by 56% and decreased total biomass by 46% compared the plants receiving SRF. At the moderate rate plants growing in soils receiving SRF had greater shoot, root, and total biomass than all fertilizer formulations. Plants receiving MBF4 had decreased shoot and total biomass by 45% and 34%, respectively, compared to plants receiving SRF. Plants receiving MBF5 had decreased shoot biomass by 39% and decreased total biomass by 30% compared to plants receiving SRF. When fertilizers were applied at low, moderate, or

high rates, the concentrations of N, P were higher in shoot tissue than in shoot tissue of plants receiving MBF4 or MBF5. Arbuscular mycorrhazal infection in plant roots did not consistently differ among plants growing in soil receiving SRF and all MBF formulations and plants growing in soils receiving no fertilizer.

When applied at low moderate or high rates, after 126 days, SRF leachate contained a greater amount of DRP, TP, NO_3, and NH_4 than leachate from MBF4 and MBF5. At the low rate SRF leachate contained 71% more DRP, 45% more TP, 93% more NO_3, and 91% more NH_4 than leachate MBF4 columns. At the low rate SRF leachate contained 73% more DRP, 49% more TP, 97% more NO_3, and 96% more NH_4 than leachate MBF5 columns. At the moderate rate SRF leachate contained 81% more DRP, 64% more TP, 88% more NO_3, and 98% more NH_4 than leachate MBF4 columns. When fertilizers were applied at the moderate

rate SRF leachate contained 85% more DRP, 69% more TP, 97% more NO_3, and 99% more NH_4 than leachate MBF5 columns. When fertilizers were applied at the high rate SRF leachate contained 74% more DRP, 65% more TP, 82% more NO_3, and 97% more NH_4 than leachate MBF4 columns. When fertilizers were applied at the high rate SRF leachate contained 74% more DRP, 77% more TP, 97% more NO_3, and 99% more NH_4 than leachate MBF5 columns.

When fertilizers were applied at low, moderate, or high rates, the concentrations of N, P were higher in shoot tissue than in shoot tissue of plants receiving MBF4 or MBF5. When fertilizers were applied at low, moderate, or high rates the concentrations of K, Ca, Mg, Zn, Al and Na in shoot tissue did not differ (data not shown). When fertilizers were applied at low rate, the concentrations of N, P, K, Ca, Mg, Mn, Al, Zn, and Na in shoot tissue did not differ (data not shown). When fertilizers were applied at moderate rate the concentrations of N, K, Ca, Mg, Mn, Al, Zn, and Na in shoot tissue did not differ. When fertilizers were applied at high rate P concentration was higher in root tissue of plants receiving SRF than MBF4 or MBF5. When fertilizers were applied at high rate, the N concentration in root tissue was higher in plants receiving SRF and MBF4 than MBF5. When fertilizers were applied at low, moderate, or high rates, Fe concentration in root tissue was higher in plants receiving MBF5 than SRF or MBF4.

Correlations were determined using DRP, TP, NH_4, and NO_3 and days since fertilizers were applied to compare leaching rates among fertilizers. Correlation coefficients (R^2 values) were variable and ranged from 0.13 to 0.32 in the DRP and TP equations (data not shown). Correlation coefficients (R^2 values) were variable and ranged from 0.12 to 0.70 in the NO_3 and NH_4 equations (data not shown).

4. Discussion

When applied at low moderate or high rates, regardless of whether the fertilizers were pellets, banded, or broadcast, SRF leachate contained much greater amounts of NO_3, NH_4, DRP, and TP than leachate from MBF4 and MBF5. Correlations were determined using DRP, TP, NH_4, and NO_3 and days since fertilizers were applied to compare leaching rates among fertilizers. The correlation coefficients (r^2 values) were variable and usually low in the DRP, TP, and NH_4 correlations, but generally higher in the NO_3 correlations. The MBF fertilizers seem to prevent DRP, TP and NH_4 leaching better than NO_3 leaching. Statistical comparisons of DRP, TP, NO_3, and NH_4 leaching from the GLM models and mean separation and least square means tests gave similar results as the correlation equations. However, statistical comparisons of DRP, TP, NO_3, and NH_4 leaching from the GLM models and mean separation and least square means tests gave a higher degree of significance among means.

St. Augustine grass growing in soils receiving SRF had greater plant biomass shoot and root N and P content than all MBF formulations regardless of fertilizer form or the amount of fertilizer applied. St. Augustine grass growing in soils receiving SRF (Osmocote 14-14-14) had 33%–49% greater biomass than those growing in MBF formulations. Entry and Soka [6, 7] found similar results when Soft spring wheat, (*Triticum aestivum* L.) Kentucky bluegrass (*Poa pratensis* L.), and Kochia (*Kochia scoparia* L.) received (Osmocote 14-14-14) these same MBF fertilizers. However, plants growing in soils receiving SRF had 15%–55% greater plant biomass than those growing in MBF formulations [6, 7]. The growth rate of plants in soils receiving SRF was greater than those growing in soil receiving MBF formulations presumably because in soils receiving SRF, the nutrients were more available to the plant. The MBF formulations contained more N and P than the SRF fertilizers, but a significant amount of the nutrients were bound to the $Al_2(SO_4)_3 \cdot 18H_2O$ or $Fe_2(SO_4)_3 \cdot 3H_2O$-, starch-chitosan-lignin exchange matrix, and more slowly available to plants. A small fraction of N and P is probably immobilized in the matrix and only available to plants over months or years. Future studies need to modify the MBF fertilizer matrix to increase plant growth while reducing N and P leaching. When applied at low, moderate, or high rates Fe concentration in root tissue was higher in plants receiving MBF5 than SRF or MBF4 because Al and Fe are incorporated in the MBF fertilizers to reduce P leaching. In some crops higher plant Fe concentrations may be undesirable. Other phosphorus binding compounds such as $Al_2(SO_4)_3 \cdot 18H_2O$ could replace $Fe_2(SO_4)_3 \cdot 3H_2O$ in some MBF formulations.

Direct losses of P from fertilizer leaching or runoff usually result when fertilizer application is coincident with heavy rain events [19]. Our results imply that, even if the slow release fertilizers available on the market today were applied at rates to meet crop or turf P nutrition over a growing season and plants grew at their maximum potential, it would be difficult for them to take up a sufficient amount of fertilizer P to prevent leaching. Therefore, even if agricultural and turfgrass operators were to apply nutrients in amounts anticipated to meet plant requirements over the growing season, substantial amounts of N and P could be leached. The problem is made more severe because some turfgrass operators and homeowners often apply nutrients in quantities exceeding Plant requirements [20]. Several studies indicated that sediment bound P concentrations in runoff generally increase as soil P concentrations increase [21–24]. Long-term overfertilization of soils is recognized as potentially contributing to eutrophication of surface waters [15, 25].

Conventional SRF formulations such as single super phosphate (SSP), monoammonium phosphate (MAP), and diammonium phosphate (DAP) were developed with the goal of minimizing the production costs per unit of soluble P. The study of SSP, MAP, and DAP modification to reduce susceptibility to P runoff and leaching has been limited [23]. Slow-release fertilizers have been employed to reduce direct fertilizer runoff losses. Nutrient leaching from slow release fertilizers is reduced through degradation of an organic or inorganic coating around a core of inorganic fertilizer. Quin et al. [26] describe coating a DAP with a slurry of elemental sulfur which provides a short-term barrier

to water. Field trials demonstrated an approximately 40% reduction of P runoff during the first runoff event after application. Nash et al. [27] conducted laboratory dissolution studies comparing SSP and a dry sulfur-coated superphosphate, in which sulfate of ammonia was the binding agent. The authors found that the water-extractable P was greater than the coated superphosphate fertilizer treatments (6.6%) compared to 4.8% from superphosphate treatments. The rapid dissolution of the S-coated superphosphate resulted in the rapid solubilization of the sulfate of ammonia in the extraction procedure and with it removal of the sulfur coat and protection against P dissolution in the granules [24].

Commercial slow release fertilizers can be classified into two basic groups: low solubility and polymer-coated water soluble fertilizers [28]. The polymer-coated slow release fertilizers are water soluble and can exhibit consistent nutrient release rates. However average soil temperature and moisture need to be known. The fertilizers are characterized by one or more polymeric resins surrounding the fertilizer. The duration of nutrient release is controlled by the porosity of the resin coating. A more porous coating results in quicker release. When polymer-coated slow release fertilizers are applied to the soil, the water in the soil enters the fertilizer granule through micropores dissolving the nutrients. Nutrients are then steadily released through the same pores. The rates of nutrient release of polymer-coated slow release fertilizers are influenced by soil temperature; the higher the soil temperature, the greater the release rate [28]. Release rate is hypothesized to not be significantly influenced by microbiological decomposition, soil moisture, soil type, or pH. However, all polymers eventually degrade in soil [29–32] and the degradation rate influences nutrient release from the polymer.

The MBF formulations in our study cover a range of common inorganic nutrient compounds combined with $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ and the high ionic exchange compounds, starch, chitosan, and lignin. These formulations allow nutrients to bind with the $Al_2(SO_4)_3 \cdot 18 H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$-lignin-chitosan matrix substantially reducing leaching. Once N and P are bound to the $Al(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$-lignin-chitosan matrix, they become slowly available to plants over one or more growing seasons. After the starch-chitosan-lignin matrix with $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ is applied to soil, the soil microorganisms degrade the starch in the matrix comparatively rapidly creating some ionic exchange sites. The chitosan degrades less rapidly than starch but more rapidly than lignin and is expected to retain most of its ionic exchange sites for about a year in most soil environments. The lignin component in the matrix degrades more slowly than starch or chitosan and retains its ionic exchange sites for more than a year in most soil environments. Nutrient availability and leaching is expected to be controlled to a large degree by varying the relative amounts of starch-chitosan-lignin matrix with $Al_2(SO_4)_3 \cdot 18H_2O$ and/or $Fe_2(SO_4)_3 \cdot 3H_2O$ in the mixture. MBF application rates must be based on the amount of N and P released to meet plant growth. Therefore their application rates will necessarily not be comparable to

existing conventional or slow release fertilizers which because of more rapid availability, but also more leaching, are applied to soil based on the amount of nutrient in kg fertilizer ha^{-1} applied. Conventional rate calibration research for MBF fertilizers in field settings has not yet been performed.

Mycorrhizal colonization in plant roots did not differ among the unfertilized controls, SRF, MBF4, and MBF5 formulations. Entry and Soka [6, 7] found similar results. Mycorrhizal colonization was assessed at the termination of the experiment when roots were growing throughout the soil. *Glomus interadicies* is an arbuscular mycorrhizal fungi species that will form associations with a broad range of host plants in soils containing high concentrations of nitrogen and phosphorus. *Glomus interadicies* was added to the matrix to enhance plant uptake of N and P. In most soils arbuscular mycorrhizal spores are probably not necessary in the MBF formulations.

The impact of, MBF fertilizers to reduce N and P leaching in the field may not be less readily apparent in agricultural soils with loamy to clayey textures. Similarly agricultural production fields with long histories of high N or P rate applications would be less likely to exhibit changes in nutrient response or leaching results initially with conversion to MBFs because of nutrient enrichment in the soil [33–37]. Fertilizer N and P will also have become incorporated into organic matter complexes which will result in these nutrients being released as organic matter is decomposed [33, 34, 38]. The efficacy of MBF fertilizers to reduce N and P input to surface and ground water should be more apparent on highly leached sandy soils than soils containing high concentrations of silt, clay, or organic matter.

5. Conclusions

These new fertilizer formulations do not depend on organic or inorganic coatings to reduce N and P leaching and with further testing and development could be more effective than commercial fertilizers. The MBFs must be formulated to equal or improve plant growth relative to commercial fertilizers. Although further greenhouse and field testing are necessary, results of this initial investigation are promising. Cost estimates of these MBF fertilizers have been calculated to be $0.03–0.08 kg^{-1} above the cost of conventional fertilizers. One of the main goals of future research should be to reduce the cost of MBF production. MBFs initially may be economically feasible for use by homeowners on their lawns, turf grass operators such as golf course managers, nursery managers, and growers of high value agricultural crops. The MBF formulations could prove important in soils whose water drains into nutrient-affected watersheds such as Chesapeake Bay, Florida Everglades, and rivers flowing into the Great Lakes.

As nutrients are applied to a soil they can accumulate to the maximum retention capacity of the soil, which is controlled by soil physical and chemical properties, the resident biota, and the rate of nutrient uptake by vegetation. Excessive application of any fertilizer eventually will load soil beyond its maximum retention capacity. Nutrients added to the soil above that limit via any mode of application

eventually can be released to water flowing over and/or through the soil. Improved technology cannot substitute fully for adhering to sound land management practices. In the long term N and P contamination of water can be prevented only by applying nutrients in quantities relative to the inherent capacity of the soil to retain nutrients and the quantities removed via harvest. However, new MBF formulations that release nutrients at a rate comparable to plant uptake can help reduce nutrient leaching and ultimately eutrophication.
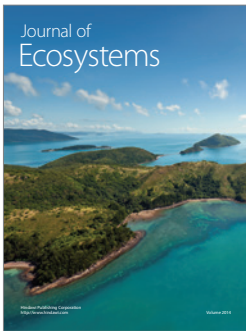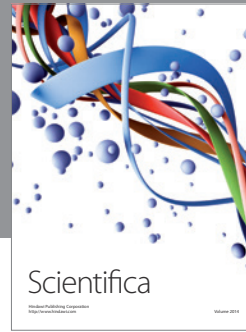
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