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Matrix-Based Fertilizers Reduce Nutrient Leaching While Maintaining Kentucky Bluegrass Growth

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Abstract We tested the efficacy of matrix-based fertilizers (MBFs) to improve Kentucky bluegrass (*Poa pratensis* L.) growth while reducing NH, NO_3, dissolved reactive phosphorus (DRP), and total phosphorus (TP) compared to commercial slow-release fertilizer (SRF) Polyon®, ESN®, and Avail® in greenhouse column studies. The MBFs covered a range of inorganic N and P in compounds that are relatively loosely bound (MBF6) and more tightly bound compounds (MBF7) with $Al(SO_4)_3 18H_2O$ and/or $Fe_2(SO_4)_3 3H_2O$ and with high ionic exchange compounds starch, cellulose, and lignin. The total amount of NO_3 and NH_4 leached was greater from columns receiving Polyon® and ESN® fertilizers than all other treatments. The MBF6+Avail® or MBF7+Avail® fertilizers leached 64–68% less NO_3 than Polyon® (43-0-0) and ESN® (46-0-0), and 73–76% less TDP and TP than Avail® (10-34-0). A greater amount of NO_3 was leached from the MBF6+Avail® and the MBF7+Avail® treatments than the other MBF fertilizer treatments. Shoot and root biomass were greater when plants received the Avail®, MBF6+Avail®, and MBF7+Avail® fertilizer treatments than the other fertilizer treatments. When combined with small quantities of commercial SRFs, these new MBFs were able to maintain plant growth while reducing N and P leaching. These new MBF formulations do not depend on organic or inorganic coatings to reduce N and P leaching and with further testing and development could be effective commercial fertilizers.

Keywords Matrix-based fertilizers · Starch · Cellulose · Lignin aluminum sulfate · Iron sulfate

1 Introduction

Eutrophication is widespread and rapidly expanding in fresh surface waters and coastal seas of the developed world. In most temperate lakes, streams, and coastal ecosystems, N or P are the elements most limiting to production of plant material such as algae. The incidence of harmful algal blooms in lakes, streams, and coastal oceans has dramatically increased in recent years (Bricker et al. 1999). Transport of P from agricultural soils to surface waters has been linked to eutrophication in freshwater and estuaries (Owens and Shipitalo 2006; Bush and Austin 2001; Broesch et al. 2001; Daniel et al. 1998). 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.

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We developed matrix-based fertilizers (MBFs) that reduced NH_4, NO_3, dissolved reactive phosphate (DRP), and total P (TP) leaching in column studies. The MBF formulations in our studies cover a range of common inorganic nutrient compounds combined with $Al(SO_4)_3$ $18H_2O$ and/or $Fe_2(SO_4)_3$ $3H_2O$, plus starch, cellulose, and lignin. Starch, cellulose, and lignin were chosen because of their high concentration of ionic exchange sites and their decomposition characteristics. The $Al(SO_4)_3 18H_2O$ and/or $Fe_2(SO_4)_3$ $3H_2O$ were added to the MBFs to complex with N and P and to also bind with the starch–cellulose and lignin matrix, increasing N and P immobilization sites. Nutrients bound to the $Al(SO_4)_3 18H_2O$ and/or $Fe_2(SO_4)_3 3H_2O$–starch–cellulose–lignin matrix become increasingly available to plants as the matrix components degrade. The organic components in the matrix should degrade starch > cellulose > lignin in the order of more to less rapid (Donnelly et al. 1990; Entry et al. 1991). We chose not to formulate MBFs using nutrient–Cl compounds because in water, chloride can react with O_2 to form hypochlorous acid and hypochlorites (Öberg 2002; Ayers 1997) which combine with organic matter to form a wide range of chloroamines (Xue et al. 2008; Ivahnenko and Barbash 2004). These can have carcinogenic effects (Geter et al. 2004; Zeighami et al. 1990), retard fetal growth (Bove et al. 2007; Porter et al. 2005; Whitaker et al. 2005) and increase low-serum cholesterol and low-density lipoprotein (Nieuwenhuijsen et al. 2000) in humans.

In previous experiments, Osmocote® 14-14-14 a slow-release fertilizer (SRF), combined with $Al(SO_4)_3 18\ H_2O$ and $Fe(SO_4)_3$ $3H_2O$, leached 78–84% more NH_4, 58–78% more TP, and 61–77% more DRP than MBF formulations (Entry and Sojka 2007, 2008). The SRF treatment leached 34% less NO_3, than MBF7. Total plant weight did not differ among fertilizer treatments. Entry and Sojka (2007) 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 (*Triticum aestivum* L.) plants growing in soils receiving SRF had greater shoot, root, and total biomass than all MBF formulations. Entry and Sojka (2007) and Sojka and Entry (2007) found that SRF leachate contained a greater amount of NO_3, NH_4, DRP, and TP than leachate from MBFs regardless of fertilizer rate, or whether fertilizers were broadcast, banded, or applied as pellets. Despite improvements in losses of nutrients, St Augustine grass growing in soils receiving MBFs decreased shoot biomass by 49% to 56% and had decreased total biomass by 33% to 46% compared to SRF. We recognized the need to identify MBF formulation strategies that retained the ability to reduce nutrient leaching, but which enabled optimal plant growth, yield, and quality.

The MBFs must be formulated to equal or improve plant growth relative to commercial fertilizers. The MBFs bind nutrients to the $Al(SO_4)_3 18H_2O$ and/or $Fe_2(SO4)_3 3H_2O$–starch–cellulose–lignin matrix and application rates are based on nutrients released to meet plant growth. Therefore, MBF application rates (based on N and P analysis of the mixtures) will not be comparable to conventional or slow-release fertilizers which release nutrients in more direct relationship to the amount of nutrient applied. In this respect, the concept and mode of action of MBFs is a synthetic analog of the kind of nutrient release that occurs with nutrients in manure sources. In this study our objectives were to determine the efficacy of the matrix-based fertilizers with and without additional slow-release fertilizers to improve Kentucky bluegrass (*Poa pratensis* L.) growth while reducing NH_4, NO_3, dissolved reactive phosphorus (DRP), and total phosphorus (TP) leaching.

2 Materials and Methods

2.1 Fertilizer Treatments

The MBF formulations are comprised of inorganic chemicals combined with starch, cellulose, and lignin (Sigma, St. Louis, MO). Treatment 1 was a control; no fertilizer was applied to the columns (Table 1). Treatment 2 was 3.0 g of Polyon® (43-0-0) slow-release fertilizer which was equal to 338.7 mg N and 0 mg P per column and 191 kg N ha^{-1} and 0 kg P ha^{-1}. Treatment 3 was 3.0 g of ESN® (46-0-0) slow-release fertilizer which was equal to 242 mg N and 0 mg P per column and 202 kg N ha^{-1} and 0 kg P ha^{-1}. Treatment 4 was 3.0 g of the Avail® (10-34-0) slow-release fertilizer which was equal to 105 mg N and 445 mg P per column and 133 kg N ha^{-1} and 557 kg P ha^{-1}. Treatment 5 was MBF6 applied at a rate of 200 mg N and 149 mg P per column and 255 kg N ha^{-1} and 189 kg P ha^{-1}. Treatment 6 was

Table 1 Chemical compounds used to comprise the slow-release fertilizers, Polyon®, ESN®, and Avail®, and the matrix-based fertilizers with and without additional Avail®

Treatment	1	2	3	4	5	6	7	8
Fertilizer rate	CONT	Polyon®	ESN®	Avail®	MBF6	MBF7	MBF6 Avail®	MBF7 Avail®
mg compound per column								
NH_4 NO_3	000.0	860.0	920.0	300.0	000.0	000.0	000.0	000.0
P_2O_5	000.0	000.0	000.0	1020.0	400.0	120.0	400.0	120.0
K_2O	000.0	000.0	000.0	180.0	360.0	180.0	360.0	180.0
$Ca(NO_3)_2$ $4H_2O$	000.0	000.0	000.0	000.0	472.0	472.0	472.0	472.0
$Al(NO_3)_3$ $9H_2O$	000.0	000.0	000.0	000.0	750.0	750.0	750.0	750.0
$NH_4(H_2PO_4)$	000.0	000.0	000.0	000.0	310.0	230.0	310.0	230.0
$Ca(H_2PO_4)_2$	000.0	000.0	000.0	000.0	000.0	468.0	000.0	468.0
Fe (P_2O_7)	000.0	000.0	000.0	000.0	334.0	334.0	334.0	334.0
$Al(PO_4)_3$	000.0	000.0	000.0	000.0	000.0	360.0	000.0	360.0
$Al(SO_4)_318H_2O$	000.0	000.0	000.0	000.0	000.0	366.0	000.0	366.0
$Fe_2(SO_4)_3$ $3H_2O$	000.0	000.0	000.0	000.0	800.0	800.0	800.0	800.0
$Al(OH_4)_33H_2O$	000.0	000.0	000.0	000.0	1.000	1.000	1.000	1.000
Starch	000.0	000.0	000.0	0.000	1,000	1.000	1.000	1.000
Cellulose	000.0	000.0	000.0	0.000	1.000	1.000	1.000	1.000
Lignin	000.0	000.0	000.0	0.000	1.000	1.000	1.000	1.000
Total mg N column	000.0	338.7	242.0	105.0	200.0	107.0	235.0	142.0
Total mg P column	000.0	000.0	000.0	445.0	149.0	435.0	297.0	583.0
Total N kg N ha^{-1}	000.0	191.0	202.0	133.0	255.0	136.0	299.0	180.0
Total P as kg P ha^{-1}	000.0	000.0	000.0	557.0	189.0	554.0	275.0	740.0

MBF7 applied at a rate of 107 mg N and 435 mg P per column and 136 kg N ha^{-1} and 554 kg P ha^{-1}. Treatment 7 was MBF6 applied at a rate of 200 mg N and 149 mg P per column and 255 kg N ha^{-1} and 189 kg P ha^{-1}+1.0 g Avail®, which is equal to 35 mg N and 148 mg P per column and 44 kg N ha^{-1} and 186 kg P ha^{-1} for a total of 235 mg N and 297 mg P per column and 299 kg N ha^{-1} and 275 kg P ha^{-1}. Treatment 8 was MBF7 applied at a rate of 107 mg N and 435 mg P per column and 136 kg N ha^{-1} and 554 kg P ha^{-1} + 1.0 g Avail®, which is equal to 35 mg N and 148 mg P per column and 44 kg N ha^{-1} and 186 kg P ha^{-1} for a total of 142 mg N and 583 mg P per column and 180 kg N ha^{-1} and 740 kg P ha^{-1}.

2.2 Column Description

A screen with 2.00-mm wire spacing was cut into squares (125×125 mm) and secured at the bottom of each 10-cm diameter×30-cm long polyvinyl chloride cylinder. A 10-cm diameter polyvinyl screen with 0.10-mm mesh was then placed on at the bottom of each 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 h prior to the start of leachate collection as described below. The soil was a coarse-loamy sand and classified as a mixed non-acid, mesic Xeric Torriorthent. Soil physical and microbiological properties are presented in (Sojka et al. 2005; Entry et al. 2004).

2.3 Experimental Design

The experiment was arranged in a completely randomized design (Kirk 1995) with eight fertilizer treatments (described above) by nine replications for a total of 90 columns planted with Kentucky bluegrass. We collected and analyzed leachate at 30, 60, 90, 120, 150, 180, and 210 days for a total of 504 leachate measurements.

2.4 Fertilizer Placement, Growing Conditions, and Harvest

The MBF formulations were added as a powder, and slow-release fertilizers (Polyon®, ESN® and Avail®) were added as granular pellets and broadcast into the top 5 cm of soil (Fig. 1; Table 1). We then placed a 2×2-cm starter patch (approximately 10 g) of Kentucky bluegrass on top of each column. Plants were watered with 100 mL of water daily to maintain field capacity. Leachate did not flow through columns when 100-mL water was applied. We collected leachate at 30, 60, 90, 120, 150, 180, and 210 days after fertilizer placement 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. Subsamples were analyzed for NO_3, NH_4, DRP, and TP as described below. Throughout the experiment plants were exposed to light having a photosynthetic active radiation of 400–1,000 mol m^{-2} s^{-1} and a 14–16-h photoperiod. 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. Shoot and root tissue were dried at 80°C for 48 h and weighed for biomass.

2.5 Chemical Analysis

Leachate was Analyzed for NO_3 and NH_4 Using a Lachat Automated Ion Analyzer (Quickchem 8000 Systems, Milwaukee, WI) following methods described in APHA (1998). Total P and DRP in leachate were determined by digesting 25 mL aliquots in an autoclave at 103.5 kPa and 121°C for 60 min with 4.0-mL acidified ammonium persulfate (APHA 1998). Three samples from each soil type were dried at 65EC for 72 h and passed through a 2-mm sieve. Total N was determined using standard microkjeldahl procedures modified for NO_3 (Bremmner 1996). After drying and weighing, plant root and shoots were 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 500°C, 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 (Perkin-Elmer, Boston, MA).

2.6 Statistical Analysis

All data sets were tested for normal distribution with Statistical Analysis Systems (SAS Institute Inc. 2001) and then analyzed using general linear models (GLM) procedures for a completely random design. In all analyses, residuals were equally distributed with constant variances. Differences reported throughout are significant at a $p \leq 0.05$, as determined by the least squares means test. The GLM models of nutrients leached for fertilizer type × sample day were significant, therefore, statistical comparisons of NO_3, NH_4, DRP, and TP fertilizer type × sample day were performed (Kirk 1995; Snedecor and Cochran 1994).

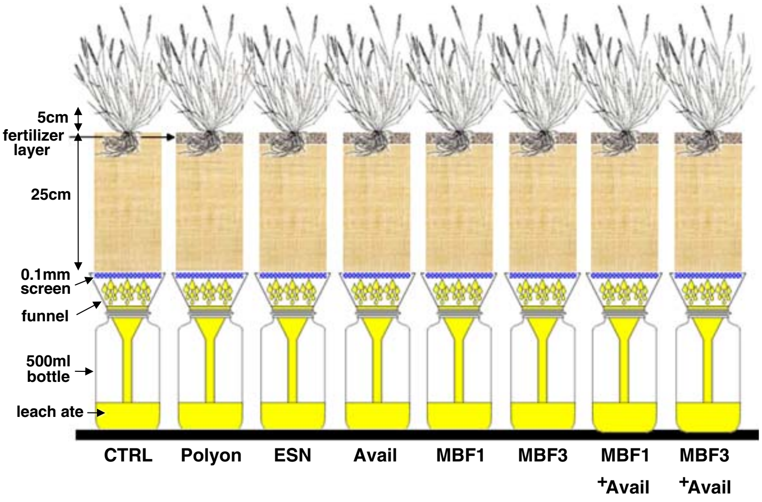

Fig. 1 Diagram of the column apparatus

3 Results

3.1 Total Nutrients Leached Among Fertilizer Treatments

Columns receiving MBF7+Avail® had less N (180 kg N ha^{-1}) applied than columns receiving Polyon® (191 kg N ha^{-1}; Table 1), and ESN®, (202 kg N ha^{-1}) but leached at least 84% NO_3 and 70% less NH_4 while maintaining plant growth. Columns receiving MBF7 + Avail® had more P (740 kg P ha^{-1}) applied than columns receiving Avail® (557 kg P ha^{-1}), but leached 73% less DRP and 74% less TP while maintaining plant growth (Table 2). Columns receiving MBF6+Avail® had more N (299 kg N ha^{-1}) applied than columns receiving Avail® (133 kg N ha^{-1}), but leached a similar amount of NO_3 and 38% less NH_4 while maintaining plant growth. Columns receiving MBF6+Avail® had less P (275 kg P ha^{-1}) applied than columns receiving Avail® (557 kg P ha^{-1}), but leached 76% less DRP and 73% less TP while maintaining plant growth (Table 3). Columns receiving MBF7 had a similar amount of N applied (136 kg N ha^{-1}) than columns receiving Avail® (133 kg N ha^{-1}), but leached at least 84% less NO_3 and 64% less NH_4. Columns receiving MBF7 had nearly the same amount of P (554 kg P ha^{-1}) applied as columns receiving Avail® (557 kg P ha^{-1}), but leached 97% less DRP and 93% less TP.

3.2 Nutrients Leached at Sampling Times

Thirty and 60 days after planting, the amount of NO_3 leached was greater from columns receiving the MBF treatments and was not consistently different than columns receiving the slow-release fertilizer treatments. Ninety, 120, and 150 days after planting the amount of NO_3 leached was greater from columns receiving Polyon® and ESN® fertilizers than all other treatments. At 120 and 150 days after planting a greater amount of NO_3 was leached from columns receiving the MBF6+Avail® than MBF7+Avail®. The total amount of NH_4 leached at each date was greater from columns receiving Polyon® and ESN® than all other treatments. In the columns that received Polyon® and ESN®, 75–78% of the total amount NO_3 and 68–72% of the total amount NH_4 leached from columns was leached in the first 120 days after

Table 2 Mean nitrate (NO_3) and ammonium (NH_4) concentrations in reverse osmosis water leached through columns of a sandy loam amended with the slow-release fertilizers, Polyon®, ESN®, and Avail®, and the matrix-based fertilizers with and without additional Avail®[a]

Fertilizer	Day 30		Day 60		Day 90		Day 120		Day 150		Day 180		Day 210		Total leached	
	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4	NO_3	NH_4
mg L^{-1} leachate																
Control	3.94 e	0.00 c	4.15 d	0.02 c	3.52 d	0.05 b	1.17 de	0.04 d	0.43 c	0.05 b	0.19 c	0.21 a	0.10 b	0.02 b	13.33 e	0.39 d
Slow-release fertilizer Polyon®	64.83 d	0.24 a	124.53 b	1.46 a	218.44 a	0.12 a	838.67 a	0.69 a	315.56 a	0.68 a	27.21 a	0.26 a	3.84 a	0.07 a	1593.08 a	3.51 a
Slow-release fertilizer ESN®	134.25 c	0.31 b	247.33 a	1.06 a	256.00 a	0.19 a	411.11 b	0.21 b	339.89 a	0.55 a	6.50 b	0.19 a	0.75 b	0.10 a	1395.85 a	2.60 a
Slow-release fertilizer Avail®	68.37 d	0.90 a	243.31 a	0.46 b	128.11 b	0.18 a	57.35 c	0.28 b	6.19 b	0.19 b	3.02 b	0.06 b	0.07 b	0.03 b	506.44 b	2.11 b
Matrix-based fertilizer 6	231.44 b	0.01 c	113.03 b	0.12 c	27.41 c	0.02 b	2.98 d	0.03 c	0.06 c	0.07 b	0.01 c	0.17 a	0.02 b	0.01 b	374.95 c	0.43 d
Matrix-based fertilizer 7	56.66 d	0.00 c	19.73 c	0.39 bc	3.43 d	0.04 b	0.19 e	0.07 c	0.03 c	0.07 b	0.01 c	0.16 a	0.01 b	0.00 b	80.06 d	0.75 d
Matrix-based fertilizer 6+Avail®	262.67 a	0.04 c	207.78 a	0.84 ab	31.12 c	0.06 b	5.20 d	0.13 cd	2.29 b	0.14 b	0.63 c	0.09 b	0.22 b	0.01 b	509.91 b	1.31 c
Matrix-based fertilizer 7+Avail®	105.71 c	0.01 c	100.56 b	0.22 bc	20.70 c	0.07 b	0.63 e	0.02 d	0.21 c	0.13 b	0.15 c	0.08 b	0.12 b	0.01 b	228.08 c	0.54 d

[a] In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=9$).

Table 3 Mean total phosphorus (TP) and total dissolved phosphorus (TDP) concentrations in reverse osmosis water leached through columns of a sandy loam soil amended with the slow-release fertilizers, Polyon®, ESN®, and Avail®, and the matrix-based fertilizers with and without additional Avail®[a]

Fertilizer	Day 30		Day 60		Day 90		Day 120		Day 150		Day 180		Day 210		total leached	
	DRP	TP	DRP	TP	DRP	TP	DRP	TP	DRP	TP	DRP	TP	DRP	TP	DRP	TP
mg L^{-1} leachate																
Control	0.68 b	2.45 b	0.90 b	2.20 b	0.77 b	0.94 b	0.57 b	0.79 d	0.41 c	0.65 c	0.30 c	0.34 d	0.33 d	0.29 d	3.96 c	7.49 c
Slow-release fertilizer Polyon®	0.92 b	2.19 b	0.22 b	1.26 b	0.14 c	0.53 b	0.01 c	0.77 d	0.03 c	0.51 c	0.02 c	0.14 d	0.01 d	0.04 d	1.35 d	5.42 c
Slow-release fertilizer ESN®	0.98 b	2.25 b	0.16 b	0.96 b	0.15 c	0.73 b	0.09 c	0.68 d	0.11 c	0.63 c	0.40 c	0.12 d	0.04 d	0.06 d	1.05 d	5.41 c
Slow-release fertilizer Avail®	13.13 a	14.92 a	6.42 a	14.30 a	4.82 a	16.74 a	3.89 a	13.52 a	7.30 a	10.37 a	5.49 a	6.15 a	5.51 a	5.91 a	46.57 a	81.92 a
Matrix-based Fertilizer 6	0.16 c	1.87 b	0.16 b	1.13 b	0.20 c	0.66 b	0.16 c	0.56 d	0.08 c	0.42 c	0.05 c	0.15 d	0.04 d	0.04 d	0.85 d	4.81 c
Matrix-based fertilizer 7	0.18 c	1.94 b	0.19 b	1.50 b	0.30 c	0.65 b	0.25 c	0.52 d	0.19 c	0.46 c	0.21 c	0.28 d	0.20 d	0.21 d	1.52 d	5.57 c
Matrix-based fertilizer 6+Avail®	0.04 c	2.86 b	0.19 b	1.55 b	0.31 c	0.96 b	3.18 a	8.54 d	3.45 b	5.03 b	2.32 b	1.26 c	1.74 c	1.92 c	11.22 b	22.01 b
Matrix-based fertilizer 7+Avail®	0.05 c	2.11 b	0.22 b	1.39 b	0.28 c	0.67 b	2.60 a	6.06 c	4.06 b	5.83 b	2.50 b	2.51 b	2.47 b	2.63 b	12.19 b	21.20 b

[a] In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \le 0.05$, $n=9$).

planting. In the columns that received Avail®, 95–99% of the total NO_3 and 68–72% of the total amount NH_4 leached was leached from columns after 120 days. Except for DRP on day 120, at all sampling days, columns receiving Avail® leached greater amounts of DRP and TP than columns receiving all other fertilizers. Columns that received MBF6+Avail® and MBF7 + Avail® leached greater amounts of DRP and TP than columns receiving MBF6 and MBF7. In the columns that received Avail®, 60% of the total amount DRP and 72% of the total amount of TP leached from columns was leached in the first 120 days after planting. In contrast, columns that received MBF6+ Avail® and MBF7 + Avail® leached 33% and 26% of the total amount DRP leached from columns was leached in the first 120 days after planting. In the columns that received MBF6+Avail® and MBF7+ Avail®, 63% and 48% of the total amount TP leached from columns was leached in the first 120 days after planting.

3.3 Plant Growth and Nutrients Leached mg^{-1} Nutrient Applied

When Avail® and MBF7 + Avail® were applied to columns, we found a greater amount of total plant and shoot growth mg^{-1} of total N applied than when all other fertilizers were applied (Table 4). There was a greater amount of total plant growth mg^{-1} of P when MBF6+ Avail® was applied to columns than when all other fertilizers were applied. There were greater amounts of NO_3, DRP, and TP leached mg^{-1} plant growth when Polyon®, ESN®, and Avail® were applied to columns than when MBFs were applied (Table 5). There were greater amounts of NO_3, DRP, and TP leached mg^{-1} of plant growth when Avail® was applied to columns than when MBFs were applied. There was a greater amount of NH_4 leached mg^{-1} of plant growth when Polyon®, ESN® Avail® was applied to columns than when MBFs were applied.

3.4 Nutrient Concentration in Plant Tissue

The N concentration in Kentucky bluegrass shoots was higher when plants received Polyon® and ESN® than in shoots when plants received the other fertilizer treatments (data not shown). The P concentration was higher in grass shoots when plants received Avail®

Table 4 Total plant growth and shoot growth of Kentucky bluegrass, (*Poa pratensis* L.) mg ha^{-1} nutrient applied

Fertilizer	mg nutrients applied[a]				g total plant growth mg nutrients applied[a]		g shoot growth mg nutrients applied[a]	
	TN	NO_3	NH_4	P	TN	P	TN	P
Control	000.0	000.0	000.0	000.0	0.00	0.00	0.00	0.00
Slow-release fertilizer Polyon®	338.7	000.0	338.7	000.0	0.31 c	0.00	0.12 b	0.00
Slow-release fertilizer ESN®	242.0	000.0	242.0	000.0	0.37 c	0.00	0.20 b	0.00
Slow-release fertilizer Avail®	55.0	27.5	27.5	445.0	1.87 a	0.44 b	1.17 a	0.28 a
Matrix-based fertilizer 6	200.0	165.0	35.0	149.0	0.30 c	0.40 b	0.14 b	0.19 a
Matrix-based fertilizer 7	107.0	71.0	36.0	435.0	0.59 b	0.12 c	0.25 b	0.06 b
Matrix-based fertilizer 6+Avail®	235.0	187.0	48.0	297.0	0.99 b	0.78 a	0.36 b	0.29 a
Matrix-based fertilizer 7+Avail®	142.0	92.0	50.0	583.0	1.64 a	0.30 c	1.04 a	0.25 a

[a] In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=9$).

than in shoots when plants received the other fertilizer treatments. The Al and Fe concentrations in plant shoots were not consistently higher when plants received MBFs with or without additional Avail® compared to plants that received Polyon®, ESN®, and Avail®. The K, Ca, Mg, Mn, Cu, B, and Zn concentrations in root and shoot tissue did not differ among fertilizer treatments. The N concentration in Kentucky bluegrass roots was higher when plants received Polyon® and ESN® than in shoots when plants received the other fertilizer treatments (data not shown). The N concentration in roots was lower when plants received the MBF6 and MBF7 than when plants received the other fertilizer treatments. Shoot, root, and plant biomass was greater when plants received the Avail®, MBF6+Avail®, and MBF7+Avail® fertilizers than when they received the other fertilizer treatments (Figs. 2, 3, and 4). Plant biomass was greater when plants received Avail®, MBF6+Avail®, and MBF7+Avail® than Polyon®, ESN®, and MBF6 and MBF7.

4 Discussion

The growth of Kentucky bluegrass receiving MBF6+Avail ® and MBF7+Avail® was not significantly different than plants receiving Avail® fertilizer and greater than plants receiving Polyon® and ESN® (N only) fertilizers. Entry and Sojka (2007) found that soft spring wheat (*T. aestivum* L.) plants fertilized with MBF6 and MBF7 at low, moderate, or high rates did not produce as much plant biomass as when fertilized with (Osmocote® 14-14-14). To maximize plant growth the MBFs seem to need some portion of the formulation to be a readily available nutrient source. When readily available N and P are supplied as conventional slow-release fertilizers such as Osmocote®, Avail®, Polyon®, and ESN® substantial N and or P leaching occurs within the first 30–120 days after application. In this study, MBF6+Avail® or MBF7+Avail® treatments received both more and less N and P than Polyon®, ESN®, and Avail®, maintained plant growth, but after 210 days, in most columns, the MBF6+Avail® or MBF7+Avail® treatments leached substantially less NO_3, NH_4, DRP, and TP than the slow-release N fertilizers Polyon®, ESN®, and Avail®.

The MBFs must be formulated to equal or improve plant growth relative to commercial fertilizers. The MBFs bind nutrients to the $Al(SO_4)_3 18H_2O$- and/or $Fe_2(SO_4)_3 3H_2O$–starch–cellulose–lignin matrix and application rates are based on nutrients released to meet plant growth, therefore their application rates (based on N and P analysis of the mixtures) will not be comparable to conventional or slow-release fertilizers which release nutrients in more direct relationship to the amount of nutrient applied. In this respect the concept and mode of action of MBFs is a synthetic analog of the kind of nutrient release that occurs with nutrients in manure sources. Fertilizers were applied at recommended quantities to attain maximum plant growth and therefore not necessarily

Table 5 Nutrients leached from columns Mg ha^{-1} nutrient applied

Fertilizer	Nutrients applied[a]				Nutrients leached g^{-1} plant growth[a]					Nutrient leached mg^{-1} nutrient applied[a]				
	TN mg^{-1} nutrient applied	NO_3	NH_4	P	TN mg nutrient leached mg^{-1} plant growth	NO_3	NH_4	DRP	TP	TN mg nutrient leached mg^{-1} mg^{-1} nutrient applied	NO_3	NH_4	DRP	TP
Control	0	0	0	0	1.736 c	1.687 d	0.049 c	0.501 a	0.948 a	000.0 d	000.0	000.0	000.0	0.000
Slow-release fertilizer Polyon®	338.7	0	338.7	0	15.411 a	15.333 b	0.285 a	0.013 d	0.052 c	4.699 a	000.0	4.699 a	000.0	0.000
Slow-release fertilizer ESN®	242	0	242	0	15.556 a	15.880 b	0.296 a	0.117 c	0.061 c	5.768 a	000.0	5.768 a	000.0	0.000
Slow-release fertilizer Avail®	105	27.5	27.5	445	2.589 c	26.515 a	0.011 c	0.238 b	0.417 b	4.843 a	18.757 a	0.780 b	0.104 a	0.184 a
Matrix-based fertilizer 6	200	165	35	149	6.351 b	6.344 c	0.007 c	0.014 d	0.081 c	1.872 b	2.272 b	0.122 c	0.005 c	0.032 b
Matrix-based fertilizer 7	107	71	36	435	1.504 c	1.491 d	0.139 b	0.028 d	0.103 c	0.755 c	1.127 b	0.021 c	0.004 c	0.121 b
Matrix-based fertilizer 6+Avail®	235	187	48	297	2.107 c	2.101 d	0.005 c	0.046 d	0.091 c	2.175 b	2.726 b	0.027 c	0.038 b	0.075 b
Matrix-based fertilizer 7+Avail®	142	92	50	583	0.982 c	0.980 d	0.002 c	0.052 d	0.091 c	1.610 b	2.479 b	0.010 c	0.020 b	0.036 b

[a] In each column, values followed by the same letter are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=9$).

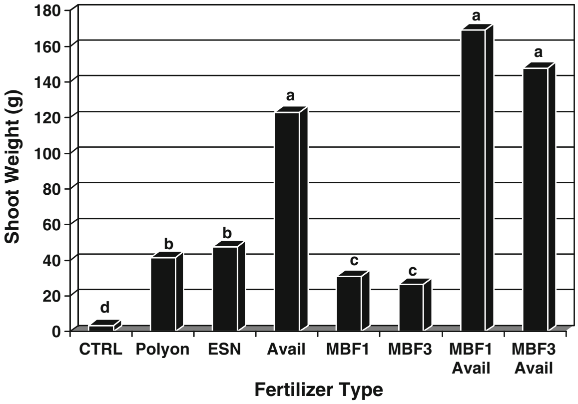

Fig. 2 Shoot weight of Kentucky bluegrass (*Poa pratensis*) after 210 days grown in soil treated with the slow-release fertilizers Polyon®, ESN®, Avail®, and MBF6 and MBF7 with and without additional Avail®. *Bars* with the *same letter* are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=9$)

at equal N and P rates. The MBFs differ in regard to commercial slow-release fertilizers in that they are comprised of chemicals having differing N and P solubility. To attain maximum plant growth, the more soluble nutrients in Avail®, Polyon®, and ESN® are applied in excess of plant uptake and the ability of the soil to retain them on soil ion exchange sites and are therefore leached (Entry and Sojka 2007, 2008). When MBFs are applied to a soil, nutrients are also applied in excess of plant uptake; however, the more soluble nutrients are bound by the Al $(SO_4)_3 18H_2O$–

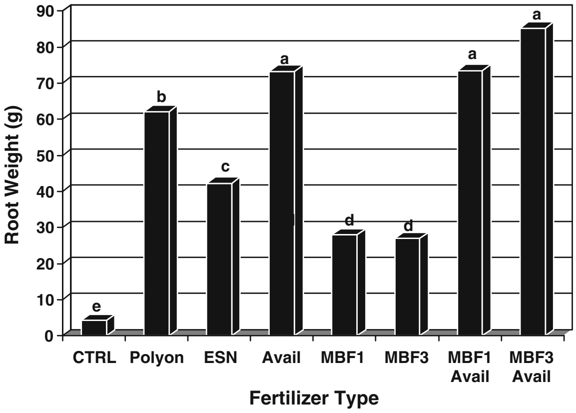

Fig. 3 Root weight of Kentucky bluegrass (*Poa pratensis*) after 210 days grown in soil treated with the slow-release fertilizers Polyon®, ESN®, Avail®, and MBF6 and MBF7 with and without additional Avail®. *Bars* with the *same letter* are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=9$)

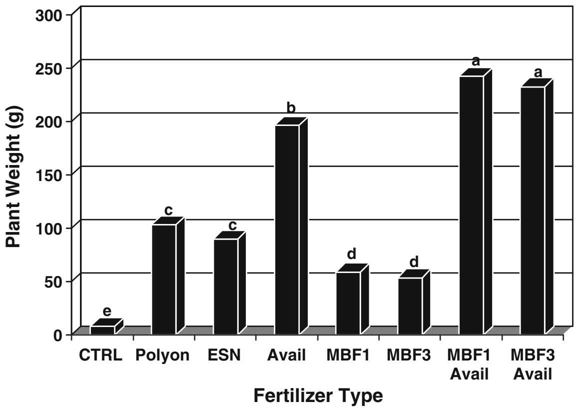

Fig. 4 Plant weight of Kentucky bluegrass (*Poa pratensis*) after 210 days grown in soil treated with the slow-release fertilizers Polyon®, ESN®, Avail®, and MBF6 and MBF7 with and without additional Avail®. *Bars* with the *same letter* are not significantly different as determined by the least square means test ($p \leq 0.05$, $n=9$)

$Fe_2(SO_4)_3 3H_2O$–starch–cellulose–lignin matrix. The amount of soluble and less soluble nutrients are based on the amount of each nutrient available for plant growth; therefore, their application rates (based on N and P analysis of the mixtures) are not comparable to conventional or slow-release fertilizers which release nutrients in more direct relationship to the amount of nutrient applied.

We analyzed plant growth mg^{-1} nutrient applied to more accurately compare plant growth from each fertilizer on a more equal basis. Regardless of the rate of MBF application, much of the N and P applied in the MBF fertilizers remained unavailable for plant uptake for the duration of the study (Entry and Sojka 2007, 2008). To obtain maximum plant growth, the MBFs must be supplied with an additional amount of more soluble N and P without increasing leaching. By analyzing results as mg nutrient leached mg^{-1} nutrient applied, we show that these nutrients are not leached. In contrast, total plant and shoot growth g^{-1} total N and P applied to the soil from MBFs was lower than Avail® alone; however, much of the N and P in Avail® was lost to leaching and thus was both unavailable for plant uptake and vulnerable to transport to surface waters.

The MBFs+Avail® resulted in the same plant growth rate as Avail® with a substantial decrease in NO_3, NH_4, DRP, and TP leached. Total plant and shoot growth g^{-1} total N and P applied to the soil from MBFs did not differ with regard to Avail®. However, greater quantities of NO_3, NH_4, DRP, and TP $mg^{-1}$of each nutrient applied were leached from soil when Avail® was applied to soil than when all other fertilizers were applied. Polyon® and ESN® do not contain P, therefore, when Polyon® and ESN® were applied to soil, shoot growth expressed as shoot weight was not as great as when Avail®, MBF6 + Avail®, and MBF67+Avail®, which contain both N and P, were applied, presumably due to a lack of available P. However, greater quantities of NO_3 and NH_4 mg^{-1} were in leachate when Polyon® and ESN® were applied than when all of the MBFs were applied. The MBFs should also slowly release additional N and P during the growing season without additional fertilizer application. In this experiment the MBFs, were applied at both higher and lower amounts of N than Polyon® and ESN® and Avail®, but only lower amounts of P than Avail®. Traditional studies where the total amount of N and P in the MBFs and commercial slow-release fertilizers are applied at equal N and P application rates to several soils would more accurately compare plant growth and leaching and are necessary to confirm these results.

We could have incorporated more readily available N and P sources directly into the MBFs and possibly achieved a similar result. We hypothesized that adding Avail® would result in less N and P leaching by taking advantage of the slow-release capabilities of Avail® compared to adding NO_3, NH_4, or the non-slow-release fertilizers, single super phosphate (SSP), monoammonium phosphate (MAP), diammonium phosphate (DAP) triple super phosphate directly into the MBF formulations. Land managers could apply MBFs either in fall or early in the growing season and apply a commercial slow-release fertilizer timed to release nutrients during the crop's exponential growth phase, thereby maximizing plant uptake and growth while minimizing nutrient runoff and leaching.

With current fertilizer technology, direct losses of P from fertilizer leaching or runoff usually result when fertilizer application is coincident with heavy rain events (Owens and Shipitalo 2006; Haygarth and Jarvis 1999). Agricultural operations fertilize plants at rates recommended for crop production or plant growth (He et al. 2006; Easton and Petrovic 2004). In addition, fertilizers vary widely in solubility and can therefore have different P loss risk when applied to different soil types (Shober and Sims 2007; Elliott et al. 2006; Penn and Sims 2002; Kleinman et al.

2002). When columns received Polyon®, ESN®, and Avail®, from 85–94% of the total amount of the NO_3 leached was leached in the first 150 days. When columns received Avail®, 76% of the total amount of DRP and 85% of the total amount of TP leached was leached in the first 150 days. Avail® and MBF67+ Avail® had the greatest amount of total plant growth g^{-1}N applied while MBF6+Avail® had the greatest amount of total plant growth g^{-1} P applied. However, Polyon® and ESN® had greater amounts of N leached g^{-1} plant growth and greater amounts of N leached mg^{-1}N applied than the MBFs. Avail® had greater amounts of P leached g^{-1} plant growth and greater amounts of P leached mg^{-1} P applied than the MBFs. These 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 the plants to take up enough fertilizer P to prevent leaching. The problem is made more severe because turfgrass operators and homeowners often apply nutrients in quantities exceeding plant requirements (de Jonge et al. 2004; Hart et al. 2003). Several studies indicated that sediment bound P concentrations in runoff increase as soil P concentrations increase (Sharpley et al. 1993, 2000; Pote et al. 1999; Cox and Hendricks 2000). Long-term over-fertilization of soils contributes to eutrophication (Sims 1993; Frossard et al. 2000). Since the P concentration in water, above which eutrophication can occur, is an order of magnitude smaller than the soil P concentration necessary for plant growth (Owens and Shipitalo 2006; Daniel et al. 1998), improved fertilizer technology is necessary to both optimize crop growth while minimizing P leaching.

Conventional fertilizers, such as SSP, MAP, and DAP, were developed to minimize the cost of soluble P. The study of SSP, MAP, and DAP modification to reduce susceptibility to P runoff and leaching has been limited (Hart et al. 2003). Slow-release fertilizers have been employed to reduce direct fertilizer runoff losses. Nutrient leaching from slow-release fertilizers is reduced via organic or inorganic coatings around a core of soluble inorganic fertilizer; the coatings slowly degrade, resulting in eventual acceleration of nutrient release. Quin et al. (2003) described 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. (2003) conducted laboratory dissolution studies comparing SSP and a dry sulfur-coated superphosphate, in which sulfate of ammonia was the binding agent. They found that the water-extractable P was greater from the coated superphosphate fertilizer treatments (6.6%) compared to 4.8% from superphosphate treatments. The rapid dissolution of the S-coated superphosphate resulted from the rapid solubilization of the sulfate of ammonia in the extraction procedure. With loss of the sulfur coat there was no protection against P dissolution in the granules (Hart et al. 2003).

Commercial slow-release fertilizers can be classified into two basic groups: low solubility and polymer-coated water-soluble fertilizers (Blaylock et al. 2005). The polymer-coated slow-release fertilizers are water soluble and can exhibit consistent nutrient release rates. However, average soil temperature and moisture affect the nutrient-release rates. 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 (Blaylock et al. 2005). 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 (Basfar et al. 2003; Bonhomme et al. 2003; Lehmann et al. 1998, 2000) and the degradation rate influences nutrient release from the polymer.

The MBF formulations are comprised of a range of common inorganic nutrient compounds combined with $Al(SO_4)_3$ $18H_2O$ and/or $Fe_2(SO_4)_3$ $3H_2O$ and the high ionic exchange compounds starch, cellulose, and lignin. These formulations allowed N and P that leached from Avail® to bind with the $Al(SO_4)_318H_2O$ and/or $Fe_2(SO_4)_33H_2O$–lignin–cellulose matrix substantially reducing leaching. N and P having become bound to the $Al(SO_4)_318H_2O$ and/or $Fe_2(SO_4)_33H_2O$–lignin–cellulose matrix likely will become available to most plants over the growing seasons. We postulate that nutrient availability and leaching can be largely controlled by varying the relative amounts of starch–cellulose–lignin matrix with $Al(SO_4)_3 18H_2O$ and/or $Fe_2(SO_4)_3\ 3H_2O$ in the mixture. The MBFs bind nutrients to the $Al(SO_4)_3 18H_2O$–$Fe_2(SO_4)_3 3H_2O$–starch–cellulose–lignin matrix; application rates are based on the amount of nutrients released to meet plant growth. Therefore, their application rates (based on N and P analysis of the mixtures) are not comparable to conventional or slow-release fertilizers which release nutrients in more direct relationship to the amount of nutrient applied. In this respect the concept and mode of action of MBFs is a synthetic analog of the kind of nutrient release familiar to farmers and soil fertility experts from working with manure sources of nutrients or from application of rock phosphates. In contrast with rock phosphates and manures, however, since the fertilizers are consistently formulated, using constituents of controlled quality, there is no danger of heavy metal contamination or excess salt accumulation.

The amount of Avail® that was necessary to supplement the MBFs was only equivalent to 12.7 kg N ha^{-1} and 43.3 kg P ha^{-1}. After the first addition of MBFs presumably small amounts of slow-release fertilizers may be added to soil or via foliar feeding, while keeping leaching to a minimum. Additions of more readily available N and P sources to the MBF formulations appear to increase plant growth while still minimizing N and P leaching. Further testing with similar commercial slow-release fertilizers as supplements to the MBF formulations and additions of more readily available N and P chemical additions to the MBFs may further increase growth while still reducing nutrient leaching compared to conventional formulations without a matrix component.

The impact of MBFs to reduce N and P leaching in the field may not be immediately apparent in previously heavily fertilized agricultural soils. Continued fertilization of a soil for a period of years results in adsorption of N and P onto clays and organic matter ionic exchange sites and complexing with the soil organic matter fraction (D'Angelo 2005; McDowell et al. 2005; Bird et al. 2002, 2003; Devevre and Horwath 2001). Thus nutrients are slowly released as mineral and organic matter is decomposed and with desorption from the enhanced exchange complex (Bird et al. 2002, 2003; Entry and Emmingham 1995). The efficacy of MBFs 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.

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 and earlier initial investigations are promising. Cost estimates of these MBFs 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 homeowner on their lawns, turf grass operators such as golf course managers and growers of high-value agricultural crops. The MBF formulations could prove important where water drainage from fertilized soils exacerbates nutrient loading of environmentally sensitive receiving waters.

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