Matrix Based Fertilizers Reduce Nitrogen and Phosphorus Leaching in Greenhouse Column Studies

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Abstract We tested the efficacy of matrix based fertilizer formulations (MBF) that reduce NH_4, total phosphorus (TP), total reactive phosphorus (TRP) and dissolved reactive phosphorus (DRP) in leachate. The MBF formulations cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF1) to more moderately bound (MBF2) and more tightly bound compounds (MBF3) mixed with Al $(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. *Glomus interadicies*, a species of arbuscular mycorrhizal fungal spores that will form mycorrhizae in high nutrient environments, was added to the MBF formulations to increase plant nutrient uptake. When N and P are released from the inorganic chemicals containing N and P the matrix based fertilizers likely bind these nutrients to the Al$(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ starch–chitosan–lignin matrix. We tested the efficacy of the MBFs to reduce N and P leaching compared to Osmocote® 14-14-14, a slow release fertilizer (SRF) in sand filled columns in a greenhouse study. SRF with and without Al and Fe leached 78–84% more NH_4, 58–78% more TP, 20–30% more TRP and 61–77% more than MBF formulations 1, 2, and 3 in a total of 2.0 liters of leachate after 71 days.

The concentration and amount of NO_3 leached among SRF and MBF formulations 1 and 2 did not differ. The SRF treatment leached 34% less NO_3, than MBF3. Total plant weight did not differ among fertilizer treatments. Arbuscular mycorrhizal infection did not differ among plants receiving SRF and MBF formulations 1, 2 and 3. Although further greenhouse and field testing are called for, results of this initial investigation warrant further investigation of MBFs.

1 Introduction

Nitrogen (N) and phosphorus (P) are the two soil nutrients that most often limit plant growth. When N and P fertilizers are added to the soil, the amount of these nutrients taken up by the plant relative to the amount of N and P applied to the soil is low because only the soluble fraction of these nutrients can be taken up by plants (Vassilev & Vassileva, 2003). Land managers and home owners may apply soluble forms of N and P as inorganic fertilizers in quantities greater than plants can assimilate, leading to leaching and often surface and ground water contamination (David & Gentry, 2000; Edwards, Twist, & Codd, 2000; Sharpley, Foy, & Withers, 2000; Vitousek et al., 1997).

Transport of P from agricultural soils to surface waters has been linked to eutrophication in fresh

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water and estuaries (Broesch, Brinsfield, & Magnien, 2001; Bush & Austin, 2001; Daniel, Sharpley, & Lemunyon, 1998). Nitrogen and P accumulation in fresh or brackish water can overstimulate the growth of algae creating conditions that interfere with the health and diversity of indigenous plant and animal populations (Pohle, Bricelj, & Garcia-Esquivel, 1991; Tveite, 1994). In freshwater, algal blooms contribute to a wide range of water-related problems including summer fish kills, foul odors, and unpalatable tastes in drinking water. Eutrophication is also widespread and rapidly expanding in estuaries and coastal seas of the developed world. In marine ecosystems, algal blooms known as red or brown tides cause widespread problems by releasing toxins and by spurring oxygen depletion as they die and decompose. The incidence of harmful algal blooms in coastal oceans has dramatically increased in recent years (Bricker, Clement, Pirhalla, Orlando, & Farrow, 1999). This increase is linked to coastal 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. Fertilizer regimens could greatly benefit from more effective time release technologies that can better protect surface and ground water.

We developed matrix based fertilizers (MBFs) that may reduce NH_4, NO_3 and total P (TP) leaching. The MBFs are comprised of a range of inorganic N and P in compounds which are relatively loosely bound (MBF1), more moderately bound (MBF2) or more tightly bound mixtures (MBF3) depending on the relative amounts of the high ionic exchange compounds starch, chitosan and lignin and $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$. The MBF are developed to reduce N and P leaching by using chemicals that have higher chemical bonding energies compared to standard fertilizer formulations, a starch, chitosan and lignin matrix designed to bind nutrients and release them slowly as the matrix degrades and $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ to further bind nutrients releases them over a longer time period. We then added *Glomus interadicies,* a species of arbuscular mycorrhizal fungal spores that will form mycorrhizae in high nutrient environments, in the MBF formulations to increase plant nutrient uptake.

The MBF formulations allow nutrients to bind with the $Al(SO_4$ H_2O and/or $Fe_2(SO_4)_3$–lignin–chitosan matrix, substantially reducing leaching. Nutrient ions having become bound to the $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$–lignin–chitosan matrix, likely will become

available to most plants over several growing seasons. When N and P are released from the inorganic chemicals containing these nutrients, the matrix based fertilizers likely bind N and P to a $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ starch–chitosan–lignin matrix. After the starch–chitosan–lignin matrix with $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ is applied to soil the soil micro-organisms can degrade the starch in the matrix comparatively rapidly and will create some ionic exchange sites. Chitosan degrades less rapidly than starch but more rapidly than lignin and is expected to retain most of it's ionic exchange sites for about one year in most soil environments. The lignin component in the matrix degrades more slowly than starch and chitosan and is expected to retain it's ionic exchange sites for several years in most soil environments. Nutrient availability and leaching can be controlled to a large degree by varying the relative amounts of starch–chitosan–lignin matrix with $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ in the mixture. Our objective was to determine if these matrix based fertilizers combined with arbuscular mycorrhizae reduce N and P leaching compared to a typical commercial slow release fertilizer (Osmocote® 14-14-14) in sand filled columns in a greenhouse study. We also tested the efficacy of MBF2 without $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ to determine the efficacy of starch–chitosan–lignin alone to reduce N and P leaching and a slow release fertilizer combined with $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ to ensure that the addition of Al and Fe alone was not solely responsible for reduced N and P leaching.

2 Materials and Methods

2.1 Fertilizer treatments

The MBF formulations are comprised of inorganic chemical combined with starch, chitosan and lignin (Sigma, St. Louis, MO). Treatment 1 was a control (CONT); no fertilizer was applied to the columns (Figure 1). Treatment 2 (SRF) was 5.0 g of the Osmocote® (14-14-14) slow release fertilizer (Scotts, Marysville, OH) which was equal to 167.7 kg N ha^{-1}, 166.9 kg P and 130.1 kg K ha^{-1}. Treatment 3 (SRF+ Al+Fe) was 5.0 g of the Osmocote® (14-14-14) slow release fertilizer equal to 167.7 kg N ha^{-1}, 166.9 kg P and 130.1 kg K ha^{-1}. The Osmocote® (14-14-14) was placed over 0.488 g $Al(SO_4)_3$ H_2O and
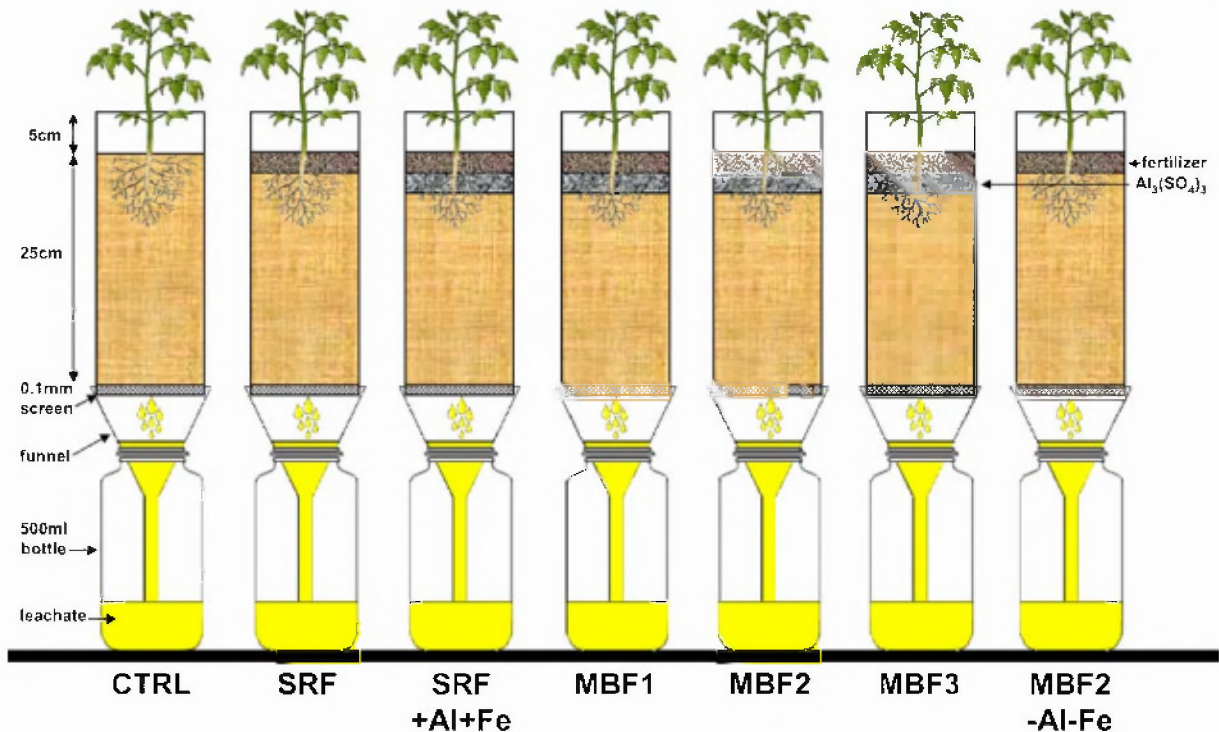
Figure 1 Diagram of column apparatus. *CTRL* = control which is column without fertilizer applied. The MBF formulations are comprised of inorganic chemical combined with starch, chitosan and lignin (Sigma, St. Louis, MO). Treatment 1 was a control (CONT); no fertilizer was applied to the columns (Figure 1). Treatment 2 (SRF) was 5.0 g of the Osmocote[®] (14-14-14) slow release fertilizer (Scotts, Marysville, OH) which was equal to 167.7 kg N ha^{-1}, 166.9 kg P and 130.1 kg K ha^{-1}. Treatment 3 (SRF+Al+Fe) was 5.0 g of the Osmocote[®] (14-14-14) slow release fertilizer was equal to 167.7 kg N ha^{-1}, 166.9 kg P and 130.1 kg K ha^{-1}. The Osmocote[®] (14-14-14) was placed over 0.488 g Al(SO$_4$)$_3$ H$_2$O

and 0.400 g Fe$_2$(SO$_4$)$_3$. Treatment 4 (MBF1), chemical composition described in Table I, was equal to 52 kg N ha^{-1}, 80 kg P ha^{-1} and 130.1 kg K ha^{-1}. Treatment 5 (MBF2), chemical composition described in Table I, was equal to 121 kg N ha^{-1} and 88 kg P ha^{-1} and 130.1 kg K ha^{-1}. Treatment 6 (MBF 3), chemical composition described in Table I, was also equal to 121 kg N ha^{-1} and 88 kg P ha^{-1} and 130.1 kg K ha^{-1}. Treatment 7 (MBF2–Al–Fe) was MBF formulation 2, chemical composition described in Table I, which was equal to 121 kg N ha^{-1}, 88 kg P ha^{-1} and 130.1 kg K ha^{-1} without Al(SO$_4$)$_3$ H$_2$O and Fe$_2$(SO$_4$)$_3$.

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2.2 Experimental design

The experiment was arranged in a completely random-ized design (Kirk, 1982) with 7 fertilizer treatments×3 crop species×3 replications×4 leachate measurements for a total of 63 columns and 252 leachate measure-ments. Soft spring wheat, (*Triticum aestivum* L.) Kentucky bluegrass (*Poa pratensis* L.) and Kochia (*Kochia scoparia* L.) were planted in columns described below. The plants were watered with 200 ml reverse osmosis water each day for 71 days. Leachate was collected as described below at 1, 22, 43 and 71 days after planting. Nitrate, NH$_4$, total phosphorus (TP), total reactive phosphorus (TRP) and dissolved reactive phos-phorus (DRP), in samples were measured in leachate at the above stated days using methods described below.

Table I Chemical compounds used to comprise three different matrix based fertilizers in mg N and P in each column

Treatment compound	1 CONT	2 SRF	3 SRF+Al+Fe	4 MBF1	5 MBF2	6 MBF3	7 MBF1 –Al–Fe
mg element/column							
$NH_4 NO_3$	000	210	210	000	000	000	000
P_2O_5	000	200	200	000	000	000	000
K_2O	000	180	180	180	180	180	180
$Ca(NO_3)_2\ 4H_2O$	000	000	000	472	236	236	236
$Al(NO_3)_3\ 9H_2O$	000	000	000	750	000	000	000
$NH_4(H_2PO_4)$	000	000	000	230	115	115	115
$Ca(H_2PO_4)_2$	000	000	000	468	234	234	234
$Fe\ (P_2O_7)$	000	000	000	334	1490	1490	1490
$Al(PO_4)_3$	000	000	000	360	000	000	000
$Al(SO_4)_3\ H_2O$	000	000	000	488	366	000	366
$Fe_2(SO_4)_3$	000	000	000	400	800	1600	800
Starch	000	000	000	1000	1000	1000	1000
Chitosan	000	000	000	1000	1000	1000	1000
Lignin	000	000	000	1000	1000	1000	1000
G. intradices	0.000	0.000	0.000	10	10	0.010	10

The MBF formulations are comprised of inorganic chemical combined with starch, chitosan and lignin (Sigma, St. Louis, MO). Treatment 1 was a control (CONT); no fertilizer was applied to the columns (Figure 1). Treatment 2 (SRF) was 5.0 g of the Osmocote® (14-14-14) slow release fertilizer (Scotts, Marysville, OH) which was equal to 167.7 kg N ha^{-1}, 166.9 kg P and 130.1 kg K ha^{-1}. Treatment 3 (SRF+Al+Fe) was 5.0 g of the Osmocote® (14-14-14) slow release fertilizer was equal to 167.7 kg N ha^{-1}, 166.9 kg P and 130.1 kg K ha^{-1}. The Osmocote® (14-14-14) was placed over 0.488 g Al(SO$_4$)$_3$ H$_2$O and 0.400 g Fe$_2$ (SO$_4$)$_3$. Treatment 4 (MBF1), chemical composition described in Table I, was equal to 52 kg N ha^{-1}, 80 kg P ha^{-1} and 130.1 kg K ha^{-1}. Treatment 5 (MBF2), chemical composition described in Table I, was equal to 121 kg N ha^{-1} and 88 kg P ha^{-1} and 130.1 kg K ha^{-1}. Treatment 6 (MBF 3), chemical composition described in Table I, was also equal to 121 kg N ha^{-1} and 88 kg P ha^{-1} and 130.1 kg K ha^{-1}. Treatment 7 (MBF2-Al-Fe) was MBF formulation 2, chemical composition described in Table 1, which was equal to 121 kg N ha^{-1}, 88 kg P ha^{-1} and 130.1 kg K ha^{-1} without Al(SO$_4$)$_3$ H$_2$O and Fe$_2$(SO$_4$)$_3$.

2.3 Column description

A 2.00 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 (Figure 1). A 14 cm diameter funnel was placed below each column in the rack and secured. Three kilograms of sand was placed in each column (columns were filled to 25 cm) leaving a 5 cm space at the top of each column. Sand in columns was a combination of the following size grains by weight: 0.28%≥3.35 mm, 4.86%≥2.362 mm, 21.64%≥ 1.379 mm, 11.05%≥1.000 mm, 28.9%≥0.600 mm, 24.26%≥0.246 mm, 6.60%≥0.149 mm, 1.00%≥ 0.125 mm and 1.40%>0.125 mm. Sand in columns was loosely packed and then repeatedly washed with reverse osmosis water to flush nutrients that could be loosely held to sand particles. Washed sand was used

in this experiment to ensure all N and P in leachate would be from the fertilizers rather than from soil nutrients and to achieve maximum leaching. Columns were allowed to drain for 1 h prior to the start of leachate collection. Reverse osmosis water was poured over plant and fertilizer in each column and leachate was collected in a 200 ml beaker.

2.4 Fertilizer placement and growing conditions

We placed the amounts of Fe$_2$(SO$_4$)$_3$ and/or Al(SO$_4$)$_3$ H$_2$O into columns receiving SRF+Al and Fe, MBF1, MBF2, and MBF3. Osmocote® 14-14-14 or MBF formulations were placed directly above the Fe$_2$(SO$_4$)$_3$ and/or Al(SO$_4$)$_3$ H$_2$O. The SRF and MBF2–Al and Fe, treatments without Fe$_2$(SO$_4$)$_3$ and Al(SO$_4$)$_3$ H$_2$O, were placed directly on the surface of the sand and incorporated into the top 3 cm of sand (Figure 1). We

then placed 0.05 g of soft spring wheat (*T. aestivum* L.), Kentucky bluegrass (*P. pratensis* L.) and Kochia (*K. scoparia* L.) seed in each column and covered them with 1.0 cm of sand. Seeds were watered with 100 ml of reverse osmosis water daily. Leachate did not flow through columns when 100 ml water was applied. We collected leachate 1, 22, 43 and 71 days after applying fertilizer formulations by giving plants 500 ml reverse osmosis water in lieu of the scheduled daily application of 100 ml of reverse osmosis water. Leachate was analyzed within one week for NO_3 and NH_4, TP, TRP and DRP. Plants were exposed to light having a photosynthetic active radiation of 400–700 μmol^{-2} s^{-1} and a 14–16 h photoperiod.

2.5 Harvesting and arbuscular mycorrhizae assessment

After 72 days, 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 cleared by placing them in a solution of 2.5% (w/v) KOH. The roots in the KOH solution were then placed in an autoclave for 5 min and then rinsed in 2% HCl for 24 h. Roots were then placed in 0.05% (w/v) trypan blue in acidic glycerol for 24 h (Koske & Gemma, 1989). Roots were observed for hyphal colonization under a 200× microscope by the cross hair intersection method (McGonigle, Miller, Evans, Fairchild, & Swan, 1990). 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 80°C for 48 h and weighed for shoot and root biomass.

2.6 Chemical analysis

Nitrate and ammonium were determined using a Lachat Automated Ion Analyzer (Quickchem 8000 Systems, Milwaukee, WI) using the method as described by Greenberg, Clescerl, & Eaton (1992). Total phosphorus (TP), total reactive P (TRP) and dissolved reactive phosphorus (DRP) in leachate was 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 (Greenberg et al., 1992). At harvest, plant root and shoot material were weighed and 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). An additional 0.25 g subsample was ashed at 500°C and analyzed for P, K, Ca, Mg, Mn, Fe, Cu, B and Zn using a inductively coupled plasma emission spectrometer (Perkin-Elmer, Boston, MA).

2.7 Statistical analysis

Nitrate and ammonium, DRP, TRP and TP values were tested for normal distribution. Data were then analyzed using general linear models (GLM) procedures for a completely random design using Statistical Analysis Systems (SAS Institute Inc., 1996). In all analysis, residuals were equally distributed with constant variances. Differences reported throughout are significant at $p \leq 0.05$, as determined by the Least Squares Means test.

3 Results

The first day after initiating the experiment, NH_4, NO_3, DRP, TRP and TP leachate concentrations did not differ among fertilizer treatments. Interactions in GLM models of leached nutrients for plant species× fertilizer formulation×sample day and plant species× sample day were not significant, therefore, statistical comparisons of NH_4, NO_3, DRP, TRP and TP are presented for fertilizer formulations because GLM models showed these interactions were significant at $p \leq 0.05$ (Snedecor & Cochran, 1980). SRF and SRF+ Al leached greater quantities of NH_4, TP, and DRP than MBF1, MBF2, MBF3 and MBF1–Al–Fe (Table II). MBF1–Al–Fe leached greater quantities of NH_4, TP, and DRP than MBF1, MBF2 and MBF3. The amount of NO_3 leached among SRF, SRF+Al and Fe and MBF1 and MBF2 did not differ. However, there was 34% less NO_3 leached from the SRF treatment than the MBF3 treatment. A greater quantity of NO_3 was leached from the MBF2–Al–Fe formulation than from SRF, SRF+Al+Fe, MBF1, MBF2 and MBF3 formulations. There was no consistent difference in the amount of TRP leached among the SRF, SRF+Al, MBF1, MBF2 and MBF3 formulations. SRF, SRF+Al and Fe leached higher concentrations and amounts of DRP than MBF1 and MBF3 formulations. The MBF2–Al–Fe formulation leached greater amounts of TP, DRP and TRP than all

Table II Total amount of NH_4, NO_3, total phosphorus (TP), total reactive phosphorus (TRP) and dissolved reactive phosphorus (DRP) added to sand columns leached from sand columns, nutrients remaining in sand columns growing wheat, beans or grass over 71 days

Fertilizer	Nutrients added			Nutrients leached					Nutrients remaining			Nutrients leached[a]		
	NH_4	NO_3	P	NH_4	NO_3	Total P	TRP	DRP	NH_4	NO_3	P	NH_4	NO_3	P
	(mg nutrients in sand)			(mg nutrient kg^{-1} leachate)					(mg nutrients in sand)			(%)		
Control	0.00d	0.00d	0.00d	0.04d	0.11c	0.12e	0.16d	0.07d	0.00c	0.00c	0.00 d	0.00 d	0.00 c	0.00 c
SRF	110.25 a	110.25 a	87.32 c	3.58a	0.19c	2.44a	0.99bc	2.70a	100.32 a	93.91 a	79.81 c	9.74 a	0.52 b	7.01 a
SRF+Al+Fe	110.25 a	110.25 a	87.32 c	4.05a	0.15c	2.91a	1.47b	3.29a	99.71 a	103.62 a	78.22 c	11.02 a	0.41 b	8.78 a
MBF formulation 1	111.92a	56.00 b	159.80 b	0.66c	0.29bc	0.54d	0.69c	0.61d	104.76 a	49.21 b	156.41 b	0.59 c	0.50 b	0.38 b
MBF formulation 2	56.00 b	56.00 b	243.51 a	0.78c	0.22bc	1.03c	1.30b	1.04c	47.35 b	47.91 b	237.57 a	2.78 b	0.78 b	1.38 b
MBF formulation 3	56.00 b	56.00 b	243.51 a	0.58c	0.43b	0.62d	0.79c	0.63d	48.82 b	49.82 b	239.55 a	2.07 b	1.53 a	0.84 b
MBF formulation 1 & Al-Fe	111.92a	56.00 b	243.51 a	1.77b	2.05a	1.97b	2.16a	2.09b	48.73 b	49.44 b	234.64 a	1.58 b	3.65 a	1.30 b

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

a Percent nutrients leached from sand

other MBF formulations. The control treatment (no fertilizer applied) leachate contained less NH_4, DRP, TRP and TP than all fertilizer treatments. The amount of NO_3, NH_4, and P added to the soils were different in the SRF and SRF+Al treatments than the MBF1, MBF2, MBF3 and MBF1–Al–Fe treatments. A greater percent of the NH_4 and TP added to the sand was leached from the SRF and SRF+Al treatments than the MBF1, MBF2, MBF3 and MBF1–Al–Fe treatments. A greater percent of the NO_3 added to the sand was leached from MBF3 and the MBF1–Al–Fe treatments than the MBF1, MBF2, SRF and SRF+Al treatments.

Plants growing in MBF2 and MBF3 treatments had greater shoot dry weight than plants growing in all other fertilizers (Table III). Total plant weight did not differ among fertilizer treatments. The amount of shoot N, root N, shoot P and root P taken up by plants over 70 days did not differ among fertilizer treatments. Shoot N, root N, shoot P and root P taken up by plants receiving fertilizer treatments were higher than those growing in the control treatment (plants that did not receive fertilizer). The concentration of K, Ca, Mg, Mn, Fe, Cu, B and Zn in root and shoot tissue did not differ among treatments (data not shown). Arbuscular mycorrhizal infection did not differ among plants receiving SRF, MBF1, MBF2 and MBF3 (Table II). Plants receiving the MBF2–Al–Fe formulation and control plants had lower arbuscular mycorrhizal infection in roots than all other treatments.

4 Discussion

The MBFs were formulated to supply plants with N and P at optimal rates over a range of nutrient requirements and management strategies. They contain N and P in several different chemicals designed to release N and P at varying times and amounts and over longer time periods than soluble and conventional slow release fertilizers. The MBFs contain a starch–chitosan–lignin matrix in combination with $Fe_2(SO_4)_3$ and/or $Al(SO_4)_3$ H_2O and are therefore not directly comparable to the amount of nutrient with commercially available soluble and slow release fertilizers as to the amount of nutrient applied relative to the amount of nutrient leached. A sand growing medium was used to minimize effects of residual soil N and P in the leachate.

Table III Total amount of NH_4, NO_3, total phosphorus (TP), total reactive phosphorus (TRP) and dissolved reactive phosphorus (DRP) leached from sand columns growing wheat, beans or grass over 71 days, and plant dry weight, N and P concentration and arbuscular mycorrhizal colonization

Fertilizer	Plant dry Weight			Plant nutrients				
	Shoot (g)	Root	Total	Shoot N (mg kg^{-1})	Shoot P	Root N	Root P	Myc (%)
Control	1.3 c	6.7 a	8.0 a	8000 b	369c	10100a	793b	36 b
SRF	2.4 b	5.9 a	8.3 a	15900 a	1217 a	14800 a	1866 a	49 a
SRF+Al+Fe	2.3 b	5.9 a	8.2 a	12800 a	896 ab	17000 a	2078 a	43 a
MBF formulation 1	2.5 b	6.9 a	9.4 a	13700 a	719 b	15300 a	1982 a	51 a
MBF formulation 2	5.4 a	6.7 a	12.1 a	12400 a	1289 a	13500 a	2795 a	47 a
MBF formulation 3	3.0 ab	5.7 a	8.7 a	12160 a	820 ab	13800 a	2941 a	49 a
MBF formulation 1 å Al–Fe	2.6 b	7.8 a	10.4 a	12100 a	1229 a	10300 a	2968 a	33 b

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

Myc = percent arbuscular mycorrhizal infection

The mycorrhizal plant–sand system of the commercial SRF (Osmocote 14-14-14) with or without Al leached greater quantities of NH_4, TP and DRP compared with respective values found for the MBF1, MBF2 and MBF3 formulations. The amount of NO_3 leached among SRF with or without Al and MBF1 and MBF2 formulations did not differ. The addition of $Al(SO_4)_3$ H_2O and $Fe_2(SO_4)_3$ to SRF did not influence NH_4, TP, TRP and DRP. The MBF formulations had $Al(SO_4)_3$ H_2O or $Fe_2(SO_4)_3$ as a part of the fertilizer formulation or the salts placed below the fertilizer layer to intercept and bind NH_4, TP, TRP and DRP that would leach from the fertilizer itself. However, when $Al(SO_4)_3$ H_2O and $Fe_2(SO_4)_3$ were removed from the MBF2 fertilizer, greater amounts of NH_4, NO_3, TP, TRP and DRP were leached compared to MBF1, MBF2 and MBF3 fertilizer treatments.

Direct losses of P from fertilizer usually result when fertilizer application is coincident with a hydrological factor such as heavy rain events (Haygarth & Jarvis, 1999). We found 84% of the total P was leached from these columns in the first 43 days after treatments commenced. Our results imply that, even if the slow release fertilizers were applied at rates to meet crop or turf P uptake over a growing season and plants grew at their maximum potential, it would be difficult for them to accumulate the amount of fertilizer P necessary to prevent leaching. Therefore, even if agricultural and turfgrass operators were to apply

nutrients only 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 (Hart, Quin, & Nguyen, 2003). Several studies indicated that sediment-bound TP concentrations in runoff generally increase as soil P concentrations increase (Cox & Hendricks, 2000; Pote et al., 1999; Sharpley, Daniel, & Edwards, 1993). Long-term over fertilization of soils is recognized as potentially contributing to eutrophication of surface waters (Frossard, Condron, Oberson, Sinaj, & Fardeau, 2000; Sims, 1993).

Conventional fertilizer 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 (Hart et al., 2003). 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, Braithwaite, Nguyen, Blennerhassett, and Watson (2003) 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 in 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. The authors 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, and with it removal of the sulfur coat and 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, Kaufmann, & Dowbenko, 2005). 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. coating. When polymer coated slow release fertilizers are applied to the soil, the water in the soil enters the fertilizer granule through micropores which dissolves the nutrients. Nutrients are then steadily released through the pores. The rate 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 hypothized to not be significantly influenced by microbiological decomposition, soil moisture, soil type or pH. However, all polymers eventually degrade in soil (Basfar, Idriss Ali, & Mofti, 2003; Bonhomme et al., 2003; Lehmann, Miller, & Kozerski, 2000; Lehmann, Miller, Xu, Singh, & Reece, 1998) and the degradation rate will influence nutrient release from the polymer.

Although further greenhouse and field testing are called for, results of this initial investigation are promising because, in this greenhouse study, MBFs reduced NH_4 in leachate by as much as 82%, TP in leachate by as much as 75%, TRP in leachate by as much as 31% and DRP in leachate by as much as 77%. These MBF formulations initially may be economically feasible for use by homeowners on their lawns, turfgrass operators such as golf course managers and growers of high value agricultural crops. The MBF formulations could prove important in soils whose water flow drains into nutrient-affected waters such as Chesapeake Bay, Florida Everglades and rivers flowing into the Great Lakes.

Mycorrhizal colonization in plant roots did not differ among SRF, MBF1, MBF2 and MBF3 formulations with or without $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$. Mycorrhizal colonization was assessed at the termination of the experiment when roots were growing throughout the soil. The mycorrhizal associations with *G. interadicies* probably formed in the first few weeks of the experiment and subsequently, as roots grew and suberized, the colonizations at that location in the root diminished. *G. interadicies* is an arbuscular mycorrhizal fungi species that will form associations with a broad range of host plants in soils containing high concentrations of N and P and was added to the matrix to enhance nutrient uptake. The amount of N, P K, Ca, Mg, Mn, Fe, Cu, B and Zn in in plant tissue taken up by plants over 70 days did not differ among fertilizer treatments. Plants can acquire nutrients from the chemicals in MBF fertilizers in similar proportions as Osmocote® (14-14-14) slow release fertilizer.

The MBFs cannot be expected to reduce N and P leaching in all soils and conditions. However, one may blend a the MBF for specific plants, soils and environmental conditions. Nutrient availability and leaching is expected to be controlled to a large degree by varying the relative amounts of starch–chitosan–lignin matrix with $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ in the mixture. The proportions of starch–chitosan–lignin in the matrix may be altered to bind N and P more or less tightly, and changing the overall degradation rate of the matrix and thus alter release of these nutrients for plant uptake. Starch degrades more rapidly than chitosan, which degrades more rapidly than lignin. The lignin component in the matrix degrades more slowly than starch and chitosan and is expected to retain it's ionic exchange sites for several years in most soil environments. Increasing the amount of starch and chitosan should increase nutrient release whereas increasing the concentration of lignin is expected to decrease nutrient release to plants. The relative proportions of $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ in the matrix can also be altered. Increasing the amount of $Al(SO_4)_3$ H_2O and/or $Fe_2(SO_4)_3$ in the matrix will increase nutrient binding,

especially P, which should make nutrients available over a longer time period.

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. Continual excessive application of any fertilizer eventually will load soil beyond it's maximum retention capacity. Nutrients added to the soil above that limit via any mode of application (e.g., natural and anthropogenic aerial deposition, application of fertilizer) eventually are 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, our data suggests that new MBF formulations that release nutrients at a rate comparable to plant uptake can reduce nutrient leaching and ultimately eutrophication.

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