Matrix based fertilizers reduce nitrogen and phosphorus leaching in three soils

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Abstract

We compared the efficacy of matrix based fertilizers (MBFs) formulated to reduce NO_3^-, NH_4^+, and total phosphorus (TP) leaching, with Osmocoate® 14-14-14, a conventional commercial slow release fertilizer (SRF) and an unamended control in three different soil textures in a greenhouse column study. The MBFs covered a range of inorganic N and P in compounds that are relatively loosely bound (MBF 1) to more moderately bound (MBF 2) and more tightly bound compounds (MBF 3) mixed with $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ 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 a $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ starch–chitosan–lignin matrix. One milligram (8000 spores) of *Glomus intradices* was added to all formulations to enhance nutrient uptake. In all three soil textures the SRF leachate contained a higher amount of NH_4^+, NO_3^- and TP than leachate from all other fertilizers. In all three soils there were no consistent differences in the amount of NH_4^+, NO_3^- and TP in the MBF leachates compared to the control leachate. Plants growing in soils receiving SRF had greater shoot, root and total biomass than all MBFs regardless of $Al(SO_4)_3H_2O$ or $Fe_2(SO_4)_3$ additions. Arbuscular mycorrhizal infection in plant roots did not consistently differ among plants growing in soil receiving SRF, MBFs and control treatments. Although the MBFs resulted in less plant growth in this experiment they may be applied to soils growing plants in areas that are at high risk for nutrient leaching to surface waters.
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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 overall N and P use efficiency is low because only the soluble fraction of these nutrients can be taken up by plants (Vassilev and Vassileva, 2003). Land managers and home owners commonly 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 (Vitousek et al., 1997; David and Gentry, 2000; Edwards et al., 2000; Sharpley et al., 2000).

Transport of P from agricultural soils to surface waters has been linked to eutrophication in fresh water and estuaries (Bush and Austin, 2001; Broesch et al., 2001; Daniel et al., 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 (Tveite, 1994; Pohle et al., 1991). Nonpoint N sources were responsible for more than 90% of N inputs to more than half of the 86 rivers studied in United States. Nonpoint P sources contributed over 90% of the P in a third of these rivers. Along the coastline of the North Atlantic Ocean nonpoint sources of N are some 9-fold greater than inputs from wastewater treatment plants (Bricker et al., 1999). Eutrophication is also widespread and rapidly expanding in most temperate lake, stream and coastal ecosystems. The incidence of harmful algal blooms has dramatically increased in recent years (Bricker et al.,

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1999). This increase is linked to eutrophication and other factors, such as changes in 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 cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF 1) to more moderately bound (MBF 2) and more tightly bound compounds (MBF 3) mixed with $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. We 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. Our objective was to determine if MBFs combined with arbuscular mycorrhizae would reduce N and P leaching compared to a slow release fertilizer (SRF) in sand, sandy loam and loam textured soils in a greenhouse column study.

2. Materials and methods

2.1. Fertilizer treatments

The MBF formulations in our study cover a range of common inorganic nutrient compounds combined with $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$. Starch, chitosan and lignin were chosen because of their high concentration of ionic exchange sites and their decomposition characteristics. Nutrients bound to the $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ starch–chitosan–lignin matrix become increasingly available to plants as the organic components in the matrix degrade. The organic components in the matrix should 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 (MBF 1) to more tightly (MBF 3) by increasing the concentration of $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ and by varying the amounts of starch, chitosan and lignin in the matrix. When the matrix is applied to soil the soil microorganisms will degrade the starch in the matrix comparatively rapidly while chitosan will degrade less rapidly. Lignin is expected degrade the slowest and should retain most of its ionic exchange sites for a longer time in most soil environments.

The MBF formulations are comprised of inorganic chemicals combined with starch, chitosan and lignin (Sigma, St. Louis, MO). Treatment 1 was a control; no fertilizer was applied to the columns (Table 1). Treatment 2 was 5.0 g of the Osmocote® (14-14-14) SRF which was equal to 345 μg N and 344 μg P per column and 167.7 kg N ha^{-1} and 166.9 kg N ha^{-1} (Table 1). Osmocote® (14-14-14) has a 3–4 month nutrient release pattern at 70 °C. Treatment 3 was MBF 1 which received 313.0 μg N and 164.0 μg P per column and was equal to 152 kg N ha^{-1} and 80 kg P ha^{-1}. Treatment 4 was MBF 2 which received 249 μg N and 181 μg P per column and was equal to 121 kg N ha^{-1} and 88 kg P ha^{-1}. Treatment 5 was MBF 3 which received 60 μg N and 294 μg P per column and was equal to 29 kg N ha^{-1} and 143 kg P ha^{-1}. We added treatments 6–8 to determine the effect of $Al(SO_4)_3H_2O$ and $Fe_2(SO_4)_3$ on N and P leaching in the columns. Treatment 6 was MBF 3 + Al − Fe which MBF 3 was placed over 0.488 g $Al(SO_4)_3H_2O$ without $Fe_2(SO_4)_3$. MBF 3 + Al − Fe received 60.0 μg N and 294.0 μg P per column and was equal to 29 kg N ha^{-1} and 143 kg P ha^{-1}. Treatment 7 was MBF 3 − Al + Fe placed over 1.600 g $Fe_2(SO_4)_3$ without $Al(SO_4)_3H_2O$. MBF 3 − Al + Fe

Table 1
Chemical compounds used to comprise three different matrix based fertilizers in mg N and P in each column[a]

| Treatment | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
Compound	CONT	SRF	MBF 1	MBF 2	MBF 3	MBF 3 +Al − Fe	MBF 3 −Al + Fe	MBF 3 −Al + Fe
NH_4NO_3	0.000	0.210	0.000	0.000	0.000	0.000	0.000	0.000
P_2O_5	0.000	0.200	0.000	0.000	0.000	0.000	0.000	0.000
K_2O	0.000	0.180	0.180	0.180	0.180	0.180	0.180	0.180
$Ca(NO_3)_24H_2O$	0.000	0.000	0.472	0.472	0.236	0.236	0.236	0.236
$Al(NO_3)_39H_2O$	0.000	0.000	0.750	0.750	0.000	0.000	0.000	0.000
$NH_4(H_2PO_4)$	0.000	0.000	0.230	0.230	0.115	0.115	0.115	0.115
$Ca(H_2PO_4)_2$	0.000	0.000	0.468	0.468	0.234	0.234	0.234	0.234
$Fe(P_2O_7)$	0.000	0.000	0.334	0.334	1.490	1.490	1.490	1.490
$Al(PO_4)_3$	0.000	0.000	0.360	0.360	0.000	0.000	0.000	0.000
$Al(SO_4)_3 H_2O$	0.000	0.000	0.488	0.366	0.000	0.488	0.000	0.000
$Fe_2(SO_4)_3$	0.000	0.000	0.400	0.800	1.600	0.000	1.600	0.000
Starch	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Chitosan	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000
Lignin	0.000	0.000	1.000	1.000	1.000	1.000	1.000	1.000

[a](mg compound in each column) MBF 1 is matrix based fertilizer formulation 1 = 152 kg N ha^{-1} and 80 kg P ha^{-1}; MBF 2 is matrix based fertilizer formulation 2 = 121 kg N ha^{-1} and 88 kg P ha^{-1}; MBF 3 is matrix based fertilizer formulation 3 = 29 kg N ha^{-1} and 143 kg P ha^{-1}. SRF = slow release fertilizer 5.0 g of Osmocote® (14-14-14) which includes NH_4NO_3, P_2O_5 and K_2O.

received $60.0\,\mu g$ N and $294.0\,\mu g$ P per column and was equal to $29\,kg\,N\,ha^{-1}$ and $143\,kg\,P\,ha^{-1}$. Treatment 8 was MBF $3 - Al - Fe$ MBF $3 - Al + Fe$ which was MBF 3 without $Al(SO_4)_3H_2O$ or $Fe_2(SO_4)_3$ which received $60.0\,\mu g$ N and $294.0\,\mu g$ P per column and was equal to $29\,kg\,N\,ha^{-1}$ and $143\,kg\,P\,ha^{-1}$. We added the 8000 spores of *G. interadicies* in $1.00\,ml$ of reverse osmosis water to all MBF treatments (per column) to increase plant nutrient uptake.

2.2. Column description

A $2.0\,mm$ wire screen was cut into squares ($125 \times 125\,mm$) and secured to the bottom of each $10.0\,cm$ diameter $\times 30\,cm$ long polyvinyl chloride cylinder (Fig. 1). 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.

2.3. Soil descriptions

Soils having three different textures were used to determine the effectiveness of the fertilizers to reduce leaching over a range of soil types. The Brown's Creek soil was a loam and was classified as a fine, montmorillonitic, mesic Xerollic Haplargid. The Simco soil was a coarse-loamy sand and classified as a mixed non-acid, mesic Xeric Torriorthents. The Kuna soil is a sandy loam and classified as a mixed, mesic lithic Xerollic Camborthids (Collett, 1982). Soil physical and microbiological properties are presented in Entry et al. (2002, 2004). Soil chemical concentrations are presented in Table 2.

2.4. Experimental design

The experiment was arranged in a completely randomized design (Kirk, 1982) with eight fertilizer treatments × three soil textures with three replications. There were a
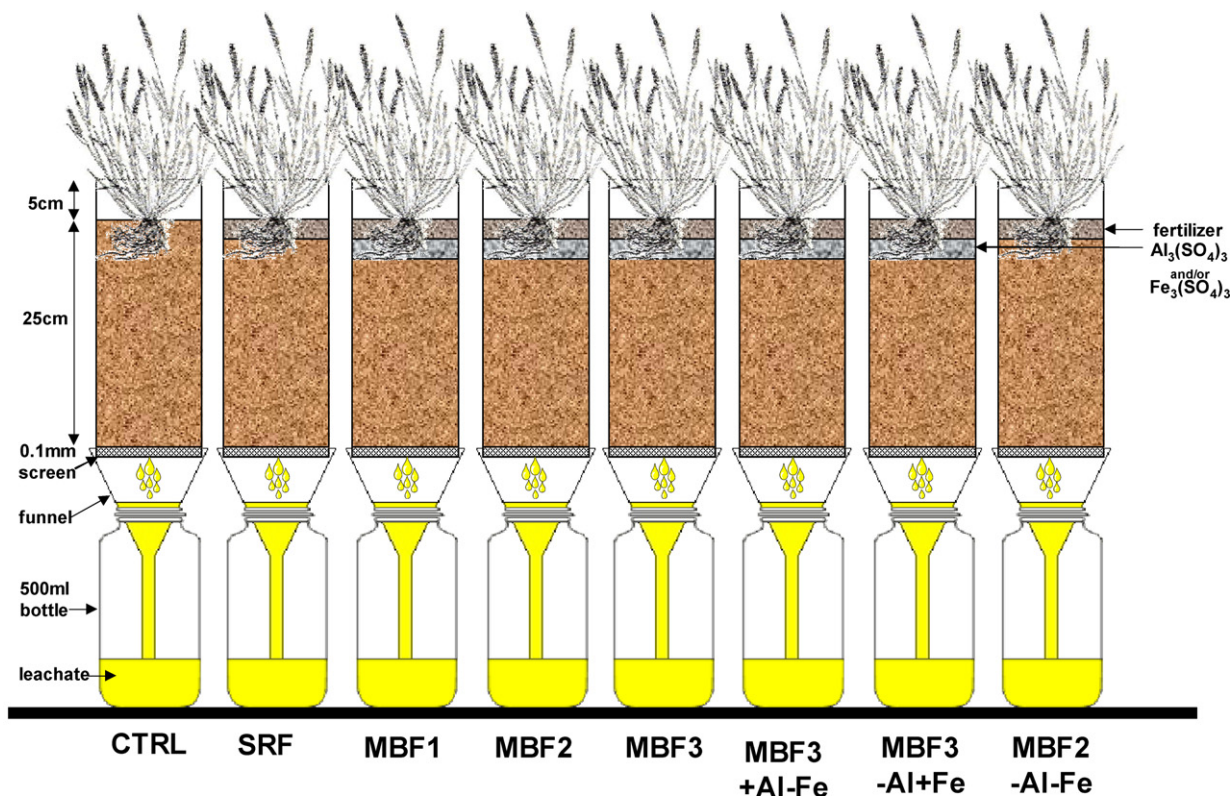
CTRL = control which is column without fertilizer applied. SRF = slow release fertilizer which received 345 µg N and 344 µg P. MBF1 = matrix based fertilizer 1 which received 313 µg N and 164 µg P. MBF2 = matrix based fertilizer 2 which received 249 µg N and 181 µg P. MBF3 = matrix based fertilizer 3 which received 60 µg N and 294 µg P. MBF3 +Al-Fe = matrix based fertilizer 3 which received 60 µg N and 294 µg P. MBF3 –Al+Fe = matrix based fertilizer 3 which received 60 µg N and 294 µg P. MBF3 -Al-Fe = matrix based fertilizer 3 which received 60 µg N and 294 µg P.

Fig. 1. Diagram of column apparatus. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF $3 + Al - Fe$). Treatment 7 was matrix based fertilizer formulation 3 with $0.488\,g$ $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF $3 - Al - Fe$). Treatment 8 was matrix based fertilizer formulation 3 without $Al(SO_4)_3H_2O$ and $Fe_2(SO_4)_3$ (MBF $3 - Al - Fe$).

Table 2
Extractable nutrient concentration in a loam, sand, and loamy sand soils[a]

Soil	C	N	P	Fe	Mn	S	Si	Al	Zn
	(g C kg^{-1} soil)	(mg element kg^{-1} soil)							
Loam	0.47 b	8300 a	1440 a	250 a	22 b	728 a	470 a	14 a	8.7 a
Sandy Loam	0.69 a	5900 b	861 b	120 b	35 a	462 b	329 a	5 b	7.6 a
Sand	0.28 c	6500 b	846 b	150 b	15 c	759 a	411 a	8 b	11.3 a

[a] In each column and soil, values followed by the same letter are not significantly different as determined by the least-square means test ($p \leqslant 0.05$, $n = 3$).

total of 72 columns and 360 leachate measurements. Plants were given 100 ml reverse osmosis water each day for 16 weeks. Samples were measured for NH_4, NO_3, and TP in leachate at 21, 42, 63, 84 and 112 days.

2.5. Fertilizer placement and growing conditions

We placed the above stated amounts of $Fe_2(SO_4)_3$ and/or $Al(SO_4)_3H_2O$ at a depth of 5 cm in columns receiving MBF treatments 6–8. The MBF formulations were placed directly above the $Fe_2(SO_4)_3$ and/or $Al(SO_4)_3H_2O$. The slow release Osmocote® 14-14-14 fertilizer not receiving additional $Fe_2(SO_4)_3$ and/or $Al(SO_4)_3H_2O$ was mixed into the top 5 cm of soil. We then placed 0.5 g of white soft spring wheat (*Triticum aestivum* L.cv. Frame) seed on top of each column. Seeds were covered with 0.5 cm of soil. Seeds were watered with 100 ml of water daily to maintain field capacity of the soil. Leachate did not flow through columns when 100 ml water was applied. We collected leachate 21, 42, 63, 84 and 112 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. Subsamples were analyzed for NO_3^- and NH_4^+ and TP as described below. Throughout the experiment plants were exposed to light having a photosynthetic active radiation of 400–700 µmol m^{-2} S^{-1} and a 14–16 h photoperiod.

2.6. Harvesting and arbuscular mycorrhizae assessment

After 112 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 g of roots were randomly selected from each plant and placed 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 and Gemma, 1989). Roots were observed for hyphal colonization under a 200× microscope by the cross hair intersection method (McGonigle et al., 1990). Approximately 100 intersections were scored and used to determine percent of root length infected. Root tissue excluding roots examined for mycor-

rhizal infection and shoot tissue was dried at 80 °C for 48 h 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 as described by Greenberg et al. (1992). Total P 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). Three soil samples from each soil type were dried at 65 °C for 72 h and passed through a 2 mm sieve. Total C was estimated by dry ashing at 525 °C and assuming C equal to 50% of loss on ignition (Nelson and Sommers, 1996). Total N was determined using standard microkjeldahl procedures modified for NO_3^- (Bremmner, 1996). A 2 g subsample of soil was extracted with 10 ml 1 N ammonium acetate (Sims, 1989) and analyzed for Mn, Fe, Al, Si, S and Zn were determined using inductively coupled plasma emission spectrometry (ICP). 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 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 a inductively coupled plasma emission spectrometer (Perkin-Elmer, Boston, MA).

2.8. Statistical analysis

Nitrate, NH_4^+ and TP values were tested for normal distribution. Data were then analyzed using general linear models (GLM) procedures for a completely random design with Statistical Analysis Systems (SAS Institute Inc., 1996). In all analyses, residuals were equally distributed with constant variances. Differences reported throughout are significant at $p \leqslant 0.05$, as determined by the least-squares means test.

3. Results

The GLM of leached nutrients for soil type × fertilizers × sample day, soil type × fertilizers, and soil

type × sample day were not significant, therefore, statistical comparisons of NH_4^+, NO_3^- and total P are presented for fertilizer treatments because GLM showed these interactions were significant at $p \leqslant 0.05$ (Snedecor and Cochran, 1980).

After 112 days, SRF leachate contained a greater amount of NH_4^+, NO_3^- and TP than leachate from all other fertilizers (Figs. 2–4). In all three soils, MBFs reduced NH_4^+ in leachate by a minimum of 50%, NO_3^- leachate by a minimum of 46% and TP in leachate by a minimum of 200%. In all three soils there were no consistent differences in the amount of NH_4^+ NO_3^- and TP in the MBF leachates than in the control leachate. Plants growing in soils receiving SRF had greater head weight, shoot, root and total biomass than all fertilizer formulations (Table 3). All fertilizer formulations and SRF plants had greater head weight, shoot, root and total biomass than plants growing in soils receiving no fertilizer (control). 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). Plants growing in the loam soil receiving SRF treatment had greater shoot and root N concentrations than all MBF formulations except for the MBF 1 shoot N concentration. Plants growing in the sand and sandy loam soils receiving SRF treatment had greater shoot N concentrations than all
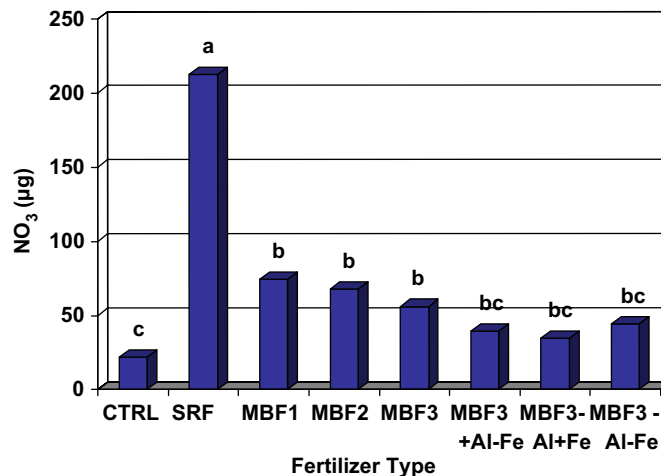

Fig. 3. Total amount of NO_3 leached from soil columns growing wheat over 112 days. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF 3 + Al − Fe). Treatment 7 was matrix based fertilizer formulation 3 with 0.488 g $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF 3 − Al+ Fe). Treatment 8 was matrix based fertilizer formulation 3 without $Al(SO_4)_3H_2O$ and $Fe_2(SO_4)_3$ (MBF 3 − Al − Fe). Bars having same letter are not significantly different as determined by the least-square means test $(p \leqslant 0.05)$, $n = 360$.
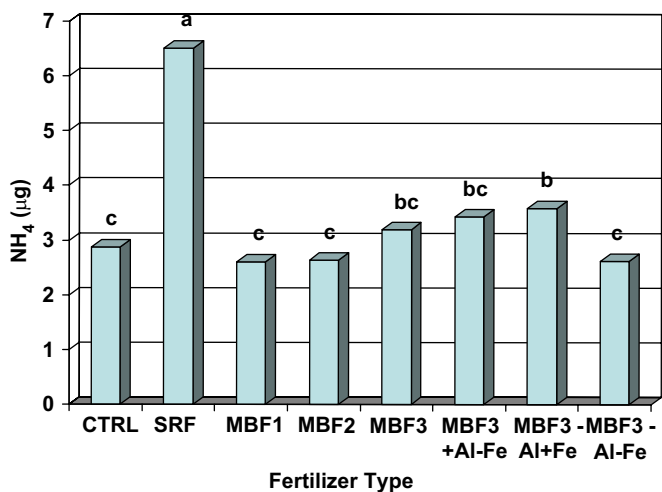

Fig. 2. Total amount of NH_4 leached from soil columns growing wheat over 112 days. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF 3 + Al − Fe). Treatment 7 was matrix based fertilizer formulation 3 with 0.488 g $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF 3 − Al+ Fe). Treatment 8 was matrix based fertilizer formulation 3 without $Al(SO_4)_3H_2O$ and $Fe_2(SO_4)_3$ (MBF 3 − Al − Fe). Bars having same letter are not significantly different as determined by the least-square means test $(p \leqslant 0.05)$, $n = 360$.

Fig. 4. Total amount of total phosphorus (TP) leached from soil columns growing wheat over 112 days. Treatment 1 was a control; no fertilizer applied to the column (CONT). Treatment 2 was a slow release fertilizer (SRF). Treatment 3 was matrix based fertilizer formulation 1 (MBF 1). Treatment 4 was matrix based fertilizer formulation 2 (MBF 2). Treatment 5 was matrix based fertilizer formulation 3 (MBF 3). Treatment 6 was matrix based fertilizer 3 without $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF 3 + Al − Fe). Treatment 7 was matrix based fertilizer formulation 3 with 0.488 g $Al(SO_4)_3H_2O$ and without $Fe_2(SO_4)_3$ (MBF 3 − Al+ Fe). Treatment 8 was matrix based fertilizer formulation 3 without $Al(SO_4)_3H_2O$ and $Fe_2(SO_4)_3$ (MBF 3 − Al − Fe). Bars having same letter are not significantly different as determined by the least square means test $(p \leqslant 0.05)$, $n = 360$.
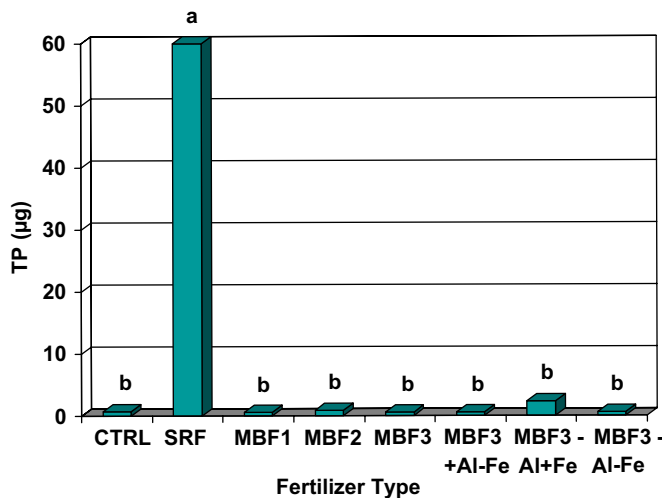
Table 3
Wheat height, biomass, and head weight after 112 days growth in a loam, sand, and loamy sand soil in greenhouse conditions[a,b]

Soil	Treatment	Height (cm)	Head weight (g)	Shoot biomass (g)	Root biomass (g)	Plant biomass (g)	Mycorrhizal infection (arbuscules/mm)	Shoot N	Shoot P	Root N	Root P
									(mg kg^{-1})		
Loam	Control (no fertilizer)	44.0 c	6.5 c	11.5 d	12.7 c	24.2 c	3.7 b	8300 b	168.2 c	5333 b	3553 c
	SRF	49.0 b	17.2 a	26.9 a	29.5 a	56.4 a	40.9 a	16060 a	732.6 a	7833 a	8567 a
	MBF 1	57.9 a	12.6 b	21.8 b	24.0 b	40.0 b	20.6 a	10700 ab	278.2 b	5200 b	4123 bc
	MBF 2	57.6 a	12.6 b	21.0 b	23.1 b	44.2 b	27.7 a	8300 b	304.6 b	4300 b	3806 bc
	MBF 3	56.8 a	9.7 b	16.4 c	18.1 b	34.5 b	13.0 ab	7333 b	235.9 b	3933 b	4367 b
	MBF 3 + Al − Fe	54.3 a	9.4 b	16.2 c	17.8 b	33.9 b	15.6 ab	7633 b	282.7 b	4800 b	5373 b
	MBF 3 − Al + Fe	50.4 a	8.6 b	15.0 c	16.5 b	31.5 b	43.3 a	8467 b	221.0 b	4000 b	4123 bc
	MBF 2 − Al − Fe	55.9 a	11.7 b	19.2 bc	21.1 b	34.2 b	19.6 ab	8530 b	276.6 b	4333 b	4553 b
Sand	Control (no fertilizer)	24.8 b	0.8 c	1.7 c	1.9 c	3.6 c	16.9 a	5900 c	14.6 c	4800 b	3563 c
	SRF	51.9 a	17.3 a	28.0 a	30.9 a	58.9 a	20.3 a	13733 a	614.0 a	7800 a	6073 ab
	MBF 1	50.3 a	7.7 b	15.4 b	16.9 b	38.8 b	8.0 ab	8666 b	134.7 b	5800 b	6226 ab
	MBF 2	51.7 a	8.9 b	15.9 b	17.5 b	33.4 b	21.0 a	7566 b	197.4 b	4900 b	4280 b
	MBF 3	47.6 a	6.0 b	10.1 b	12.1 b	23.1 b	28.3 a	7033 b	153.7 b	4566 b	4120 bc
	MBF 3 + Al − Fe	51.4 a	6.4 b	11.7 b	12.8 b	24.5 b	6.1 b	7433 b	193.8 b	4200 b	5617 b
	MBF 3 − Al + Fe	47.1 a	6.9 b	12.4 b	13.7 b	26.1 b	5.1 b	7100 b	151.6 b	4833 b	3687 b
	MBF 2 − Al − Fe	52.7 a	8.6 b	16.3 b	17.9 b	34.2 b	20.9 a	7666 b	180.2 b	4500 b	3390 b
Sandy Loam	Control (no fertilizer)	39.5 b	2.8 c	5.9 c	6.4 c	12.4 c	26.3 a	6466 c	47.2 c	5400 b	3300 c
	SRF	48.0 a	18.1 a	28.7 a	31.6 a	60.3 a	24.1 a	15833 a	586.9 a	7400 a	5806 a
	MBF 1	56.9 a	10.6 b	20.0 b	22.0 b	41.9 b	35.2 a	7166 b	194.8 b	5100 b	3912 bc
	MBF 2	54.0 a	10.3 b	18.4 b	20.3 b	38.7 b	15.4 a	8300 b	257.8 b	4066 b	5247 b
	MBF 3	53.0 a	9.6 b	17.8 b	19.5 b	37.3 b	17.6 a	7600 b	210.7 b	4133 b	4346 b
	MBF 3 + Al − Fe	52.0 a	9.1 b	16.5 b	18.1 b	34.6 b	24.3 a	9500 b	191.6 b	3900 b	5246 b
	MBF 3 − Al + Fe	50.9 a	8.7 b	16.3 b	17.9 b	34.2 b	29.6 a	9833 b	161.2 b	4800 b	5183 b
	MBF 2 − Al − Fe	50.1 a	8.9 b	16.2 b	17.8 b	34.0 b	26.3 a	7566 b	182.5 b	4133 b	4057 b

[a]In each column and soil, values followed by the same letter are not significantly different as determined by the least-square means test ($p \leqslant 0.05$, $n = 9$).
[b]MBF 1 is matrix based fertilizer formulation 1 = 152 kg N ha^{-1} and 80 kg P ha^{-1}; MBF 2 is matrix based fertilizer formulation 2 = 121 kg N ha^{-1} and 88 kg P ha^{-1}; MBF 3 is matrix based fertilizer formulation 3 = 29 kg N ha^{-1} and 143 kg P ha^{-1}.
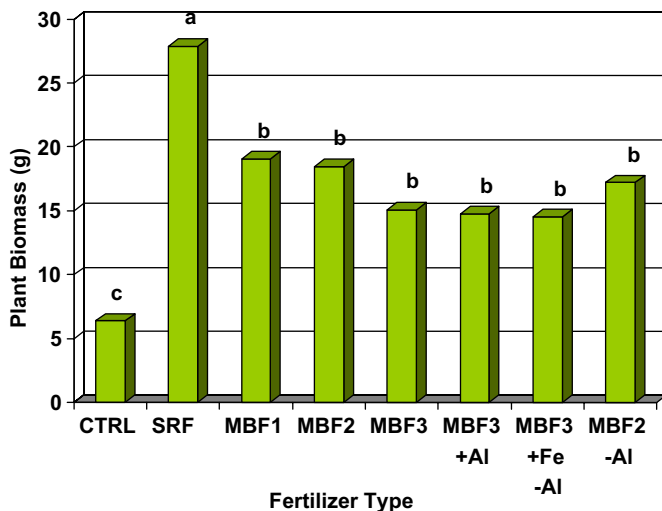

Fig. 5. Total amount of plant biomass from soil columns growing wheat over 112 days.

MBF formulations. Plants growing in soils receiving SRF had greater shoot P content than all MBF formulations. All fertilizer and SRF plants had greater shoot P content than plants growing in soils receiving no fertilizer (control). The concentration of K, Ca, Mg, Mn, Fe, Cu, B and Zn in root and shoot tissue did not differ ($p \leqslant 0.05$) among treatments (data not shown) (Fig. 5, Table 2).

4. Discussion

We found that 70–86% of the NH_4^+, 75–84% of the NO_3^- and 84% of the total P was leached from the soil columns in the first 63 days after the Osmocote$^{\circledR}$ (14-14-14) SRF was applied (data not shown). Plants growing in soils receiving SRF had greater plant biomass (growth) shoot and root N and P content than all MBF formulations regardless of $Al(SO_4)_3H_2O$ or $Fe_2(SO_4)_3$ additions. Plants growing in soils receiving SRF had 15–55% greater plant biomass than those growing in MBF formulations 112 days after application. The growth rate of plants in soils receiving SRF was greater than those growing in soil receiving MBF formulations in the 112 day time period, presumably because in soils receiving SRF, the nutrients were more available to the plant. Shoot biomass, shoot N and P, and head weight were greater in plants given SRF than the MBF formulations. The MBF formulations contained more N and P than the SRF, but a significant amount of the nutrients were bound to the $Al(SO_4)_3H_2O$, or $Fe_2(SO_4)_3$, starch, chitosan and 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 should include a fertilizer rate study to determine the amount of the MBFs that can be applied to soils to increase plant growth equal to plant growth obtained by

fertilization with the SRF while still reducing N and P leaching.

Direct losses of P from fertilizer leaching or runoff usually result when fertilizer application is coincident with heavy rain events (Haygarth and 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 SRFs 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 (Hart et al., 2003). Several studies indicated that sediment bound P concentrations in runoff generally increase as soil P concentrations increase (Sharpley et al., 1993; Pote et al., 1999; Cox and Hendricks, 2000). Long-term overfertilization of soils is recognized as potentially contributing to eutrophication of surface waters (Sims, 1993; Frossard et al., 2000).

Conventional fertilizers 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). SRFs have been employed to reduce direct fertilizer runoff losses. Nutrient leaching from SRFs is reduced through degradation of an organic or inorganic coating around a core of inorganic fertilizer. Quin et al. (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 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. 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., 2004).

Commercial SRFs can be classified into two basic groups: low solubility and polymer coated water soluble fertilizers (Blaylock et al., 2005). The polymer coated SRFs 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 SRFs 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 rates of nutrient release of polymer coated SRFs are influenced by soil temperature, the higher the soil temperature, the greater the release rate (Blaylock et al., 2005). Release rate is hypothesized to be not 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., 2000, 1998) 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 $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ and the high ionic exchange compounds starch, chitosan and lignin. These formulations allow nutrients to bind with the $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$–lignin–chitosan matrix substantially reducing leaching (Entry and Sojka, 2007). Nutrient ions having become bound to the $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$–lignin–chitosan matrix will slowly become available to most plants over several growing seasons. These matrix based formulations cover a range of inorganic N and P in compounds that are relatively loosely bound (MBF 1) to more moderately bound (MBF 2) and more tightly bound compounds (MBF 3) mixed with $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ and with the high ionic exchange compounds starch, chitosan and lignin. When N and P are released from the chemicals containing these nutrients the MBFs likely bind N and P to a $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ starch–chitosan–lignin matrix. After the starch–chitosan–lignin matrix with $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ is applied to soil the soil microorganisms will degrade the starch in the matrix comparatively rapidly and will create some ionic exchange sites. The chitosan will degrade less rapidly than starch but more rapidly than lignin and is expected to retain most of its ionic exchange sites for at least one year in most soil environments. The lignin component in the matrix will degrade more slowly than starch and chitosan and is expected to retain its ionic exchange sites for several years 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 $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ in the mixture. The MBFs bind nutrients to the $Al(SO_4)_3H_2O$ and/or $Fe_2(SO_4)_3$ starch–chitosan–lignin matrix and application rates are based on the amount of nutrients released to meet plant growth, therefore their application rates will necessarily not be comparable to conventional or SRFs, which release nutrients based on the amount of nutrient applied.

Mycorrhizal colonization in plant roots did not differ among SRF, MBF 1, MBF 2 and MBF 3 formulations

with or without $Al(SO_4)_3H_2O$ 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 nitrogen and phosphorus. *G. interadicies* was added to the matrix to enhance plant uptake of N and P.

The impact of MBF to reduce N and P leaching in the field may not be readily apparent in most cases, especially in agricultural soils. Fertilization on the same soils for years will result in N and P sorption on clay and organic matter ionic exchange sites (D'Angelo, 2005; McDowell et al., 2005; Bird et al., 2002, 2003; Devevre and Horwath, 2001). 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 (Bird et al., 2003, 2002; Entry and Emmingham, 1995) . The efficacy of MBF 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. The use of ^{15}N and ^{31}P labeled chemical components in MBF may be the most accurate method to determine the quantities of these nutrients leached from the fertilizer in most soils.

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. Although further greenhouse and field testing are called for, results of this initial investigation are promising. Cost estimates of these MBF has 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, 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.

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 its 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 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 reduce nutrient leaching and ultimately eutrophication.

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