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Nitrogen Recovery and Loss from Kentucky Bluegrass Fertilized by Conventional or Enhanced-Efficiency Urea Granules

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Abstract: Easy handling and low unit N cost make prilled urea (46-0-0) a popular fertilizer. While incomplete recovery of granular urea applications by turfgrass is documented, field evaluations of NH₃ volatilization mitigation by coatings or bioinhibitor efficiency enhancements are limited. Meanwhile, NH₃ emissions reduce air quality and contribute to nutrient loading of water resources. Our objectives were to quantify 3- and 6-d ammonia emission and 9-week turfgrass recovery of unincorporated granular fertilizer application to turfgrass. In 2014 and 2015, commercial urea-N fertilizers were broadcast over a mature Kentucky bluegrass (*Poa pratensis* L. ‘Midnight’) lawn at 43 kg ha⁻¹. Treatments included conventional urea and three enhanced-efficiency fertilizers; a blended fertilizer with 25% of its urea-N supplanted by polymer- and polymer-/sulfur-coated prills, or two stabilized urea fertilizers both amended by N-(n-butyl) thiophosphoric triamide (NBPT) and dicyandiamide (DCD) inhibitors. Using a 51% ‘trapping-efficiency’ flux chamber system under the field conditions described, 23.1 or 33.5% of the conventional urea-N was lost as NH₃ over the respective 3- or 6-d period following application. Alternatively, dual amendment by NBPT and DCD resulted in approximately 10.3 or 19.6% NH₃-N loss over the respective 3- or 6-d periods, and greater fertilizer-N recovery by the turfgrass over the 9-week experiments.

Keywords: ammonia; best management practice; turfgrass; urease inhibitor; volatilization

1. Introduction

In the presence of nitrate or sulfate, ammonia enhances the formation and growth of airborne particulate that is statistically correlated with adverse human health effects [1–4]. Ammonia deposition to surfaces, the primary atmospheric removal mechanism, is considered a significant threat to terrestrial and aquatic ecosystem health [5,6]. The majority of atmospheric ammonia in the US and Canada originates from livestock operations and fertilizer application [7,8].

Numerous investigations into ammonia loss following urea fertilizer application to turfgrass systems have been summarized [9–11]. Environmental and edaphic conditions shown to directly influence ammonia volatilization from urea fertilizer applications include temperature, wind speed, soil organic matter, and soil pH and moisture levels [12–14]. These and more recent studies have employed varying application and collection methods. As a result, ammonia-N volatilization from turfgrass systems is reported to range from 0.04 to 60% of urea-N fertilizer applied [11,13,15–17].

While urea fertilizer is subject to several fates following granular application to turfgrass, direct assimilation by plant roots and/or vegetative tissue is most desirable. Diffusion of the diminutive and polar urea molecule into the plant symplast is passive, yet reliant on hydration and a favorable

concentration gradient [18]. Over a 48-hour period following a foliar urea-N application of 50 kg ha⁻¹, assimilation by perennial ryegrass (*Lolium perenne* L.) was observed to exceed 17 kg ha⁻¹ [19].

Alternatively, urea is hydrolyzed into ammonia and carbon dioxide by urease [20], an enzyme ubiquitous to soil, thatch, and turfgrass leaf and shoot surfaces [21]. The position of urea at hydrolysis significantly influences the fate of its products [10]. Prompt incorporation of granular urea into soil, either mechanically [22–24] or via precipitation/irrigation-facilitated dissolution and infiltration [13,25–27], has been shown to reduce subsequent ammonia volatilization rate. Accordingly, best management practice (BMP) includes prompt but judicious ‘watering-in’ of urea fertilizer applications to turfgrass [9,28,29].

Yet given the perennial nature of turfgrass, limited availability and/or opportunity often preclude(s) mechanical incorporation and/or irrigation/rainfall concomitance when scheduling granular urea-N fertilization events. To that end, N-(n-butyl) thiophosphoric triamide (NBPT, C₄H₁₄N₃PS) is one of a few compounds so dependably inhibitive of biological N transformation that it has been commercially adopted [30]. Under aerobic conditions, this soluble alkane decomposes to N-(n-butyl) phosphorotriamide [31] and inhibits urease activity by forming a tridentate bond that binds its active site [32]. Subsequent meta-analyses indicate NBPT amendment of urea supports a near 50% relative-reduction in NH₃ loss following broadcast application of urea to agricultural and horticultural production systems [33–35]. More recent evaluations assessing NH₃ volatilization further confirm benefits of complimenting 100 to 175 kg ha⁻¹ urea-N applications with 0.2% NBPT [36–42].

Several laboratory or greenhouse studies have been conducted to evaluate efficacy of NBPT amendment of urea granules applied to turfgrass. One to five weeks following 48 to 50 kg ha⁻¹ urea-N granular applications, N recovery in ryegrass or creeping bentgrass (*Agrostis stolonifera* L.) clippings receiving NBPT-amended treatments exceeded levels observed in urea-fertilized counterparts [22,43]. Likewise, passive measures of NH₃ volatilization in the 24 h following the described urea treatments showed the NBPT additive to reduce NH₃ volatilization [43]. A laboratory flux-chamber assessment employing fairway plugs of hybrid bermudagrass (*Cynodon dactylon* (L.) Pers. × *Cynodon transvaalensis* Burt Davy) was initiated by a 49 kg N ha⁻¹ broadcast application of urea or commercially amended (stabilized) urea fertilizer granules. Following the 7-d evaluation period, NH₃ loss from a DCD- and NBPT-amended urea accounted for 28% of the fertilizer-N. Statistically greater NH₃ loss from conventional urea or urea combined with calcium aminoethylpiperazine and heteropolysaccharide polymers amounted to 40 to 43% of the applied N [44].

A comparatively greater number of turfgrass field experiments evaluating NBPT amendment on recovery/loss of granular urea-N fertilizer applications report mixed results. Results of a multi-year Kentucky bluegrass (*Poa pratensis* L. ‘Midnight’) field study indicate NBPT amendment of granular urea improved N recovery by clippings in one out of eight measurements [45]. Following a single-year evaluation of conventional or urease inhibitor-amended granular urea-N application (49 kg ha⁻¹), no treatment influenced performance, volatilization from, or N-recovery by the Kentucky bluegrass and perennial ryegrass mixed sward [15]. Micrometeorological methods, employed to measure ammonia volatilization 0- to 10-d following a broadcast application of 112 kg N ha⁻¹ as granular urea, ammonium sulfate, or DCD- and NBPT-amended urea over a burned Kentucky bluegrass seed production field, resulted in volatilization of 15% of the conventional urea fertilizer application [46]. In absolute percentage terms, 9.3 or 11.1% less of the respective ammonium sulfate or amended-urea treatments ($p < 0.05$) were simultaneously lost as gas [46].

The estimated area of turfgrass currently managed, yet not necessarily fertilized, in the US is 1.6×10^7 ha [47]. Several regional, state, and/or local government agencies, across the US and the world, have either enacted or drafted laws/ordinances regulating fertilizer application to managed turfgrass [48,49]. Golf course superintendents, sports turf managers, and lawn care operators are committed to worker, player, and client safety, and plant health and effective management of natural resources, and they rely on rapid transfer of practical field research and resulting best management practices (BMP). Our objectives were to quantify 3- and 6-d ammonia emission and fertilizer-N recovery

over a 9-week period following unincorporated application of conventional or enhanced efficiency granular urea-N fertilizer to an intensively managed Kentucky bluegrass system.

2. Materials and Methods

A Hagerstown silt loam (fine, mixed, semiactive, mesic Typic Hapludalfs) was established by Kentucky bluegrass (*Poa pratensis* L. 'Midnight') sod in September 2012 and subsequently maintained within the Pennsylvania State Univ. Valentine Turfgrass Research Center (University Park, PA, USA). Every 6 ± 4 days from May to October 2013 and April to July 2014, the field was mowed at a 3-cm height of cut with clippings collected and discarded. In the 2014 and 2015 seasons, weeds were controlled by manual removal, plots were irrigated as necessary to prevent wilt, and climatic conditions were logged every 15 min by an onsite weather station.

A 1:1 (by mass) slurry of de-ionized (DI) H₂O and soil, collected from the upper 15-cm of the profile in April 2014, was extracted and analyzed for pH, NO₃-N, and NH₄-N levels [50–52]. Results showed neutral soil pH (7.0) and undetectable levels of ionic N forms (<5 mg·kg⁻¹ soil). In May 2014, soluble fertilizers were applied to the Kentucky bluegrass to deliver 25 kg N, 30 kg Mg, and 75 kg K₂O and S ha⁻¹.

On 24 July 2014, the experimental area was mowed and clippings removed before installing a randomized complete block design comprising six (6) blocks of five (5) plots 1.6 × 1.0 m in size. Plots were divided by 0.6-m-wide spans on their short boundaries. Chamber installation was initiated on 25 July 2014 by setting a 16.5-cm id schedule 40 poly-vinyl chloride (PVC) end cap within in each plot and repeatedly striking it with a rubber mallet. The resulting indentation in the turf canopy served as a guide to cut a 3-cm-deep trench with a 'sharp-shooter' shovel [53]. The end cap was then firmly seated within the trench to a 2.5-cm depth, removed, and the process repeated on the remaining twenty-nine plots.

At 10:00 on 25 July, a 40-mL aliquot of standard 2% boric acid (H₃BO₃) was dispensed into a pre-labeled '0-3-d trip blank' high-density polyethylene (HDPE) bottle and tightly capped. Numbered vials containing pre-weighed, urea-based fertilizer granules; corresponding to the described fertilizer treatments (Table 1) were carefully applied within the chamber 'enclosure area' of a randomly selected plot at the prescribed 43 kg ha⁻¹ urea-N rate. The treatment was then 'activated' by 0.1-mm DI H₂O (1223 L ha⁻¹) using a single-nozzle, CO₂-powered backpack sprayer and an air induction even flat-spray tip (TeeJet AI9508EVS, Spraying Systems Co., Wheaton, IL, USA).

Table 1. Described grade and enhancement of the employed granular fertilizers.

Urea Fertilizer Treatment ¹	Urea-N (g kg)	P ₂ O ₅ (g kg)	K ₂ O (g kg)	Inhibitor/Additive/Enhancement	Mass Fraction (g kg)
U	460	0	0	–	–
EEF-S1	460	0	0	Dicyandiamide (DCD) N-butyl-thiophosphoric triamide (NBPT)	10.5 0.9
EEF-S2	460	0	0	Dicyandiamide (DCD) N-butyl-thiophosphoric triamide (NBPT)	21.0 0.9
EEF-C	290	20	50	Slowly available N from polymer- and polymer-/sulfur-coated urea	72.0

¹ Urea fertilizer treatments: EEF-S1, stabilized urea (UFLEX), EEF-S2, stabilized urea (UMAX), Koch Agronomic Services, Wichita, KS, USA; EEF-C, coated-urea/urea blend (STA-GREEN), Pursell's, Sylacauga, AL, USA; U, urea, Alfa-Aesar, Ward Hill, MA, USA.

Immediately following each granular fertilizer activation, a flux chamber was installed on the plot. Each flux chamber was comprised of a PVC endcap modified by a 0.5-cm-wide by 2.7-cm-deep notch and two 0.63-cm holes in opposite sides [53]. One hole was fitted with a 3.2-mm od nylon hose connector and sealed by epoxy. The other threaded by a 14-cm length of 3.2-mm id vinyl tube (Tygon®),

Saint-Gobain, Valley Forge, PA, USA) and its internal end connected to the stem of a 60-mm id, translucent-HDPE funnel. While unquantified, these inlets provided limited illumination of the turfgrass canopy within the flux chambers over the experimental photoperiods. Lastly, each funnel mouth was fastened to the draw-side of a 60-mm case fan (12 VDC, Fanner Tech USA, City of Industry, CA, USA) by two (2) nylon zip-ties and an epoxy seal.

While not immediately activated, the purpose of this case fan was to facilitate intake air mixing, i.e., disruption of laminar flow between the inlet and outlet port of each chamber. The 12 V supply wires for the fan were run out the 0.5-cm-wide notch, and the flux chamber was then driven to a 2.5-cm soil-penetration depth using a rubber mallet. Firm seating of each flux chamber was confirmed by resistance to dislodging efforts and visible pinching of the fan wire jacket between the chamber and vegetation. Using one hand to apply pressure to the top of the flux chamber, the intake hose was then cinched to seal the chamber where the tube expanded over the tapered funnel stem, and the plot number and time recorded.

Once the four fertilizer treatments had been applied, activated, and instrumented to randomly selected plots in a block, the remaining zero-N 'control' plot was treated with DI H₂O as described above and equipped with a flux chamber. The plot number and time was recorded, and the process initiated on the next block.

Once all treatments were applied and chambers installed, a dispensetter was used to add 80 mL of stock 2% standardized boric acid solution to each 250-mL scrubbing flask (Scienceware, Bel-Art Products, Wayne, NJ, USA). The flask intake stem was fitted by a 0.5-m length of 3.2 mm id vinyl tube, and the flask firmly sealed. Lastly, the described vinyl tube was fastened to the nylon hose connector of its dedicated flux chamber. During the post-treatment filling of gas scrubbing flasks in blocks B, D, and E, 80-mL aliquots of boric acid were dispensed directly into '0-3-d trip blank' labeled HDPE bottles and tightly capped.

Three vacuum manifolds, constructed from 0.8-m lengths of 5.1-cm PVC pipe, were placed within block borders and connected to all gas scrubbing flask vacuum stems in adjacent blocks. A 7-m length of 3.2-mm id tube was then used to connect each manifold to a centrally located vacuum splitter fitted with 3.2-mm od nylon hose connectors. A 1.5-m length of thick-walled vacuum hose connected the vacuum splitter to an industrial-grade vacuum pump (DV-142N, JB Industries, Aurora, IL, USA). Once all scrubbing flask/manifold/vacuum splitter connections were secured, the vacuum pump was actuated to draw 142 L·min⁻¹ over the 6-d experimental period.

Lastly, all case fan power supply wires were connected in two parallel-configured loops. A timer relay (Schneider Electric, LLC, Schaumburg, IL, USA) alternated 12 VDC delivery on 2-minute intervals. Two fully charged 7-Ah batteries connected to either a 60 W solar panel charging module or a 120 VAC to 12 VDC 4-A transformer (drawing from vacuum pump extension cord) facilitated continual fan operation. During each 6-day period the PVC chambers were in place, the plots were neither mowed nor irrigated.

From 10:00 to 11:30 on 28 July, each plot was revisited in the order of treatment applications 3 d prior. The vinyl tube connecting the scrubbing flask to the manifold was clamped before unsealing and decanting the boric acid solution into a pre-labeled 120-mL, wide-mouth HDPE bottle. A dispensetter was used to replace 80-mL of stock 2% standardized boric acid solution to the scrubbing flasks, and each flask was resealed. As 3-d previous, 80-mL aliquots of boric acid were dispensed directly into '3-6-d trip blank' labeled HDPE bottles. All bottles were transported to the laboratory and stored at 4 °C. On 31 July, the gas scrubbing flask contents were again collected as described, and the bottles were tightly capped for subsequent transport and laboratory storage at 4 °C. With the exception of the flux chambers, all volatilization measurement equipment was collected from the plots. The remaining granular fertilizer for each plot treatment; i.e., fertilizer mass required to treat the remaining 1.579 m² of plot area (1.6 m²–2.128 × 10⁻² m² flux chamber area), was applied by hand. Once all non-control plots received their assigned 43 kg ha⁻¹ urea-N treatment, the flux chambers were removed and the EEFC plots were 'activated' by 0.1-mm DI H₂O (1223 L ha⁻¹) as previously described. All other

plots, including the controls, were 'activated' by 0.1-mm (1223 L ha⁻¹) of a dilute fertilizer solution supplying P₂O₅ and K₂O at respective rates of 2.97 kg and 7.41 kg ha⁻¹. This marked initiation of the full-plot fertilizer-N recovery trial; i.e., zero days after full plot treatment (0 DAFPT).

The plots remained flagged over the subsequent 61-d experiment to prevent inadvertent mowing. Purposefully avoiding the prior location of the flux chamber in each plot, a dedicated rotary deck-mower was used to collect clipping yields at a 3-cm height of cut over a 1.6-m-long and 0.56-m-wide swath on 8, 17, and 26 August (8, 17, and 26 days after full plot treatment; DAFPT) and 3, 10, 17, and 30 September 2014 (34, 41, 48, and 61 DAFPT). Immediately following these yield measures, all remaining turf was mowed and clippings were collected and discarded offsite. Clippings yields were dried to constant mass in a forced-air oven (65 °C) and transferred to desiccators for storage. Each mass of dry clipping samples was determined at 1-mg resolution and recorded. For each experimental unit, a 1-g subsample from each clipping yield event was ground to pass a 0.5-mm sieve and analyzed for total N [54] by medium temperature furnace combustion (EA-1110 CHNS analyzer, CE Instruments, Milan, Italy).

Each date-specific product of yield and tissue N was calculated as N offtake (kg N ha⁻¹) on a per-plot basis [55] and represents apparent N recovery for the time period from the last mowing event, either 0 DAT or more recent clipping yield collection. Control-adjusted fertilizer-N recovery for each fertilized experimental unit and date was calculated by subtracting the control plot offtake on a per block basis.

A similar experiment was initiated 4 September 2014 on an adjacent section of the Kentucky bluegrass system. However, the plots were 0.61-m-square and only the 2.128 × 10⁻² m² flux chamber areas in each plot were fertilized, activated, and instrumented (all as previously described). Likewise, on 7 September, the gas scrubbing flask contents were collected, replaced with 80-mL of stock 2% standardized boric acid solution, and each flask was resealed. Bottles containing the 0 to 3-d samples and 3-6-d trip blanks were tightly capped and transferred to the laboratory for storage (4 °C). The gas scrubbing flask contents were again collected on 10 September 2014, transferred into labelled bottles, and stored as described. All volatilization measurement equipment was removed, and no further data was collected from the September experiment.

In 2015, an identical pair of studies was conducted in unique sections of the described Kentucky bluegrass system. The first was initiated 28 July and employed the identical plot number, plot size, fertilizer treatments and methodology as the July 2014 study described above. Following termination of the volatilization measures 3 August 2015, the full-plot fertilizer granules were applied, chambers removed, and treatments activated as described. The plot area remained flagged to prevent inadvertent mowing.

A second volatilization study was initiated the following day, by installation of thirty 0.61-m-square plots in randomized complete block design on an adjacent section of the described system. Flux chamber installation in the center of each was initiated, and only the 2.128 × 10⁻² m² flux chamber areas in each plot were fertilized, activated, and instrumented (all as previously described). On 7 August, the gas scrubbing flask contents were collected, replaced with 80 mL of stock 2% standardized boric acid solution, and each flask was resealed. Bottles containing the 0 to 3-d samples and 3-6-d trip blanks were tightly capped and transferred to the laboratory for storage (4 °C). During each 6-day period the PVC chambers were in place, the plots were neither mowed nor irrigated. The gas scrubbing flask contents were again collected on 10 August 2015, transferred into labelled bottles, and stored as described. All volatilization measurement equipment was removed, and no further data was collected from the second 2015 study.

Termination of the first volatilization study 3 August marked initiation of the subsequent 63-d full-plot fertilizer-N recovery trial. The described rotary deck-mower was used to collect clipping yields at a 3-cm height of cut over a 1.6-m-long by 0.56-m-wide swath on 13, 20, and 27 August (10, 17, and 24 DAFPT); 4 and 16 September (32 and 44 DAFPT); and 5 October 2015 (63 DAFPT). Immediately

following these yield measures, all remaining turf was mowed, and clippings were collected and discarded offsite.

The mean pH level of the four, field-dispensed, date-specific, 2% boric acid ‘trip blanks’ collected from each experiment conducted in 2014 and 2015 was determined in the laboratory. A 15-mL sample of each recovered boric acid solution was decanted into an HDPE beaker, then titrated with standardized 0.01 N HCl to its collection-date specific pH endpoint using a digital burette. The volume of each remaining sample was measured by graduated cylinder and recorded. Titrated NH₃-N for each flux chamber (per 3-d period) was calculated as shown (Equation (1)).

$$\left[\begin{array}{c} \text{titrated NH}_3 - \text{N}, \\ \text{kg ha}^{-1} \end{array} \right] = \left[\begin{array}{c} \text{L titrant} \\ 2.13 \times 10^{-6} \text{ha} \end{array} \right] \left[\begin{array}{c} 0.01 \text{ eq H}^+ \\ \text{L titrant} \end{array} \right] \left[\begin{array}{c} 1.4 \times 10^{-2} \text{kg NH}_3 - \text{N} \\ \text{eq NH}_4^+ \end{array} \right] \quad (1)$$

To determine volatilized NH₃-N from treatment, titrated NH₃-N (kg ha⁻¹) was multiplied by its specific ratio of collected-to-titrated boric acid, then corrected for background NH₃-N by subtracting volatilized NH₃-N measured from the control plot within its experiment block. Lastly, fertilizer-N volatilized as NH₃ (kg ha⁻¹) is the product of volatilized NH₃-N from treatment and the chamber efficiency multiplier (1.965, Appendix A).

The 41- and 48-DAFPT clipping yields and N offtakes measured in 2014 were summed to standardize the number of data collection events over both experiments. All repeated measures of volatilized NH₃-N ($n = 192$), clipping yield ($n = 360$), N offtake ($n = 360$), or fertilizer-N recovery ($n = 288$) dependent variables were combined for global analysis using the MIXED procedure (SAS Institute, v. 8.2). The employment of identical treatment levels and similar cultural, climatic, and edaphic conditions compelled the designation of ‘experiment’, and all subsequent interaction terms were designated as random variables. Significance of N-fertilizer treatment effect (TRT) was F-tested by the expected mean squares of its respective experiment interaction term, while the DAIT or DAFPT effect and its interaction with TRT was F-tested by the residual [56].

3. Results

Mean, maximum, and minimum air temperature recorded over the four 6-d ammonia volatilization collection periods ranged from 20.6 to 23.5, 28.5 to 33.5, and 10.0 to 14.1 C, respectively. Water-tight containers were employed to protect AC wiring and vacuum pump connections during respective 1.9-, 1.3-, and 1.0-cm precipitation events occurring 28 July, 30 July, and 6 September 2014, as well as during a 1.5-cm precipitation event occurring 30 July 2015.

Adjusted for chamber efficiency and 0- to 3-d following initiation, flux-chamber mean ammonia-N volatilization from control (unfertilized) plots was 0.080 kg ha⁻¹, with measures observed over a range of 0 to 0.417 kg ha⁻¹. From 3- to 6-d following initiation, the flux-chamber mean ammonia-N volatilization from the control (unfertilized) plots was 0.124 kg ha⁻¹, with measures ranging from 0 to 0.831 kg ha⁻¹.

3.1. Volatilization of Urea Fertilizer Nitrogen as Ammonia

Fertilizer-N volatilized as NH₃ was influenced by the main effect of fertilizer treatment (TRT), days after initial treatment (DAIT), and their interaction (Table 2).

Table 2. Analysis of variance by fixed effect and dependent variable. Mean separation of clipping yield and N offtake, and cumulative fertilizer-N volatilized as NH₃ or recovered in clippings, by fertilizers. EEF-S1, stabilized urea (UFLEXX), EEF-S2, stabilized urea (UMAXX), EEF-C, coated-urea/urea blend (STA-GREEN).

Source	Clipping				Fertilizer-N					
	df		yield	N offtake	df		Volatilized as NH ₃	df		Recovered in clippings
	num	den	<i>P</i> (FR < <i>F</i> _{crit})		num	den	<i>P</i> (FR < <i>F</i> _{crit})	num	den	<i>P</i> (FR < <i>F</i> _{crit})
TRT	4	4	<0.0001	<0.0001	3	9	0.0002	3	3	0.0329
DAFPT/DAIT ¹	5	315	<0.0001	<0.0001	1	152	<0.0001	5	250	<0.0001
TRT X DAFPT/DAIT	20	315	0.4980	0.2744	3	152	<0.0001	15	250	0.9702
Nitrogen fertilizer TRT	Mean clipping			Cumulative fertilizer-N						
	yield	N offtake		Volatilized as NH ₃			Recovered in clippings			
	kg ha ⁻¹			kg ha ⁻¹						
EEF-S1	220.3	10.0		8.3 (19.3%)			31.1 (72.4%)			
EEF-S2	219.5	10.1		8.6 (19.9%)			31.3 (72.9%)			
EEF-C	209.8	9.5		11.0 (25.6%)			28.3 (65.8%)			
Urea	206.7	9.3		14.4 (33.5%)			26.9 (62.5%)			
Control	119.2	4.9		–			–			
LSD ² a = 0.05	7.13	0.60		1.99			2.76			

¹ DAFPT, days after full-plot treatment; DAIT, days after initial treatment. ² LSD, least significant difference.

The main effect of DAIT revealed that 6.49 kg ha^{-1} fertilizer-N volatilized over the 0- to 3-d period following unincorporated applications of granular fertilizer, a greater emission than the mean value of 4.07 kg ha^{-1} observed over the 3- to 6-d period.

The main effect means of fertilizer-N volatilized as NH_3 and the associated Fisher's Protected least significant difference (LSD, 5%) were multiplied by two for presentation as cumulative fertilizer-N volatilized as NH_3 (Table 2). Cumulative fertilizer-N loss from conventional urea over the 6-d period totaled 14.4 kg ha^{-1} , amounting to 33.5% of the original $43 \text{ kg urea-N ha}^{-1}$ application. Over the same period, cumulative fertilizer-N loss from the original 43 kg ha^{-1} EEF-C fertilizer application totaled 11.0 kg ha^{-1} (25.6%). Cumulative 0- to 6-d ammonia-N loss from the respective EEF-S1 or -S2 fertilizer treatment totaled 8.3 or 8.55 kg ha^{-1} and comprised, on average, 19.6% of the original $43 \text{ kg urea-N ha}^{-1}$ application (Table 2).

All granular treatments released over half the total amount of fertilizer-N volatilized within 3 d (Figure 1). This was most apparent of the 0-to 3-d NH_3 emission resulting from unincorporated application of conventional urea. This emission equaled 9.95 kg ha^{-1} and exceeded that of all other fertilizer treatments (Figure 1). Fertilizer-N volatilization from the EEF-C fertilizer, 0- to 3-d following unincorporated application, equaled 7.12 kg ha^{-1} and exceeded the dual-inhibitor-enhanced fertilizer treatments (Figure 1). Ammonia-N volatilization, 0- to 3-d following unincorporated applications of the EEF-S1 and -S2 fertilizers, were similar and averaged 4.45 kg ha^{-1} . Between 3.87 and 4.47 kg ha^{-1} of fertilizer-N was measured as volatilized NH_3 over the 3- to 6-d period following broadcast application, yet no differences among fertilizer treatments were observed (Figure 1).

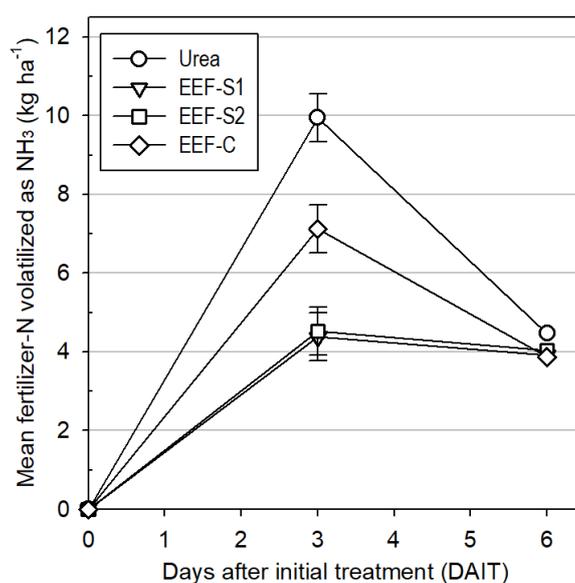


Figure 1. Mean ammonia volatilization by days after initial treatment (DAIT) and fertilizer; EEF-S1, stabilized urea (UFLEXX), EEF-S2, stabilized urea (UMAXX), EEF-C, coated-urea/urea blend (STA-GREEN). Where present, error bars designate the least significant difference (LSD) at a 0.05 α -level.

3.2. Turfgrass Growth and Recovery of Fertilizer Nitrogen

The N-limited status of the Kentucky bluegrass system over the two experimental seasons is confirmed by the observed disparity in mean clipping yield and N offtake (kg ha^{-1}) between fertilized and unfertilized (control) plots (Table 2). Across all fertilizer treatments and over the 9-week clipping yield collection period, 62.5 to 72.9% of the fertilizer-N was recovered. The EEF-S1 and -S2 treatments resulted in greater mean clipping yield and cumulative fertilizer-N recovered in clippings than the EEF-C and conventional urea fertilizer treatments (Table 2).

While fertilizer treatment did not interact with days to influence clipping yield or fertilizer-N recovery, the EEF-C treatment resulted in 30% less clipping yield than all other treatments 8- to 10-DAFPT. Likewise, the EEF-C-treated plots showed clipping yield and cumulative fertilizer-N recovered in clippings that equaled or exceeded levels simultaneously observed of EEF-S1 and -S2 fertilized plots 41- to 63-DAFPT (data not shown). These results were not unexpected, given that fertilizer prill coatings, whether sulfur and/or polymer, are engineered to delay dissolution of the soluble N source within [9].

4. Discussion

Flux chamber field measures of 0- to 6-d percent ammonia-N loss in the current field study agree with values published using micrometeorological or flux chamber field measures following granular urea-N treatment of turfgrass or pasture at similar or heavier application rates. Over two repeated 8-d periods initiated by 100 kg urea-N ha⁻¹ granular fertilizer applications to a Kentucky bluegrass and creeping red fescue (*Festuca rubra* (L.) ssp. *rubra* Gaudin) lawn mixture, volatilization losses of 6.7 to 15.1% of the applied fertilizer-N were observed [27]. Ten days following granular urea treatment of hybrid bermudagrass or zoysiagrass (*Zoysia japonica* Steud.) sod fields, cumulative ammonia-N volatilization losses were observed to range from 11.7 to 20.1% of the original 146 kg urea-N ha⁻¹ application [17]. Over nine experiments initiated by 30 kg urea-N ha⁻¹ granular fertilizer applications to a ryegrass and white clover (*Trifolium repens* L.) pasture [57], 8-day cumulative ammonia-N losses between 7.4 and 20.2% of urea-N applied resulted.

Given fertilizer prill coatings, whether sulfur and/or polymer, are engineered to delay dissolution of soluble N sources within, reduced volatilization from the EEF-C treatment relative to conventional urea was expected [9]. In an un-mowed 10-d lab incubation, reduction in NH₃ volatilization from sulfur- or polymer-coated urea fertilizer treatments were observed relative to conventional urea. More specifically, the polymer-coated urea fertilizer evaluated in that lab study resulted in zero NH₃ emission [16]. The EEF-C fertilizer employed in this field study contained 24.8% of a polymer- and polymer-/sulfur-coated urea-N (Table 1) sourced from the same producer. Not unexpectedly, the EEF-C fertilizer treatment emitted 23.6% less cumulative NH₃ than the conventional urea treatment over 6 d of field measures (Table 2).

Under the described conditions, and relative to identical application of conventional urea, both NBPT- and DCD-amended EEF-S fertilizers reduced cumulative fertilizer-N volatilization by a mean absolute percentage of 13.9. These results are consistent with those of a field study measuring NH₃ volatilization over a 4-d period following four monthly applications of 49 kg urea-N amended with 0, 0.245, 0.49, or 0.98 kg NBPT per hectare (0.5, 1, or 2% by mass) [58]. Amendment by NBPT resulted in an 11% mean absolute reduction in fertilizer-N volatilized as NH₃. Perhaps of greater noteworthiness, the 13.9% absolute reduction observed herein resulted from only 0.09% NBPT amendment of the granular urea.

Increased recovery of NBPT-amended fertilizer observed in our study agrees with published reports. For example, five weeks after fertilizing perennial ryegrass pots with solutions supplying 56.6 kg ha⁻¹ urea-N, either alone or in combination with NBPT, phenyl-phosphorodiamidate, or hydroquinone, mean N recovery in shoots receiving urea + NBPT exceeded levels observed in all other treated pots [59]. Likewise, over 4 weeks following monthly applications of a 49 kg urea-N amended with 0.5, 1, or 2% NBPT by mass, increased Kentucky bluegrass clipping yield was observed relative to urea alone [58]. In a follow-up study, and 6 weeks following 49 kg ha⁻¹ urea-N applications to Kentucky bluegrass field plots, 0.25% amendment of urea-N by NBPT resulted in greater plant recovery and soil availability of fertilizer-N than urea alone [60].

5. Conclusions

Turfgrass requires greater quantities of N than any other mineral nutrient, and N sufficiency is promptly supported by application of soluble N fertilizer(s) like urea. Current best

management practices (BMPs), e.g., 'soil incorporation' of urea fertilizer by cultivation, coincidental rainfall or scheduled irrigation event(s), may be precluded by inopportunity or playability requirements. When such circumstances prevail over a 3- or 6-d period following broadcast application, this field research shows commercial NBPT+DCD-amendment of urea prevents respective volatilization of 5.5 or 6.0 kg NH₃-N ha⁻¹, and indeed enhances N-fertilizer efficiency. Likewise, and under the described conditions, supplanting 25% of conventional urea-N with polymer- and polymer-/sulfur-coated urea prevents volatilization of 2.8 or 3.4 kg NH₃-N ha⁻¹ over the respective 3- or 6-d period following broadcast application. If no other soluble N-fertilizer source is available to support a critically important granular application under the described conditions, then employ of a NBPT+DCD-amended urea fertilizer constitutes a recommended best management practice, particularly in PM2.5 (particulate matter, <2.5 μm) non-attainment regions.

Supplementary Materials: The following are available online at <http://www.mdpi.com/2073-4395/8/8/144/s1>, Dataset S1: NH3Volatile.csv, Dataset S2: TURFcy_Noff.csv.

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Appendix A.

Appendix A.1. Trapping-Efficiency Trial Methods

In July 2016, a completely randomized design of six plots, 1.0- × 0.8-m in size, was installed in a similarly maintained turfgrass lawn within the Valentine Turfgrass Research Center. Each plot was marked and prepared for a chamber seating as described in the Materials and Methods section. Three randomly selected plots were prepared exactly as the described unfertilized (control treatment) flux chamber plots. The remaining three plots housed a flux trapping-efficiency chamber.

The flux trapping-efficiency chambers were modified by installation of a rubber septum on the opposite end of the intake tube and case fan. A 20-mL HDPE beaker was filled with 15 mL of 0.227 M (NH₄)₂SO₄ and set within the circular chamber trench to reside directly beneath the rubber septum. The beaker was then covered by the flux trapping-efficiency chamber, and the chamber driven to a 2.5-cm soil-penetration depth using a rubber mallet.

Scrubbing flask preparation and tube connections were conducted as described previously. A hypodermic needle containing 3 mL of 10 M KOH was then inserted into the septum, and its contents emptied into the beaker containing (NH₄)₂SO₄. Thus, three replicate control flux chambers and three flux trapping-efficiency chambers were fully prepared prior to activating the vacuum pump in July 2016. Complete volatilization of N from the (NH₄)₂SO₄ aliquot would generate the equivalent of 43 kg ha⁻¹ NH₃-N within the head space of each trapping-efficiency chamber.

Appendix A.2. Trapping-Efficiency Trial Results

The mean volatilized ammonia recovered in the flux-chamber trapping-efficiency trial ($n = 3$), once corrected for mean 'background' ammonia simultaneously collected from unfertilized plots using conventional flux chambers, was 21.88 kg ha⁻¹. Assuming complete conversion of NH₄⁺ to NH₃ within the 15-mL aliquots of 0.227 M (NH₄)₂SO₄ over the 0- to 3-d period, the trapped quantities of ammonia-N signify a mean efficiency (±95% confidence interval) of 50.9% (±16.4%) for the respective static- or flux-chamber systems. The reciprocal of the trapping efficiency determined for the described flux chamber system equals 1.965.

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