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Field Quantification of Ammonia Emission following Fertilization of Golf Course Turfgrass in Sub/Urban Areas

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Abstract: Low cost and favorable handling characteristics make urea (46-0-0) a leading nitrogen source for frequent, foliar N fertilization of golf course putting greens in season. Yet few field investigations of resulting NH_3 volatilization from putting greens have been directed. Meanwhile, NH_3 emissions degrade air and surface water quality. Our objective was to quantify NH_3 volatilization following practical, low-N rate, and foliar application of commercial urea-N fertilizers. Over the 2019 and 2020 growing seasons in University Park, PA, USA, an industrial vacuum pump, H_3BO_3 scrubbing flasks, and sixteen dynamic flux chambers were employed in four unique experiments to measure NH_3 volatilization from creeping bentgrass putting greens (*Agrostis stolonifera* L. 'Penn G2') in the 24 h period ensuing foliar application of urea based-N at a 7.32 or 9.76 kg/ha rate. Simultaneous and replicated flux chamber trapping efficiency trials showing 35% mean NH_3 recovery were used to adjust NH_3 volatilization rates from treated plots. Under the duration and conditions described, 3.1 to 8.0% of conventional urea N volatilized from the putting greens as NH_3. Conversely, 0.7 to 1.1% of methylol urea liquid fertilizer (60% short-chain methylene urea) or 0.7 to 2.2% of urea complimented with dicyandiamide (DCD) and *N*-(*n*-butyl) thiophosphoric triamide (NBPT) volatilized as NH_3.

Keywords: biological inhibitor; creeping bentgrass; dicyandiamide (DCD); flux chamber; methylene urea; *N*-(*n*-butyl) thiophosphoric triamide (NBPT); nitrogen; nutrient fate; putting green; urea

1. Introduction

Foliar fertilization, or frequent spray application of soluble nutrient forms, is an increasingly popular method for ensuring nutritional sufficiency of intensively managed turfgrass in season [1]. A common ingredient of commercial liquid fertilizers, urea-N is routinely applied by golf course superintendents [2,3].

Urea, $CO(NH_2)_2$, is a plant-available *N*-form subject to two possible outcomes following foliar application. The more desirable is symplast assimilation [4]. This fate of foliarly applied urea-N has been observed to account for as much as 7 kg/ha d^{-1} on creeping bentgrass (*Agrostis stolonifera* L.) putting greens [5]. Alternatively, foliarly applied urea is hydrolyzed into ammonia (NH_3) and carbon dioxide (CO_2) by urease [6], an enzyme ubiquitous to soil, thatch, and turfgrass leaf and shoot surfaces [7].

Edaphic and/or environmental conditions, as well as the position of urea at hydrolysis, significantly influence the fate of its products [8,9]. Incorporation of urea into acidic soil facilitates ammonia transformation into the plant-available ammonium form [10,11]. Likewise, NH_3 volatilization from turfgrass receiving urea-N spray application has been successfully mitigated by prompt irrigation [12,13].

Best management practices for N fertilization have long included prompt but judicious "watering in" of urea fertilizer applications to turfgrass [14]. Yet clientele expectations and/or explicit label instructions for products included in the spray application sometimes preclude irrigation or precipitation concomitance when scheduling foliar urea fertilization events.

Fortunately, numerous urea + urease inhibitor combination products are marketed to professionals seeking to prevent gaseous loss. Under aerobic conditions, *N*-(*n*-butyl) thiophosphoric triamide (NBPT, $C_4H_{14}N_3PS$) transforms into *N*-(*n*-butyl) phosphorotriamide and impedes urease activity by making a trifurcate bond to its active site [15,16]. There currently exists a slew of evidence relating NBPT amendment of urea to near 50% relative reductions in ammonia emission following application to agricultural and horticultural production systems [17–20].

Field experiments evaluating turfgrass recovery, or loss, of NBPT–complimented urea-N applications are limited and report mixed results. Results of a multiyear Kentucky bluegrass (*Poa pratensis* L.) field study that complimented 49 or 98 kg/ha urea-N drench applications (1630 L ha^{-1}) with NBPT (1.1 kg/ha) did not show the NBPT amendment to be beneficial to turfgrass [21]. However, over four 96-h measurement periods following a 49-kg urea-N application to Kentucky bluegrass, treatments complimented with 0, 0.245, 0.49, or 0.98 kg NBPT ha^{-1} (0, 0.5, 1, or 2% by mass) showed 18% of the conventional urea-N volatilized as NH_3–N compared to 7% of the urea-N fertilizer complemented with up to 2% NBPT [22]. A multiyear putting green study employing a 20 kg urea-N ha^{-1} rate reported 11% of conventional urea volatilized over a single day following foliar application, whereas only 3 to 5% of urea-N volatilized when complimented by dicyandiamide (DCD) and NBPT [23].

Most atmospheric ammonia in North America originates from livestock production and fertilizer application. In the presence of sulfate or nitrate, NH_3 constitutes the most significant and influential precursor to smog formation, i.e., particulate matter < 2.5 μm in diameter ($PM_{2.5}$). Elevated ammonia and $PM_{2.5}$ levels are monitored in numerous non-attainment regions in the US (Figure 1 [24]) and abroad and are statistically correlated to adverse health effects [25]. Furthermore, ammonium deposition to surfaces, the primary atmospheric removal mechanism, is considered a serious threat to terrestrial and aquatic ecosystem health [26]. Modern golf course superintendents rely on practical field research results to maximize their fertilizer use efficiency. Our experiment objective was to employ a requisite number of dynamic flux chambers to simultaneously quantify NH_3 volatilization from creeping bentgrass putting greens 0- to 24-h following foliar application of urea based-N at a 7.32 or 9.76 kg/ha rate using commercially available fertilizers.
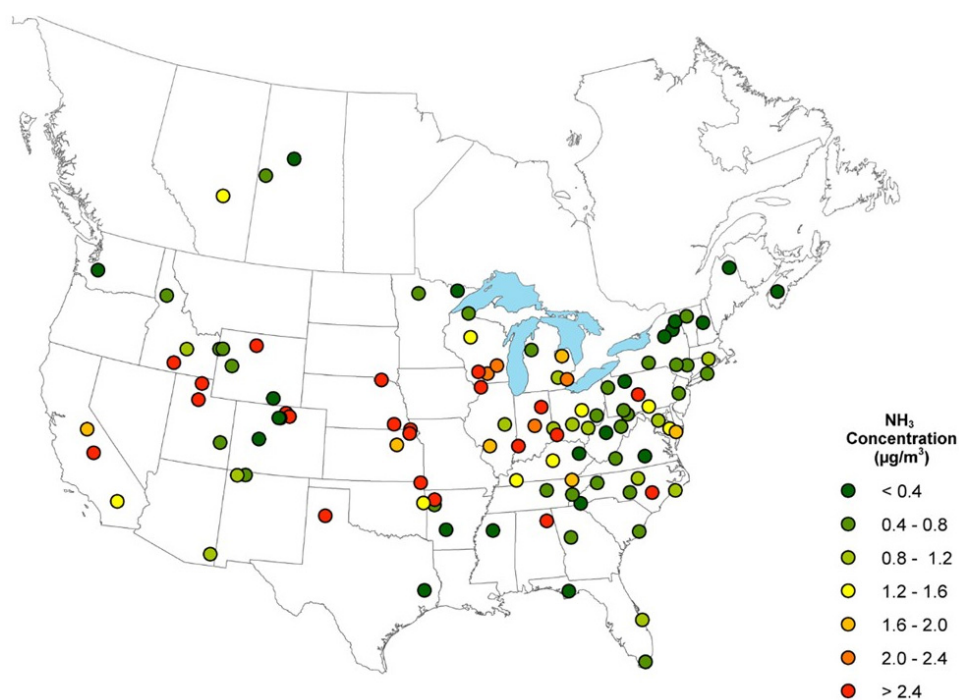
Figure 1. Mean surface NH_3 concentrations across the USA and Canada in 2020 [24].

2. Materials and Methods

In June 2019, the rootzone of a 'Penn G2' creeping bentgrass putting green maintained within the PSU Valentine Turfgrass Res. Center (University Park, PA, USA) was sampled to a 15-cm depth for routine soil fertility analysis by the PSU Agric. Anal. Services Laboratory. Maintenance of the putting green system in growing months included semi-monthly application of paclobutrazol plant growth regulator (Trimmit 2SC, Syngenta Crop Protection, Greensboro, NC, USA) at label rates, irrigation to prevent wilt, and mowing 6 ± 1 days each week at a 3.1-mm height of cut. Clippings were collected and not returned.

Following mowing on 8 July, two separate randomized complete block designs, each comprised of sixteen (16) plots in four (4) blocks, were installed. All 1.83×0.76 m (1.39 m^2) plots were separated by a 0.61-m boundary on their short-side border. Following mowing on 9 July, liquid *N*-fertilizer treatments (Table 1) were applied to all plots in four blocks (Table 1) to supply 9.76 kg N/ha (0.2 lbs N per 1000 ft^2). A CO_2–powered backpack sprayer applied all treatments in 815 L ha^{-1} carrier volume, per a 25-mesh nozzle strainer and even-spray tip (TeeJet® 1108EVS, Spraying Systems Co., Glendale Heights, IL, USA) equipped spray wand. An unfertilized control plot was treated in each block using de-ionized H_2O. Each application of described foliar treatment to an experimental unit was immediately followed by installation of its dedicated ammonia-measuring closed flux-chamber [3,23].

Table 1. Years, runs, fertilizer sources and rates, and fertilizer components and additives employed in the experimental trial.

Number (Year) of 24 h Evaluations	Fertilizer *N* Rate, kg/ha	Fertilizer Source (%N–%P$_2$O$_5$–%K$_2$O)	Components and Additives
1 (2019) 1 (2020)	7.32 (0.15 lbs / M)	Urea (46-0-0)	None
		Urea + UF RXN products (30-0-0) †	180 g kg^{-1} Methylene ureas
		Urea + DCD +NBPT (46-0-0) ‡	21 g kg^{-1} DCD 1 g kg^{-1} NBPT
2 (2019)	9.76 (0.2 lbs/M)	Urea (46-0-0)	None
		Urea + UF RXN products (30-0-0)	180 g kg^{-1} Methylene ureas
		Urea + DCD + NBPT (46-0-0)	21 g kg^{-1} DCD 1 g kg^{-1} NBPT

† Nitamin 30 L, Koch Agronomic Services, Wichita, KS, USA; ‡ UMAXX, Koch Agronomic Services, Wichita, KS, USA.

Three flux trapping-efficiency chambers were modified only by installation of a 3.1 mm hole on the opposite end of the intake tube and case fan and subsequently covered by electrical tape. A 15 mL HDPE beaker, filled with 5 mL of 0.156 M $(NH_4)_2SO_4$, was then carefully placed to reside directly beneath the drill hole. Each flux trapping-efficiency chamber was then installed over the plot and beaker and driven to a 25 mm soil-penetration depth using a rubber mallet. Scrubbing flask preparation and tube connections were conducted as described previously. A hypodermic needle containing 2 mL of 10 M KOH was then inserted through the tape seal and hole, and its contents emptied into the beaker. Thus, trapping efficiency flux chambers were prepared in triplicate immediately following activation of the vacuum pump. Complete volatilization of N in the 0.156 M $(NH_4)_2SO_4$ aliquot generated the equivalent of 9.76 kg/ha NH_3-N within the chamber head space.

The following day (10 July), gas scrubbing flask contents were collected from the plots in the order foliar treatments were applied 24 h earlier. The vacuum hose connecting the scrubbing flask to the manifold was clamped before unsealing and decanting the 2% H_3BO_3 solution into labelled, 175 mL, wide-mouth HDPE bottles. The bottles were tightly-capped and boxed for transfer and subsequent titration by standardized 0.02 N HCl in the laboratory. Measurement of NH_3 emission was limited to the 24 h post-application period as it constitutes the interval between typical mowing events and/or time golf course managers withhold irrigation following foliar applications.

The adjacent sixteen plots were then mowed while condensate was dispersed from the chambers, equipment, and tubing using compressed air. The second experimental run was then initiated on the sixteen adjacent plots by assigning and applying the same fertilizer treatments, exactly as described for 9 July above, in randomized complete block design. An NH_3-collecting flux chamber was again immediately installed on each treated plot prior to treating any subsequent plot, field blanks were dispensed, and scrubbing flasks connected. The following day (11 July), gas scrubbing flask contents were collected from each plot in the order the foliar treatments were applied 24 h previous, and all volatilization-measurement equipment was removed from the putting green.

A similar experiment was established on a unique area of the 'Penn G2' creeping bentgrass putting green in late May 2019. The primary differences between this experiment run and those described above were: larger plot size (1.83×0.92 m), a lower urea-N fertilizer application rate (7.32 kg N/ha), and a proportionally lower (611 L ha^{-1}) carrier volume. Likewise, these described N fertilizer applications were initiated 24 May and reapplied every 11 ± 3 d.

Following mowing on 16 July, liquid *N*-fertilizer treatments (Table 1) were applied at a 7.32 kg N/ha rate to plots in the four blocks. A control plot in each block was identically treated with de-ionized H_2O. Each plot treatment was followed immediately by installation of a closed, NH_3-measuring flux-chamber (as described). Again, the experiment was complimented by three flux trapping-efficiency chambers. The only difference between these and those described of the first experiment run was that they employed a 5 mL aliquot of 0.117 M $(NH_4)_2SO_4$ for NH_3-generation. On 2 September, mowed plots received identical applications of 7.32 kg N/ha fertilizer treatment, followed by a NH_3-volatilization measurement campaign as described for 16 July. These two repeated measures comprised the third experiment run. Final 2019 treatments were applied 1 October and comprised 73.2 kg N (ha year)$^{-1}$ in total.

Treatments resumed on the same plots 13 May 2020. Following mowing on 8 and 29 June 2020, the 7.32 kg N/ha fertilizer treatments were reapplied as described and immediately followed by installation of a dedicated flux chamber. Ammonia emission was sampled for 24 h and data resulting from these two repeated measures comprised the fourth experiment run.

The quotient of fertilizer-N volatilized (kg/ha) by fertilizer-N applied (kg/ha) equals percent fertilizer loss as NH_3-N data and were combined for global analysis in PROC MIXED (SAS Institute, v. 9.4, Cary, NC, USA). Block nested in experiment run comprised the sole random variable per the methods of M.S. McIntosh [27]. One single degree of freedom was used to contrast mean fertilizer N volatilized (kg NH_3-N ha^{-1}) from the urea complimented by biological inhibitors (+DCD +NBPT) treatment vs. the urea complimented by urea formaldehyde reaction products (+UF RXN) treatment. The remaining degree of freedom contrasted volatilized fertilizer-N mean response of these fertilizers (pooled effect) to the conventional urea treatment. Upon confirmation of significant interaction by global ANOVA, associated simple effects [28] were identified by the LSMEANS/SLICE option and parsed by Fisher's protected least significant difference at a 5% alpha level.

3. Results

Routine agronomic soil test results showed a 1:1 soil pH of 7.1, Mehlich-3 extractable: P of 49, K of 64, Mg of 200, Ca of 1354, and S of 19 mg/kg. Mean soil CEC (by summation) was 4.3 cmol (+) kg^{-1} and H_2O-extractable levels of soil NO_3^- and NH_4^+ were not observed at detectable limits (<5 mg/kg). Cursory assessments of plot density or vigor between fertilized and control plots ostensibly confirmed the *N*-limited condition of each putting green over the experimental periods.

The experiments were initiated when still and dry atmospheric conditions were forecast as highly probable. No precipitation was recorded over the described measurement periods. An ambient temperature probe at 2 m height and <200 m from the experiment plots

recorded means of 23.6, 24.0, 22.4, and 22.0 C respective to the 24 h periods of Experiments 1, 2, 3, and 4.

To quantify fertilizer N volatilization as described, NH_3-N volatilized from control plots was measured and subtracted from all fertilized plot measurements on a block-by-block basis. Determinations of 24 h indigenous NH_3-N emission averaged 0.1 kg N/ha ($n = 24$) and were observed over a range of 0 to 0.328 kg N/ha (data not shown).

3.1. Fertilizer N Volatilization

Once prepared in aqueous solution, the fertilizer treatments were similarly translucent and fit for foliar application. Yet over the 24 h period following application, significantly greater fertilizer N was lost from the conventional urea-N fertilizer treatment (Table 2). Fertilizer N volatilized wasn't necessarily greater in experiments featuring the higher N application rates, as experiment run was not a significant source of variation (Table 2). A contrast of the first two against the last two experiment runs nearly showed a significant ($p = 0.0529$) pooled effect on fertilizer N volatilization, where the former exceeded the latter.

Table 2. Analysis of variance (ANOVA) of 0- to 24 h fertilizer N volatilized (kg/ha) and percent fertilizer loss as NH_3-N (%), by source.

| Source (All Fixed Vars)	Degrees of Freedom		Fertilizer N Volatilized	Percent Fertilizer Loss as NH_3-N
	num	den		*p*-value
Experiment	3	12	ns	ns
Treatment (TRT)	2	48	<0.0001	<0.0001
TRT × Experiment	6	48	0.0016	0.0386
TRT contrasts				
Urea +UF RXN products vs. Urea +DCD +NBPT	1	48	ns	ns
Urea vs. other two TRTs	1	48	<0.0001	<0.0001
TRT levels	*n*		TRT Means, kg/ha	TRT Means, %
Urea	24		0.521	5.87
Urea +UF RXN products	24		0.079	0.93
Urea +DCD +NBPT	24		0.103	1.24

However, a significant interaction of fertilizer treatment and experiment run was observed (Table 2), and the simple effect overwhelmingly responsible was the conventional urea fertilizer treatment (Figure 2a). Conventional urea treatment resulted in significantly more fertilizer N volatilization (kg/ha) in the first two experiment runs than in the last two experiment runs. Meanwhile, the urea fertilizers complimented by UF RXN products or biological inhibitors showed statistically equivalent volatilization regardless (Figure 2a). Results of the first two experiment runs featuring a 9.76 kg N/ha fertilizer application rate showed urea fertilizer complimented by either UF RXN products or biological inhibitors prevented NH_3-N emission of 0.64 kg/ha relative to conventional urea fertilizer treatment. Results of the last two experiment runs, featuring a 7.32 kg N/ha application rate, showed use of urea fertilizer containing either UF RXN products or biological inhibitors (+DCD +NBPT) prevented NH_3-N emission of 0.22 kg/ha relative to conventional urea fertilizer treatment (Figure 2a).

3.2. Percent Fertilizer Loss as NH_3-N

The results in units of percent fertilizer loss as NH_3-N are like those presented in units of kg/ha and confirm that over the 24 h period following application, the conventional urea-N fertilizer treatment lost significantly more of the applied fertilizer N than the two alternative sources (Table 2). The significant interaction of fertilizer treatment and experiment run was again identified, and the simple effect determined to be most responsible for it was the conventional urea treatment (Figure 2b). However, on a percent conventional urea loss as NH_3-N basis, both experiment runs featuring a high N rate only significantly differed from the 2020 low N rate experiment run (Exp. 4). Perhaps not coincidentally,

the 24 h mean air temperature observed during Experiment 4 was the lowest of the four. In accordance with the literature [8,13], pooled mean fertilizer loss as NH_3-N was highly correlated with mean temperature observed over the respective experimental periods ($n = 4$, $r = 0.81$, $p = 0.189$).
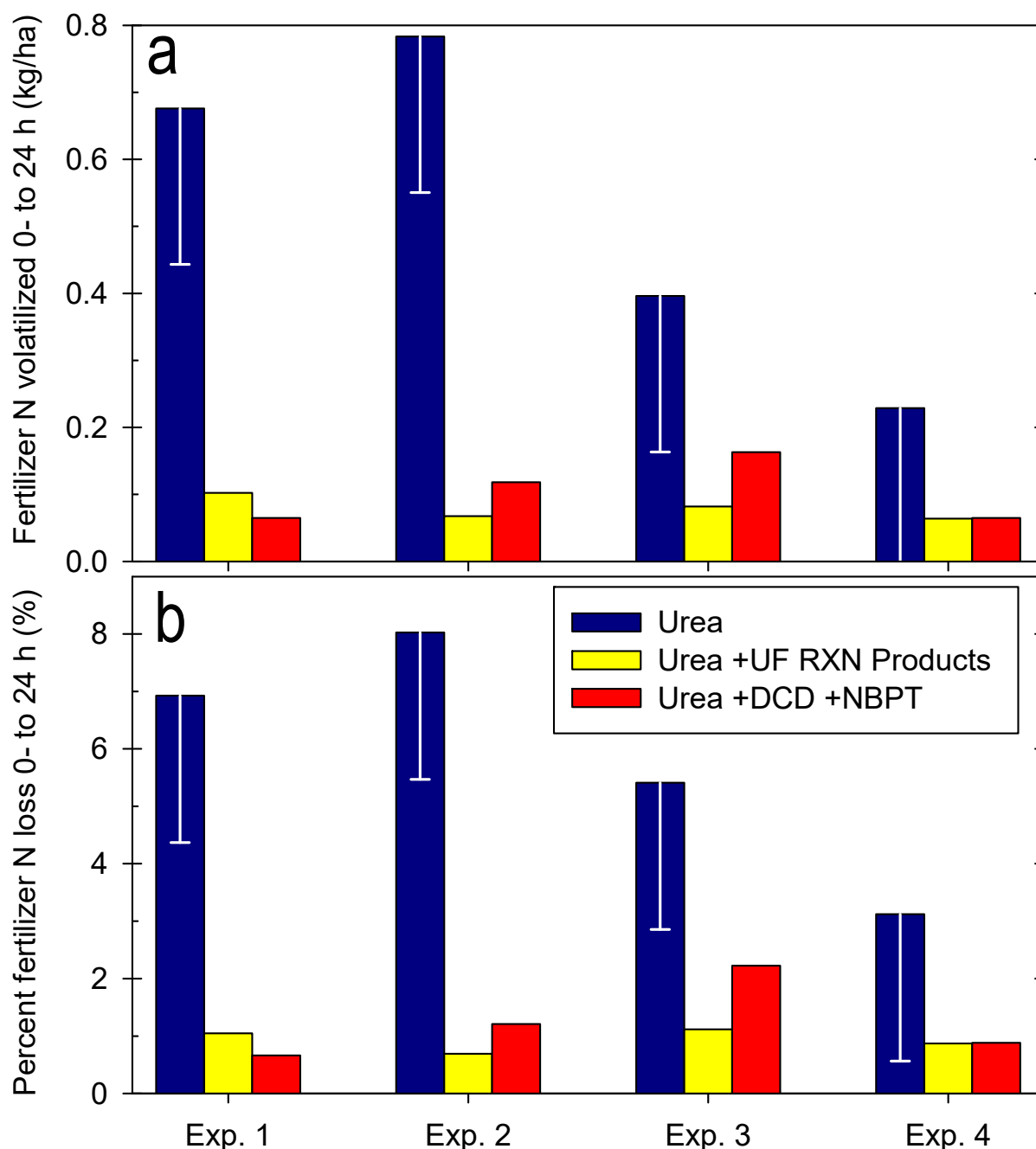
Figure 2. Comparisons of fertilizer N volatilized in mass per unit area (**a**) or percent fertilizer loss as NH_3-N (**b**) by fertilizer source and experiment. Means overlapping error bar are not significantly different from conventional urea at a 5% alpha level.

Studies describing creeping bentgrass putting green recovery of foliarly applied N report statistically less recovery over rising urea-N rates [5,29]. However, field studies reporting flux-chamber measures of NH_3 emission from at least two rates of foliarly applied urea-N conclude that loss as a percentage of urea-N applied was not significantly influenced by fertilization rate [30,31]. A similar response was observed here. Relative to experiment runs 3 and 4, the higher rate by conventional urea-N treatment consistently increased

fertilizer N volatilized in mass per area units (Figure 2a), but only half the time when analyzed as a percentage of the fertilizer N applied (Figure 2b).

4. Discussion

Related studies assessing 0- to 24 h volatilization following foliar urea-N application to a golf course putting green justified a copious N fertilization rate (20 kg N/ha) as necessarily supportive of resolute measurement by the described flux chambers [3,23]. Videlicet, meaningful conclusions are the more likely product of experiments generating a mean response significantly different from zero. Schlossberg et al. [23] went on to encourage additional field study of NH_3 volatilization from lower, more typical urea-N application rates to putting greens.

Despite ostensibly lacking an array of fertilizer N application rates supporting simultaneous comparison of NH_3 loss, the described experiments constitute a response to that encouragement. Likewise, treating experiment run as a fixed effect in combined analysis affords comparative inference into purposely varied levels of experiment run, as well as significant interactions with common treatment levels.

As a result, these findings do not unequivocally counter published conclusions arising from field studies using flux chambers to quantify NH_3 loss from plots receiving two or more rates of foliarly applied urea-N. Specifically, NH_3 volatilization loss as a percentage of urea-N applied remains independent of fertilization rate [29,30]. The authors propose rapid assimilation of urea by foliage, driven by concentration gradient at the cell membrane and precluding facilitated transport, as the mechanism responsible for this independence [32–34]. Thus, unlike ionic plant-available nutrient form reliance on facilitated diffusion, neutral urea molecules avoid crowded carrier protein gates and delayed assimilation [35,36].

In summary, over the 0 to 24 h period following a 7 to 10 kg N/ha application made under comparable environmental and cultural conditions using conventional urea fertilizer, 3–8% of foliar urea-N applications can be expected to volatilize. Conversely, 0.7 to 1.1% of methylol urea liquid fertilizer (containing 60% short-chain methylene urea) or 0.7 to 2.2% of urea complimented with DCD and NBPT volatilized as NH_3.

5. Conclusions

To date, our research fully supports the 2015 designation of NBPT-amendment of urea as a Category 1 strategy/technique for abatement of NH_3 emissions by the UNECE Task Force on Reactive Nitrogen. Category 1 techniques are deemed practical, verifiably efficient, and recommended for use in abatement strategies; relative to a broadcast application of conventional urea fertilizer [37]. When rainfall/irrigation is unavailable, yet urea N is to be foliarly-applied to a golf course putting green, the authors recommend a fertilizer complimented by urea-formaldehyde reaction products or 0.1% *N*-butyl-thiophosphoric triamide (NBPT) urease inhibitor and 2.0% dicyandiamide (DCD) nitrification inhibitor.

Conflicts of Interest: The authors declare no conflict of interest.

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