

# Comparing Closed Chamber Measures of Ammonia Volatilization from Kentucky Bluegrass Fertilized by Granular Urea<sup>1</sup>

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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, practical guidance for small-plot field assessment of ammonia (NH<sub>3</sub>) volatilization remains limited. Our objectives were to (i) develop a method for field-implementation of closed flux/dynamic chambers to measure ammonia emission over a 3-day period following granular urea application to turfgrass, and (ii) infer the significance of said measures to levels arising from simultaneous static-chamber measures. A Kentucky bluegrass (*Poa pratensis* L. 'Midnight') lawn was treated with granular urea-N at a rate of 0 or 43 kg·ha<sup>-1</sup> (38 lb/A) twice in both 2014 and 2015. Flux chamber measures of mean ammonia volatilization from urea-N fertilizer applied 3 days previous exceeded simultaneous static chamber measures by a factor of 17. Relative to static, the closed dynamic/flux chamber system described affords a more precise and efficient method for measuring ammonia volatilization from small field plots. Furthermore, over a 3-day period of dry conditions and ambient temperatures fluctuating between 10 and 31 C (50 and 88 F), as much as 23.1% of a granular urea application broadcast over a Kentucky bluegrass lawn can be volatilized as ammonia.

**Index words:** flux, gaseous emissions, methods, nitrogen, static, turfgrass.

**Species used in this study:** 'Midnight' Kentucky bluegrass (*Poa pratensis* L.).

## Significance to the Horticulture Industry

Concerns over climate instability have prompted scrutiny of large-scale anthropogenic processes worldwide, and include horticulture's influence on atmospheric dynamics. Resultantly, accurate quantification of sink/source attributes increasingly comprises agronomic/horticultural research objectives. Numerous methods of measuring gaseous efflux from horticultural systems have been developed and resulting data published. Yet it is paired method comparisons that support both meaningful interpretation of past findings and efficacy in developing future protocols. Experimental results describe how inexpensive, yet reusable, dynamic/flux chambers are quickly constructed, installed, and employed for measurement of gaseous emission from soil/media surfaces. While less costly and complex, static chambers significantly underestimate ammonia emission from fertilized turfgrass under the described conditions.

Nitrogen fertilization is essential to the function, resiliency, and aesthetics of turfgrass systems. Turfgrass requires greater quantities of N than any other plant essential nutrient, and N sufficiency is promptly supported by soluble N fertilizer application. Of the soluble sources, urea (46-0-0) is the least phytotoxic and most cost effective

on a unit N basis. Yet, results confirm that over three days of dry conditions, 23% of broadcast-applied granular urea-N can volatilize from mature turfgrass systems. For this reason, continuing best management practice (BMP) development remains a priority of horticultural and turfgrass scientists. One of the more effective granular-urea fertilization BMPs, for reducing the likelihood and extent of volatilization, is 'soil incorporation' by coincidental rainfall or scheduled irrigation event(s). However, turfgrass managers' short-term prioritization of nutrient sufficiency and clientele satisfaction often preclude rainfall/irrigation concomitance. This research confirms the cost of such inaction. Future research should employ effective chamber methods to quantify volatilization loss following unincorporated application of commercially-available 'stabilized' or 'urease inhibitor enhanced' granular urea fertilizers.

## Introduction

Numerous investigations into ammonia loss following urea fertilizer application to turfgrass systems have been summarized (Carrow et al. 2001, Petrovic 1990, Turner and Hummel 1992). 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 (Hargrove 1988, Titko et al. 1987, Torello et al. 1983). These and more recent studies have employed varying application and collection methods. As a result, ammonia-N volatilization from the 14×10<sup>6</sup> ha of turfgrass systems in the US is reported to range from 0.04 to 60% of urea-N fertilizer applied (Henning et al. 2013, Knight et al. 2007, Knight-Huckaby et al. 2012, Titko et al. 1987, Turner and Hummel 1992).

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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 (Kojima et al. 2006). Over a 48-hour period following application, Bowman and Paul (1992) observed perennial ryegrass (*Lolium perenne* L.) assimilation of foliar urea-N to exceed  $18 \text{ kg} \cdot \text{ha}^{-1}$ .

Alternatively, urea is hydrolyzed into ammonia and carbon dioxide by urease (Chin and Kroontje 1963), an enzyme ubiquitous to soil, thatch, and turfgrass leaf and shoot surfaces (Torello and Wehner 1983). The position of urea at hydrolysis significantly influences the fate of its products (Petrovic 1990). Prompt incorporation of granular urea into soil, either mechanically (Rochette et al. 2009, Sigunda et al. 2002) or via precipitation/irrigation-facilitated dissolution and infiltration (Fenn and Miyamoto 1981, Holcomb et al. 2011, Sheard and Beauchamp 1985, Titko et al. 1987), typically reduces subsequent ammonia volatilization rate. Yet limited availability and/or opportunity often preclude(s) irrigation/rainfall concomitance when scheduling granular urea-N fertilization events.

Several regional, state, and/or local government agencies across the US and world have either enacted or drafted laws/ordinances regulating fertilizer application to managed turfgrass (Hall 2015, Mitchell 2016). Meanwhile, ammonia emissions reduce air quality and contribute to non-point nutrient loading of surface water resources (Dennis et al. 2013). Thus perhaps now more than ever before, there exists a need for replicated field investigations employing proven methodologies to accurately discern fates of N fertilizers applied to turfgrass systems.

Measurement of N fertilizer emissions in replicated field-plot experiments is commonly facilitated by micrometeorological or chamber systems containing one or more acid traps to capture evolved ammonia (Sommer et al. 1991). Micrometeorological methods integrate ammonia fluxes over a large area and are less intrusive and/or influential on subject systems than chamber systems (Sheard and Beauchamp 1985, Sommer et al. 2004). Yet micrometeorological methods require spatially-isolated experimental areas, each uniformly-vegetated and equipped with an expensive and sophisticated mast assembly (Denmead 1983, Knight-Huckaby et al. 2012). Thus while accurate, micrometeorological systems are effectively precluded from multi-treatment, small-plot, field experimentation (Shigaki and Dell 2015).

Chamber systems are more commonly employed in laboratory or small-plot field research and characterized as closed static, closed dynamic, or semi-open static (Hargrove 1988, Shigaki and Dell 2015). Low cost and self-contained durability are advantages of static chamber system application in the field. Disadvantages include limited air movement and artificial tempering of diurnal fluctuations in temperature and humidity. Air flow restriction inherent to static chamber systems can impart sink attributes to plants and condensation within the chamber that seldom exist under field conditions (Hargrove 1988, Stiegler et al. 2011). However, short-term applica-

tion of static chamber systems affords inference into the relative influence of associated effects, e.g., fertilizer rate, source, and/or application method, on ammonia volatilization (Petrovic 1990).

The primary advantage of dynamic chamber systems is continuous air flow across the plot that simulates field conditions while preventing formation of condensate or an otherwise aberrant microenvironment within the chamber (Hargrove 1988, Kissel et al. 1977). Disadvantages of dynamic chamber system application in the field include significant cost, labor, and equipment requirements (Shigaki and Dell 2015).

Sports turf managers' and lawn care operators' commitments to worker, player, and client safety, plant health, and effective management of natural resources all rely on rapid transfer of practical and accurate field research results. The objectives of this research were to (i) develop a method for field-implementation of closed flux/dynamic chambers to measure gaseous emission, ammonia-N specifically, over a 3-day period following application of granular urea-N fertilizer to a Kentucky bluegrass home lawn; and (ii) infer the significance of flux chamber measures relative to simultaneous static-chamber measures.

## Materials and Methods

Kentucky bluegrass (*Poa pratensis* L. 'Midnight') sod was established Sept. 2012 in a Hagerstown silt loam (fine, mixed, semiactive, mesic Typic Hapludalfs) and subsequently maintained within the Pennsylvania State Univ. Valentine Turfgrass Research Center (University Park, PA). From May to October 2013 and April to July 2014, all plots were mowed at a 3-cm (1.2 in) height of cut every  $6 \pm 4$  days with clippings collected and discarded. Weeds were controlled by manual removal and plots were irrigated as necessary to prevent wilt.

A 1:1 (by mass) slurry of DI  $\text{H}_2\text{O}$  and soil, collected from the upper 15cm (6 in) of the profile in April 2014, was extracted and analyzed for pH,  $\text{NO}_3\text{-N}$ , and  $\text{NH}_4\text{-N}$  levels (Hartz et al. 1993, Molins-Legua et al. 2006, Thomas 1996). Results showed neutral soil pH (7.0) and undetectable levels of ionic N forms ( $<5 \text{ mg kg}^{-1}$  soil). In May 2014, granular ammonium sulfate (SULF-N), potassium nitrate (Regal Fertilizer), potassium sulfate (Lesco Inc.), and Epsom salt (PQ Corp.) fertilizers were applied to the Kentucky bluegrass to deliver 25 kg N, 30 kg Mg, and 75 kg  $\text{K}_2\text{O}$  and S  $\text{ha}^{-1}$ .

*Experiment setup.* On July 24, 2014, the experimental area was mowed and clippings removed before installing a randomized complete block design comprising six (6) blocks of three (3) plots 0.8 by 1.0 m in size. Plots in block rows were divided by 0.2-m borders and 0.5-m-wide boundaries were maintained between blocks. Chamber installation was initiated on July 25, 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 (Schlossberg et al. 2017). The end cap was then

firmly seated within the trench to a 2.5-cm depth, removed, and the process repeated on the remaining seventeen plots.

At 10:00 on July 25, a 40-mL aliquot of standard 2% boric acid ( $\text{H}_3\text{BO}_3$ ) was dispensed into a pre-labeled 'trip blank' HDPE bottle and tightly-capped. Pre-weighed urea (99.3%, Alfa Aesar, Ward Hill, MA) fertilizer granules (46-0-0, 1.5-mm mean diameter) were carefully applied within the chamber 'enclosure area' of a randomly-selected plot at a N-rate of  $43 \text{ kg ha}^{-1}$  (38 lb/A). The treatment was immediately 'activated' by 2.6mL DI  $\text{H}_2\text{O}$  ( $1223 \text{ L ha}^{-1}$ ) using a single-nozzle,  $\text{CO}_2$ -powered backpack sprayer and an air induction even flat-spray tip (TeeJet AI9508EVS, Spraying Systems Co., Wheaton, IL). A coin was then flipped to determine whether a static or flux chamber would be installed.

In the case of a static chamber assignment, 40-mL of stock 2% boric acid solution was dispensed into a labeled 50-mL high-density polyethylene (HDPE) beaker (5.1 cm tall, 4.4 cm diam.). The acid-containing beaker was set within the circular chamber trench and covered by the PVC end cap. The end cap was then driven to a 2.5-cm soil-penetration depth using a rubber mallet, allowing for a 1 cm gap between beaker brim and chamber roof. Firm seating of the PVC cap in the putting green was confirmed by resistance to dislodging efforts, and the plot number and time recorded.

Alternatively, a flux chamber was installed. Each flux chamber was also a PVC cap, modified by a 0.5-cm-wide by 2.7-cm-deep notch and two 0.63-cm holes in opposite sides (Schlossberg et al., 2017). 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 (Figure 1). 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) 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 12V 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 soil. 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 two plots in each block were fertilized and instrumented in the order determined by coin flip, the remaining plot was designated as a zero-N 'control' plot. This plot was treated with de-ionized water (DI  $\text{H}_2\text{O}$ ) as described above and equipped with a flux chamber. The



Fig. 1. The flux chambers (closed-dynamic) employed.

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 the twelve 250-mL scrubbing flasks (Scienceware, Bel-Art Products, Wayne, NJ) of the flux chambers. The intake stem was fitted with a 0.5-m length of 3.2 mm id vinyl tube and the flask sealed. The tube was then connected to the nylon hose connector of its dedicated flux chamber.

Two vacuum manifolds, constructed from 0.8-m lengths of 5.1-cm PVC pipe, were placed within block borders and fitted with hose connectors and requisite lengths of 3.2-mm id tube for connection to 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). Once all scrubbing flask/manifold/vacuum splitter connections were secured, the vacuum pump was actuated to draw  $60 \text{ L min}^{-1}$  over the 3-day 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 to each 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 the extension cord powering the vacuum pump) facilitated continual fan operation over the 3-day experimental period.

From 10:00 to 11:30 on July 28, each plot was revisited in the order of treatment applications 3-days prior. For static



chambers, the PVC end cap was carefully lifted and the underlying beaker entirely decanted into a pre-labeled HDPE bottle. For flux chambers, the vacuum hose connecting the scrubbing flask to the manifold was clamped before unsealing and decanting the boric acid solution into a pre-labelled 120 mL, wide-mouth HDPE bottle. All bottles were tightly-capped for transport to laboratory storage at 4 C. All equipment was then removed and the field experiment terminated. Identical studies were conducted in unique sections of the described lawn Sept. 4 to 7 2014, July 28 to 31 2015, and August 4 to 7 2015. During each 3-day period the PVC chambers were in place, the plots were neither mowed nor irrigated. Climatic conditions were logged every 15 minutes by an onsite weather station.

*Ammonia loss determination.* The mean pH level of the four, field-dispersed, 2% boric acid ‘trip blanks’ collected from each experimental run conducted over the 2014 and 2015 seasons 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 the remaining sample was measured using a graduated cylinder and recorded. Titrated ammonia-N ( $\text{kg ha}^{-1}$ ) collected within each boric acid trap, 3-days after treatment, was calculated using Eq. (1):

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

For each chamber trap, titrated ammonia-N was multiplied by its specific ratio of collected-to-titrated boric acid to determine ammonia-N volatilization in  $\text{kg ha}^{-1}$ . Differences between ammonia-N volatilization ( $\text{kg ha}^{-1}$ ) from paired control and urea treatment plots in each block (Eq. (2)) comprise 3-day ammonia-N volatilization from urea fertilizer in  $\text{kg ha}^{-1}$ .

$$\left[ \begin{array}{l} \text{ammonia} - \text{N} \\ \text{volatilization} \\ \text{from urea} \\ \text{fertilizer,} \\ \text{kg ha}^{-1} \end{array} \right]_{\text{block}(\text{run})} = \left[ \begin{array}{l} \text{ammonia} - \text{N} \\ \text{volatilization from} \\ \text{urea treatment,} \\ \text{kg ha}^{-1} \end{array} \right]_{\text{block}(\text{run})} - \left[ \begin{array}{l} \text{ammonia} - \text{N} \\ \text{volatilization from} \\ \text{control treatment,} \\ \text{kg ha}^{-1} \end{array} \right]_{\text{block}(\text{run})} \quad (2)$$

$\text{block}(\text{run}) = 1, \dots, 24$

All above-described variables observed of urea-N treated and/or control plots were analyzed for sample moments,

mean location (Student’s *t*), confidence interval, and normality (Shapiro-Wilk) using the UNIVARIATE procedure (SAS Institute, v. 8.2) and an alpha level of 0.05. Ammonia-N volatilization from urea measures were combined for global analysis using the MIXED procedure (SAS Institute, v. 8.2). Experimental run, block (nested in run) and all subsequent interaction sources were designated as random variables (McIntosh 1983). Significance of either the urea-N treatment (0 vs. 43  $\text{kg ha}^{-1}$ ; flux chambers) or chamber type (static vs. flux; 43  $\text{kg ha}^{-1}$  as urea-N) fixed effect was F-tested by the expected mean squares of its respective experimental run interaction term ( $\text{df} = 3$ ).

*Trapping-efficiency trial.* In July 2016, a completely randomized design of nine 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 previously. Three randomly-selected plots housed a conventional flux chamber, and were prepared exactly as unfertilized (control treatment) flux chamber plots in the previous experimental runs. Three randomly-selected plots housed a static trapping-efficiency chamber, and the remaining three plots housed a flux trapping-efficiency chamber.

The static trapping-efficiency chambers were identical to the static chambers previously described, except for a rubber septum installed in the top of each. For the static trapping-efficiency chambers, a 50-mL HDPE beaker was filled with 40-mL of 2% boric acid stock solution and set within the circular chamber trench. Likewise, a 20-mL HDPE beaker (3.8 cm tall, 3.2 cm diam.) was filled with 15-mL of 0.227 M  $(\text{NH}_4)_2\text{SO}_4$ , and set directly beneath the rubber septum on the opposite side of the chamber trench. The beakers were then covered by a static trapping-efficiency chamber, and the chamber driven to a 2.5-cm soil-penetration depth using a rubber mallet.

The flux trapping-efficiency chambers were similarly 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  $(\text{NH}_4)_2\text{SO}_4$  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  $(\text{NH}_4)_2\text{SO}_4$ . This raised the aqueous pH to a level exceeding 12, converting the  $\text{NH}_4^+$  to gaseous ammonia. Thus, three replicate static and three replicate flux trapping-efficiency chambers were fully-prepared immediately before activating the vacuum pump in July 2016. Complete volatilization of N from the  $(\text{NH}_4)_2\text{SO}_4$  aliquot generated the equivalent of 43  $\text{kg ha}^{-1}$   $\text{NH}_3\text{-N}$  within the chamber head space. Three days later, the boric acid trapping solutions were recovered from either the static chamber beakers or the flux chamber scrubbing flasks.

**Table 1. Mean, confidence interval (CI), and coefficient of variation (CV) of 0- to 3-day ammonia-N volatilization, by chamber type or granular urea-N fertilizer treatment.**

Granular urea-N treatment (kg ha <sup>-1</sup> )	chamber type	n	0- to 3-day ammonia-N volatilization from				
			treatment		urea fertilizer		
			μ (kg ha <sup>-1</sup> )	±95% CI (kg ha <sup>-1</sup> )	μ <sup>Y</sup> (kg ha <sup>-1</sup> )	±95% CI (kg ha <sup>-1</sup> )	CV (%)
0	flux	24	0.041	0.023	—	—	—
43	flux	24	5.104	0.757	5.063 (11.8%) <sup>Z</sup>	0.756	35.4
43	static	24	0.294	0.048	0.294 ( 0.7%)	0.048	38.4

<sup>Y</sup>Flux chamber estimate of ammonia-N volatilized from urea fertilizer corrected by subtracting background volatility of 0.041 kg ha<sup>-1</sup> from the observed rate of 5.104 kg ha<sup>-1</sup>. The static chamber estimate was not corrected for background volatilization.

<sup>Z</sup>Percent urea-N volatilization loss (in parentheses) calculated as the quotient of mean ammonia-N volatilization from urea fertilizer by the original 43 kg ha<sup>-1</sup> N application rate (38 lb/A).

Alirazine yellow R indicator dye was added to the remaining 0.227 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> aliquots to confirm solution pH exceeded 12.0. Trapping solutions were transferred to the lab and titrated to their original pH endpoint as described. Volatilized NH<sub>3</sub>-N was calculated as described and mean volatilized ammonia for either the flux or static chamber divided by 43 kg ha<sup>-1</sup> to determine respective chamber efficiencies.

## Results and Discussion

Mean, maximum, and minimum air temperature recorded over the four 3-d data collection periods ranged from 16.1 to 23.5, 20.6 to 30.9, and 10.0 to 18.3 C, respectively. Water-tight containers were employed to protect AC wiring and vacuum pump connections during 1.9- and 1.0-cm precipitation events occurring 28 July and 6 Sept. 2014; and during a 1.5-cm precipitation event occurring 30 July 2015, respectively.

Employment of identical treatment levels and methods, as well as similar cultural, climatic, and edaphic conditions observed over the four experimental runs, compelled the designation of 'experiment run' as a random variable. Individual Type 3 analyses of variance identified fertilizer treatment or chamber type as a significant influence of measured ammonia-N volatilization or mean ammonia-N volatilization from urea, respectively. Thus, pooled results are reported (Table 1).

*Flux chamber measures of ammonia-N volatilization.* Flux-chamber measures of ammonia-N volatilization from control (unfertilized) plots, were observed in the range of 0 to 0.212 kg ha<sup>-1</sup>. Mean ammonia-N volatilization from the 0 kg urea-N treatment was 0.041 kg ha<sup>-1</sup> and significantly different from zero (Table 1). Flux-chamber measures of ammonia-N volatilization from plots treated by 43 kg urea-N were observed in the range of 2.346 to 7.991 kg ha<sup>-1</sup>. Mean ammonia-N volatilization from plots treated with 43 kg urea-N equaled 5.104 kg ha<sup>-1</sup> and was significantly different from mean ammonia-N volatilization observed of 0 kg urea-N treated plots ( $P = 0.001$ ).

Flux chamber measurement of mean ammonia-N volatilization from urea fertilizer; i.e., the average measured from plots treated with 43 kg urea-N was 5.063 kg ha<sup>-1</sup>, after subtracting the 0.041 kg ha<sup>-1</sup> recorded in non-fertilized plots (Table 1). Mean percent urea-N volatiliza-

tion loss, calculated as the quotient of mean ammonia-N volatilization from urea-N by the original 43 kg ha<sup>-1</sup> application rate, was 11.8% (Table 1). The 95% confidence interval of mean percent urea-N volatilization loss, measured by flux chambers 0 to 3 d following treatment, accounts for 10.0 to 13.5% of the granular urea-N fertilizer applied (Table 1).

Zero- to 3-day percent ammonia-N volatilization loss measured using flux chambers in the current field study agrees with values published from micrometeorological or flux chamber field measures of granular urea-N treatment of turfgrass or pasture at similar rates. Over two repeated 8-day periods initiated by 100 kg urea-N ha<sup>-1</sup> granular fertilizer applications to a Kentucky bluegrass and creeping red fescue (*Festuca rubra* L.) lawn mixture, Sheard and Beauchamp (1985) measured 6.7 to 15.1% volatilization loss. Ten days following granular urea treatment of hybrid bermudagrass [*Cynodon dactylon* (L.) Pers. × *Cynodon transvaalensis* Burt Davy] 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<sup>-1</sup> application (Knight-Huckaby et al. 2012). Over nine experiments initiated by 30 kg urea-N ha<sup>-1</sup> granular fertilizer applications to a ryegrass (*Lolium perenne* L.) and white clover (*Trifolium repens* L.) pasture, Black et al. (1985) observed 8-day cumulative ammonia-N losses between 7.4 and 20.2% of urea-N applied.

*Static chamber measures of ammonia-N volatilization.* Static chamber measured ammonia-N volatilization from 43 kg urea-N ha<sup>-1</sup> treatment, applied exactly 3 d previous, equaled 0.294 kg ha<sup>-1</sup> (Table 1). Recent static chamber experiments report immeasurable ammonia-N volatilization from unfertilized grasslands (Bowman and Paul 1990, Schlossberg et al. 2017, Stiegler et al. 2011, Wang et al. 2004). Likewise, subtraction of any positive static chamber measure of control plot ammonia emission from the paired static chamber-measured ammonia-N volatilization from urea treatment (Eq. (2)) would only further inflate the significant disparity observed between the two chamber types. All considered, calculation of static chamber-measured ammonia-N volatilization from urea-N fertilizer (Table 1) presumed zero static chamber-measured ammonia-N volatilization from the control treatments (Schlossberg et al. 2017).

Mean percent urea-N volatilization loss, or the quotient of mean ammonia-N volatilization from urea fertilizer by the original 43 kg urea-N ha<sup>-1</sup> application rate, was 0.7% (Table 1). Thus, the significant difference in mean ammonia-N volatilization from urea fertilizer by chamber type ( $P = 0.001$ ) indicates the static chamber methodology underestimates 3-day ammonia-N volatilization from urea fertilizer applied to a Kentucky bluegrass lawn by an approximate factor of 17 (Table 1).

*Practical and comparative consideration of closed chamber techniques.* While simultaneous comparisons of static versus closed-dynamic (flux or sweeping air-flow) chamber measurements of urea-N fertilizer ammonia-N volatilization loss are limited, the disparity observed in this field study again falls squarely within the range of reported differences. Relative to closed-dynamic (flux or sweeping air-flow) chamber measures of corrected ammonia-N volatilization 0 to 24 h following a 120 kg urea-N ha<sup>-1</sup> application in the field, Wang et al. (2004) reported statistically significant and tenfold underestimation by static chamber systems. Over three separate liquid swine manure applications delivering 100 kg NH<sub>4</sub>-N ha<sup>-1</sup> to a stubble field, static chamber measures of 5-day cumulative ammonia-N volatilization underestimated simultaneous dynamic chamber measures by a factor mean of 36 (Smith et al. 2007).

Ammonia volatilization is the mass transfer of NH<sub>3</sub> gas from solution to essentially ammonia-free air above the turfgrass system, and governed by the difference in partial pressure between the two (Koelliker and Kissel 1988). Such a readily diffusive gradient is expected to be supported by typical air movement under naturally-occurring field conditions. Kissel et al. (1977) reported flux chamber field measures of ammonia volatilization plateaued at 15 volume exchanges per minute. Yet Ryden and Lockyer (1985), upon comparing wind tunnel and mass balance measures, concluded the wind tunnel method consistently overestimated ammonia volatilization when tunnel flux velocity exceeded field air speed.

Ignoring resistance loss in the present study, vacuum is calculated to flow through each of the twelve flux chamber service tubes at a 10.4 m s<sup>-1</sup> (37.4 km h<sup>-1</sup>) rate. Presuming the fans imparted turbulence supporting a piston flow pattern, an approximate flux velocity of 0.01 m s<sup>-1</sup> (0.04 km h<sup>-1</sup>) and volume exchange rate of 2.7 min<sup>-1</sup> is expected within each chamber. The specified minimum detection limit of the onsite (3-m height) cup anemometer is 1 m s<sup>-1</sup>. Onsite measures of 3-m wind speed reported on 15 min intervals over the four 3-day experimental periods indicate 141 'zero wind speed' measures. Using the empirical logarithmic law for a 0.5 m s<sup>-1</sup> air speed 3-m above a mowed plant canopy (0.03 m roughness length), a simultaneous 4-cm height air speed of 0.03 m s<sup>-1</sup> is predicted (Tennekes 1973). Thus, chamber flux velocity is conservatively estimated to not have exceeded the 4-cm external air speed >87% of the experimental periods.

The opacity of each employed chamber comprises a significant departure from field conditions, and calls into question its influence on plant uptake or volatilization of applied urea-N. The static chambers (unmodified PVC

endcaps) fully deprived underlying turfgrass of the 13- to 14-h solar photoperiod, yet the flux chamber modifications afforded limited transmission of natural irradiance. While the term 'urea uptake' is suggestive of cuticular or cellular activity, a favorable concentration gradient will sustain passive transport of the diminutive, neutral, and polar urea solute into the symplast (Schreiber 2005, Uscolaa et al. 2014). Thus, the authors do not believe majority- to complete-exclusion of solar radiation within the respective flux or static chambers affected the ammonia volatilization estimates reported. Furthermore, any resulting daylight greenhouse effect within the flux chambers was likely mitigated by influx of external air and the intermittent mixing (2 of every 4 minutes) by the interior case fan.

*Trapping-efficiency trial.* Mean volatilized ammonia recovered in the static-chamber trapping-efficiency trial (n=3) was 5.64 kg ha<sup>-1</sup>. 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<sup>-1</sup>. Safely assuming complete conversion of NH<sub>4</sub><sup>+</sup> to NH<sub>3</sub> within the 15-mL aliquots of 0.227 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> over the 3-day experimental period, the trapped quantities of ammonia-N signify a mean efficiency ( $\pm 95\%$  confidence interval) of 13.1% ( $\pm 4.7\%$ ) or 50.9% ( $\pm 16.4\%$ ) for the respective static- or flux-chamber systems.

Thus, validation of direct ammonia volatilization measurement by the described closed dynamic/flux chamber system indicates 4-times greater efficiency than by the closed static chamber system. Using the reciprocal of the trapping efficiency determined for the described flux chamber system as a multiplier (1.965), the efficiency-adjusted mean percent ammonia-N volatilization loss within 3-days of granular treatment by a 43 kg ha<sup>-1</sup> urea-N rate is estimated to be 23.1%.

The results show closed dynamic/flux chamber systems afford applied scientists an effective method for measuring gaseous emission from small field plots that, in the case of ammonia, is more precise and efficient than by static chamber systems. The authors encourage construction and use of the described flux chambers for measuring gaseous emissions of environmental or agronomic significance. Over a 3-day period of dry conditions and ambient temperatures fluctuating between 10 and 31 C, as much as 23.1% of a 43 kg ha<sup>-1</sup> granular urea-N application to a Kentucky bluegrass lawn can be lost as volatilized ammonia.

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