RESEARCH ARTICLE

Comparison of ammonia-N volatilization losses from untreated granular urea and granular urea treated with NutriSphere-N®

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Abstract

Development of novel methods to inhibit ammonia (NH_3) volatilization losses has become a strong research focus to reduce the environmental impact of agriculture and as a potential area for growth in the fertilizer industry. European Union legislation on the regulation of NH_3 emission from mineral fertilizers after 2030, will only allow urea fertilizers with reduced NH_3 emissions by at least 30% to remain in use. The recent increase in fertilizer prices has also created a renewed impetus to curb these losses. This paper details the results of an experiment comparing the rates of volatilization from granular urea treated with NutriSphere-N®, untreated urea and an unfertilized control as well as placing the results in context by conducting a review of similar studies featuring NutriSphere-N®. The study was conducted in a light and temperature-controlled growth chamber using the chamber built in air flow which collected any NH_3 volatilized from a flask containing fresh soil with applied treatment and transported the NH_3 to an acid trap where the volatilized NH_3 was captured and exhaust air was removed. The experiment ran for 3 weeks and resulting samples were analysed colorimetrically and adjusted for differences in airflow. The temporal results show that urea dominated the flux profile but the pattern of fluxes from the two fertilizer N treatments were similar. When analysed cumulatively over the duration of the experiment, the fluxes from the NutriSphere-N® treated urea were significantly ($p = .018$) (86%) lower than untreated urea and were not significantly different from the untreated control ($p = .959$).

KEYWORDS
ammonia volatilization, climate-controlled chamber, NutriSphere-N®, urea fertilizer, urease inhibitor

1 | INTRODUCTION

Globally, the livestock sector (beef and dairy cattle, swine and poultry) is estimated to be responsible for ~64% of anthropogenic ammonia (Aneja et al., 2009). Ammonia (NH_3) emissions generate substantial health damage because of the adverse effects on air quality (Ma et al., 2021). Emissions of NH_3 are mainly during the hydrolysis of urea excreted by farm livestock and other mammals or from the use of nitrogen (N) fertilizer (in the form or urea), and the breakdown of uric acid excreted by birds. Global NH_3 emissions from fertilizer N are estimated at 10–12 Tg N year^{-1} (Beusen et al., 2008) and have increased from 1.9 ± 0.03 to 16.7 ± 0.5 Tg N year^{-1} between 1961 and 2010 (Xu et al., 2019). NH_3 emissions are of concern from health, economic and environmental perspectives. First, the impact on air quality includes the formation in the atmosphere of secondary inorganic aerosols which contribute to fine particulate matter (diameter <2.5 μm, PM 2.5) which has an adverse effect on human health and the environment (Griffith et al., 2015; Wang et al., 2016). Second, the supplementation of the soils' natural stock of N with fertilizer N is the foundation of productive agricultural systems and any N volatilized as NH_3 must be replaced to sustain productivity (incurring an economic cost). Third, NH_3 lost from agricultural systems can contribute to environmental degradation through eutrophication, acidification and loss of biodiversity through dry/wet deposition of ammonia to terrestrial or aquatic ecosystems (Bergström & Jansson, 2006; Clark & Tilman, 2008; Liu et al., 2013; Zhu et al., 2016).

Urea fertilizer has a high NH_3 loss potential; surface applied urea could lose more than 40% of total N input by volatilization (Misselbrook et al., 2006). Once applied to the soil surface, urea undergoes the process of hydrolysis, where a water molecule is incorporated eventually producing carbon dioxide (CO_2) and NH_3 gas or the ammonium ion (NH_4^+) and whether surface applied or incorporated. The two forms of ammonia the ion—NH_4^+ and the gas—NH_3 are in equilibrium in the soil solution, and the balance is dependent on soil pH. At pH 6, 7, 8 and 9 NH_3 dissolved in soil solution accounts for 0.1%, 1%, 10% and 50% of the ammoniacal pool, respectively (Schmidt, 1982). Below soil pH of 8.75, NH_4^+ predominates and increases in pH indicate increases in OH−, meaning greater concentration of NH_3 (compared to NH_4^+) in the soil water with NH_3 predominating above a pH of 9.75 (Hem, 1985). During hydrolysis, the soil pH around the urea fertilizer granule increases temporarily following urea hydrolysis which shifts the $NH_4^+ - NH_3$ equilibrium towards NH_3 increasing the risk of NH_3 volatilization (Engel et al., 2011; Rochette et al., 2009). Loss from volatilization of NH_3 is greater in alkaline or calcareous soils, soils that are low in

clay, humus or environments with high temperature and humidity (Connell et al., 2011) and the literature also suggests climatic conditions, such as high rainfall, irrigation or flooding, influence yield and N use efficiency (Cahill et al., 2010).

The drive to improve the efficiency of fertilizer N has led to the development of inhibitor products designed to reduce N losses through the various N loss pathways. For example, urease inhibitors slow the process of urea hydrolysis, nitrification inhibitors slow the process of nitrification. Many urease inhibitor products work on reducing the speed of hydrolysis which helps to moderate any pH spikes surrounding the urea granule and reduces the formation of NH_3 or by deactivating the enzymes responsible for hydrolysis thereby reducing NH_3 volatilization loss. Nutrisphere-N® is a maleic-itaconic polymer (MIP) marketed as a soil urease inhibitor. Nutrisphere™ is a long chain branched polymer with an ultra-high negative charge density (1800 meq 100 g^{-1}). This charge makes the molecules stable at high ionic concentrations, which allows to hold other molecules in suspension. Adding it to a fertilizer like urea, Nutrisphere™ coats the fertilizer molecule (Smith et al., 2014). In the soil, the Nutrisphere™ coating binds to positively charged nickel ion co-factors found in the urease enzyme so these cations are no longer available for forming the urease enzyme. This results in the extraction of nickel from the urease molecule, destabilizing the molecule and rendering it ineffective (Sanders, 2007). The intended effect is to slow the enzymatic reaction of urea conversion to ammonium, like urease inhibitors, such as NBPT (N-butyl thiophosphoric triamide; Agrotain, Agrotain International LLC, St. Louis, MO) (Hopkins et al., 2008).

The aim of this experiment was to compare the volatilization level of NutriSphere-N® treated urea fertilizer with the volatilization levels from an unfertilized control and from untreated urea under controlled conditions.

2 | MATERIALS AND METHODS

2.1 | Experimental design

The experiment took place in the Program for Experimental Atmospheres and Climate (PEAC) facility at the Rosemount Environmental Research station, University College Dublin, Belfield, Ireland in a temperature and light-controlled lean in chamber environment (Conviron CMP6050). A closed system was designed to quantify the NH_3 losses from treated and untreated granular urea (Figure 1). The airflow drawn in the chamber was passing it through an acid trap containing 100 mL of 0.1 M Orthophosphoric acid (H_3PO_4) to remove atmospheric
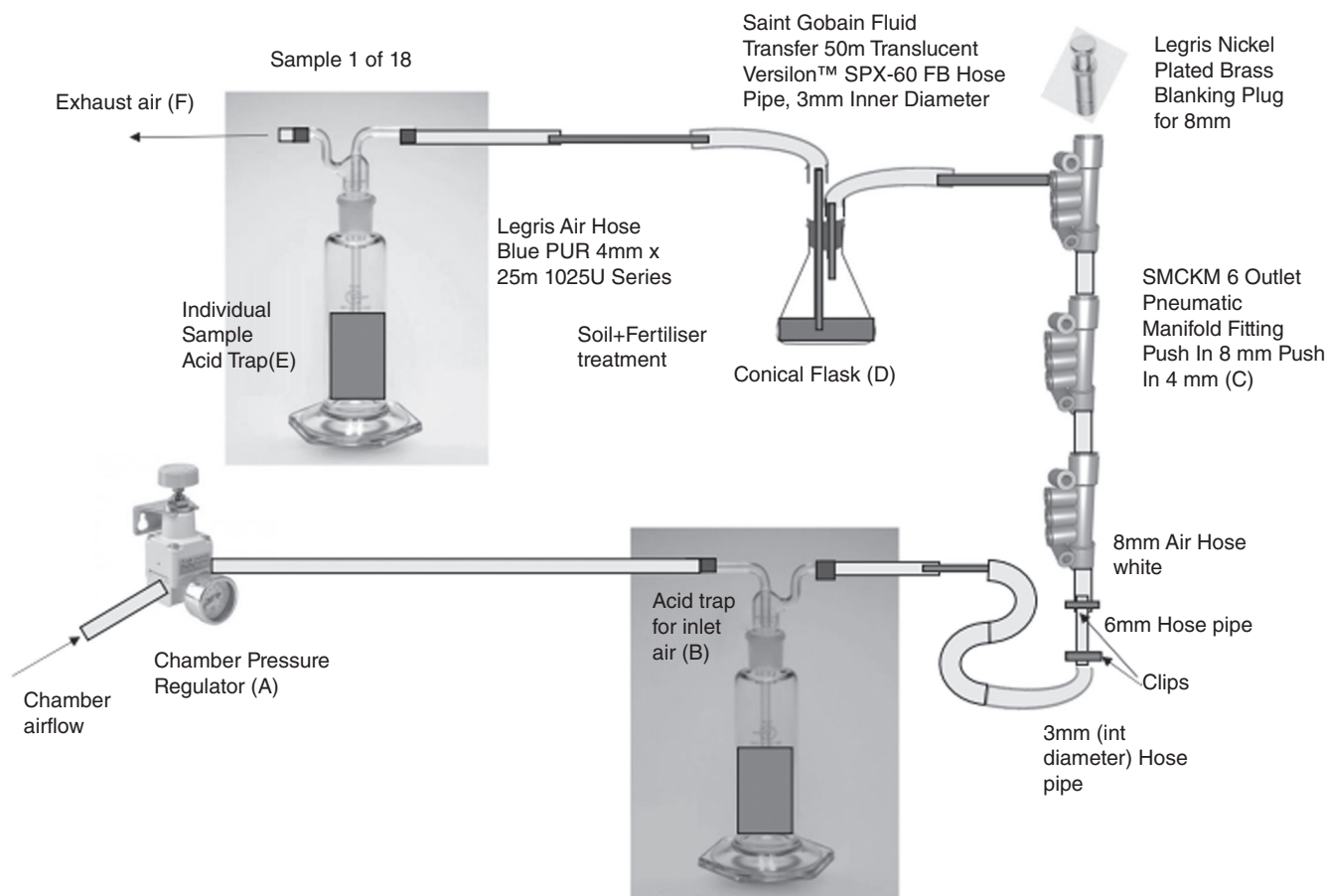
FIGURE 1 Schematic of closed system.

NH_3. This airflow was then passed through a 500 mL conical flask, containing fresh, sieved, arable soil and the applied fertilizer treatment and transported any volatilized NH_3, to an acid trap. As the chamber airflow was bubbled through the acid trap, the NH_3 present was trapped in the acid by picking up an extra hydrogen ion (H^+) in the acid which converted NH_3 to NH_4^+.

The design of the experiment was based on findings from previous work on NH_3 volatilization which showed a single acid trap containing 30 mL 0.1 M orthophosphoric acid (H_3PO_4) solution (Misselbrook et al., 2005) was adequate to measure NH_3 volatilization. To maximize the length of contact between air and acid and in agreement with Forrestal et al. (2016) we used acid trap volumes of 100 mL H_3PO_4. Previous work also found that acid trap strength of 0.01 M was adequate for laboratory gas studies (Harty et al., 2017), however, the strength of acid was increased from 0.01 to 0.1 M to avoid saturating the acid as a higher initial quantity of urea fertilizer was used (1 g). In addition, Misselbrook et al. (2005) found the airflow rates and acid strength had no significant effect on the efficiency of the trap. We used airflow sufficient to ensure the airflow bubbled through the acid trap ensuring good contact between the air containing NH_3 and the acid. The

chamber temperature ranges chosen were a night-time temperature of 16°C and a day-time temperature of 24°C to simulate summer temperature in a temperate maritime region.

A loam soil (USDA classification) used in this study was taken from an arable field at UCD Lyons Research farm (location GPS 53.29499–6.5274), and analysed at UCD soil laboratory. The soil had a pH value of 7.09 and N content of 0.28% (Elemental Analyzer, Leco Corporation, MI, USA). The soil texture comprised of 26.6% clay, 32.56% silt and 35.22% sand (Gee & Orr, 2002), 6.62% organic matter (Loss On Ignition method) and CEC 15.39 cmol kg^{-1} DW (Ammonium Acetate method).

Eighteen flasks were prepared (6 replicates per treatment), 100 ± 0.02 g of fresh biologically active soil sieved to 2 mm was added. The soil had a moisture content of $39\% \pm 0.02$ g (calculated using the % moisture formula = (Fresh Weight–Dry Weight)/Fresh Weight*100).

The volume of soil in each flask was calculated as soil weight (g)/bulk density of soil (cm^3) = 100 g/1.3 2 g cm^3 = 75.75 cm^3. The area of the soil surface 3.14 *(5.15 cm)^2 = 83.33 cm^2. The internal volume of the conical flask is calculated as 1/3 * 3.14 *(5.15 cm)^2 * 18.4 cm = 514.46 cm^3 less the volume of soil in

the flask $= 75.75\,cm^3$ giving a headspace volume of $438.96\,cm^3$. The granular fertilizer products urea and urea treated with Nutrisphere-N® (2.1 L tonne^{-1} urea) were provided by Verdesian Life Sciences Ltd. On Day 1 of the study, the fertilizer treatments were applied to the soil at a rate of 1 g urea fertilizer per 100 g fresh soil. Treatments included T1—untreated control (soil only), T2—granular urea, T3—NutriSphere-N® treated granular urea. To each acid trap, 100 mL of 0.1 M H_3PO_4 was added, the flasks were sealed and the chamber airflow was switched on. At each subsequent sampling period, the exhaust air flow rate at the air outlet pipe of each sample was measured (Hotwire Anemometer—RS PRO). Next, the chamber airflow was shut down, and the acid trap volume was restored to 100 mL with de-ionized (DI) water and decanted into labelled and dated sample bottles. Acid traps were rinsed and replenished with fresh acid, stoppers were replaced and chamber airflow was switched on. Samples were brought to laboratory for analysis.

2.2 | Laboratory method

Samples were analysed for NH_4^+ concentrations using colorimetric analysis on a spectrophotometer (Shimadzu UV-1280). The UV absorbance of NH_4^+ present in the sample was measured at 635 nm. The method uses phenol which reacts with NH_4^+ to form an intense blue colour. The intensity is proportional to the amount of NH_4^+ present. Alkaline hypochlorite and sodium nitroprusside solutions are used as oxidant and catalyst, respectively.

Atmospheric concentration of ammonia was calculated as per Woodley et al. (2018).

$$C_a = \frac{C_s \times V_s}{V_a}$$

where C_s $(mgNL^{-1})$ is the measured concentration of NH_3-N in the acid trap solution, V_S (L) is the measured volume of acid trap solution and V_a (m^3) is the measured volume of air passed through the acid trap solution. Air volume (V_a) was determined using the measured instantaneous air volumetric flow rates.

The ammonia emission rate or flux rate (mg/m^2 day) was determined (per Shah et al., 2006) using the enclosure method as follows:

$$Flux = (C_{out} - C_{in}) * \frac{Q}{A}$$

where Q is airflow rate (m^3/day) provided by the chamber;

A is the treated surface area in the conical flask (m^2);

and C_{in} and C_{out} are measured inlet and outlet (mg/m^3).

Since C_{in} has been passed through an inlet acid trap C_{in} is set to zero and the difference between C_{in} and C_{out} is the value for C_{out}.

2.3 | Data adjustments

The following adjustments were made to the data.

2.3.1 | Outlier removal

On sampling occasion 5, the airflow levels were set too low to deliver consistent bubbling for all samples. Because of concern about the unreliability of this result, all details related to this sample were removed from the result set and were instead replaced with the average NH_4^+ concentrations for sampling periods 4 and 6 (the average of the results for samples taken the day before and day after sampling occasion 5).

2.3.2 | Volume differences

Sample volumes were replenished with DI water to bring all samples to 100 mL for analysis. For any acid trap sample volumes >100 mL, the NH_4^+ concentration was adjusted to what it would be at 100 mL volume to ensure the results were comparable.

2.3.3 | Sample dilution

During analysis where the concentration of sample was too high, colour saturation took place in the sample following the addition of reagent and the results of colorimetric analysis were not reliable. In these cases, the samples were diluted either 1 in 10 or 1 in 50 and re-analysed. The resulting NH_4^+ concentration was adjusted back by the dilution factor (×10 or ×50) to give the original sample concentration.

2.3.4 | Flow rates

The absence of flow rate regulators (as a result of long delays in delivery associated with the Covid-19 pandemic), resulted in differences in flow rate between samples (Table 1). The average and standard deviation of the flow rate for each treatment on each sampling occasion is shown. Flow rates should be controlled, as differences could contribute to differences in the magnitude of fluxes.

TABLE 1 The flow rate in cubic cm per minute (CCM) sampled at the exhaust airflow at each sampling period.

Sample period

Sample	Treatment	1 17/06/20	2 18/06/20	3 19/06/20	4 20/06/20	5 21/06/20	6 22/06/20	7 23/06/20	8 25/06/20	9 27/06/20	10 29/06/20	11 02/07/20	12 06/07/20
1	Urea	121.80	126.00	118.80	11.40	n/a	155.40	269.40	145.80	155.40	110.40	136.80	172.20
2	NutriSphere-N	147.00	151.20	172.20	19.20	n/a	117.20	278.40	100.20	124.80	5.40	118.80	153.00
3	Control	109.80	236.40	219.00	19.20	n/a	147.64	259.80	101.40	103.80	77.40	116.40	141.60
4	NutriSphere-N	137.40	184.80	106.20	14.40	n/a	190.85	248.40	123.00	123.60	124.20	117.00	168.60
5	Control	118.20	121.20	187.20	16.80	n/a	160.66	267.00	103.80	127.80	18.60	139.80	224.40
6	Urea	120.60	178.80	132.00	14.40	n/a	228.80	214.20	103.20	101.40	146.40	139.20	264.40
7	NutriSphere-N	100.20	148.20	139.80	19.80	n/a	158.40	294.00	129.60	121.20	138.00	119.40	162.60
8	Control	138.60	171.00	184.20	15.00	n/a	200.41	278.40	131.40	133.80	200.40	160.80	192.60
9	Urea	118.80	121.80	148.80	17.40	n/a	181.21	301.20	150.00	110.40	133.20	136.80	207.60
10	Urea	106.20	135.00	53.40	9.00	n/a	46.20	324.00	121.80	145.20	184.80	135.00	164.40
11	NutriSphere-N	152.40	104.40	127.20	14.40	n/a	137.40	232.20	121.20	118.20	184.80	135.60	132.00
12	Control	116.40	121.20	115.80	11.40	n/a	240.00	241.80	80.40	106.80	127.20	117.00	173.20
13	Urea	115.80	190.20	161.40	14.40	n/a	164.40	213.00	88.80	124.80	27.00	111.60	174.60
14	NutriSphere-N	126.60	240.60	106.80	10.80	n/a	165.00	223.60	91.20	124.80	127.20	102.60	3.60
15	Control	112.20	138.60	127.20	13.80	n/a	184.80	280.80	112.80	116.40	4.80	135.00	111.60
16	Urea	111.00	264.00	153.60	11.40	n/a	159.60	285.00	114.60	136.80	198.60	180.00	225.00
17	Control	117.60	181.60	151.80	12.60	n/a	195.60	289.20	127.80	113.40	7.80	177.60	196.80
18	NutriSphere-N	121.80	168.60	225.60	12.00	n/a	160.80	259.80	117.60	113.40	9.00	142.80	190.20

However, the average differences in flow rates between treatments are unlikely to alter the significance of the results.

2.4 | Statistics

Statistical analysis was conducted using SPSS Statistics version 24 (2016–2017, International Business Machines (IBM) Inc., Armonk, NY, USA). A generalized linear modelling approach was used to test for the fertilizer N treatment effect on NH_3-N loss using the analysis of variance analysis (ANOVA). The factor analysed was the effect of fertilizer treatment formulation on cumulative NH_4^+ concentration. Cumulative NH_4^+ data were first checked for normality before analysis. As the data were not normally distributed cumulative NH_4^+ values were log transformed prior to analysis. Differences between fertilizer treatments were determined using the Tukey's post hoc test at the 95% confidence level.

3 | RESULTS

The fertilizer treatments were applied at a rate of 1 g urea fertilizer per 100 g fresh soil which equates to 460 mg NH_3-N. Analysis of the cumulative NH_4^+ results (Figure 2), shows NH_3 fluxes from untreated urea were 28.54 mg N, which represents a volatilization rate of 6.2%; and fluxes from NutriSphere-N® treated urea were 3.78 mg N, which represents a volatilization rate of 0.008%, while fluxes from the control were 0.05 mg N 0.00011%. Fluxes from urea were significantly higher (86.7%) than the fluxes from NutriSphere-N® treated urea ($p = .018$) and significantly higher (99.8%) than the untreated control

($p = .006$). The fluxes from the NutriSphere-N® treated urea were not significantly different from the untreated control ($p = .959$).

Figure 3 shows the daily flux of NH_3-N ($mg\,N\,m^{-2}\,day^{-1}$) NH_3-N. The highest fluxes of NH_3-N for the fertilized treatments occurred between 22 June and 6 July (sampling periods 6–12). On average, untreated urea generated the highest fluxes in the experiment, while urea treated with NutriSphere-N shows much lower fluxes of NH_3, and both fertilizer treatments produced peak fluxes on 27 June.

The pattern of fluxes from the two fertilizer N treatments were similar, NH_3-N fluxes commenced on 17 June (sampling period 1 of the study), with extremely low NH_3-N flux volumes. The fluxes gradually increased until 21 June (sampling period 5 of the study) when the rates of increase in fluxes were much greater. Fluxes peaked for the fertilizer treatments on 27 June, sampling period 9 of the study.

Analysis of the acid traps collected for each individual sampling period (Figure 4) shows that urea dominated the concentrations. The concentrations for the first four sampling periods—(acid traps sampled daily) were low <0.25 mg N. From sample period 5, the concentrations started to increase for urea (2.31 mg N); increasing to 4.44 mg N at sample period 6 and 11.65 mg N at sample period 7. For sampling periods 8, 9 and 10, the acid trap sampling took place every 2 days with the acid trap concentrations representing 2 days of measurement. At sampling period 8, this trend for higher concentrations from urea continues with 46.42 mg N and peaked on sample period 9 at 108.69 mg N for urea. NutriSphere-N® treated urea concentration also peaked at sample period 9, though the peak was much lower at 42.14 mg N. Concentrations for both fertilizer treatments started to reduce at sample period 10 with 58.97 mg N for urea, while NutriSphere-N® had returned virtually to the same level as the control. For periods 11
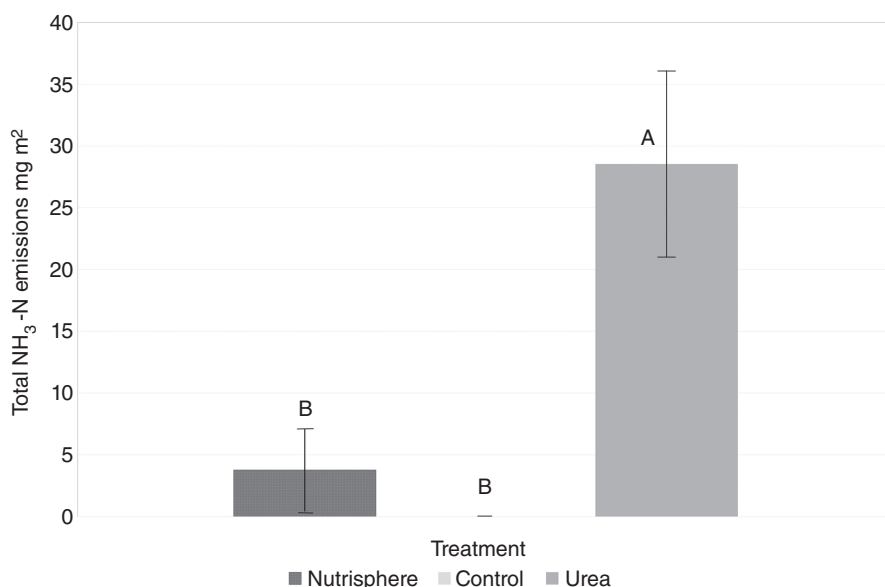

FIGURE 2 Cumulative Ammonia Emissions for the study period (total 21 days). $N = 6$, Error Bars = SE.
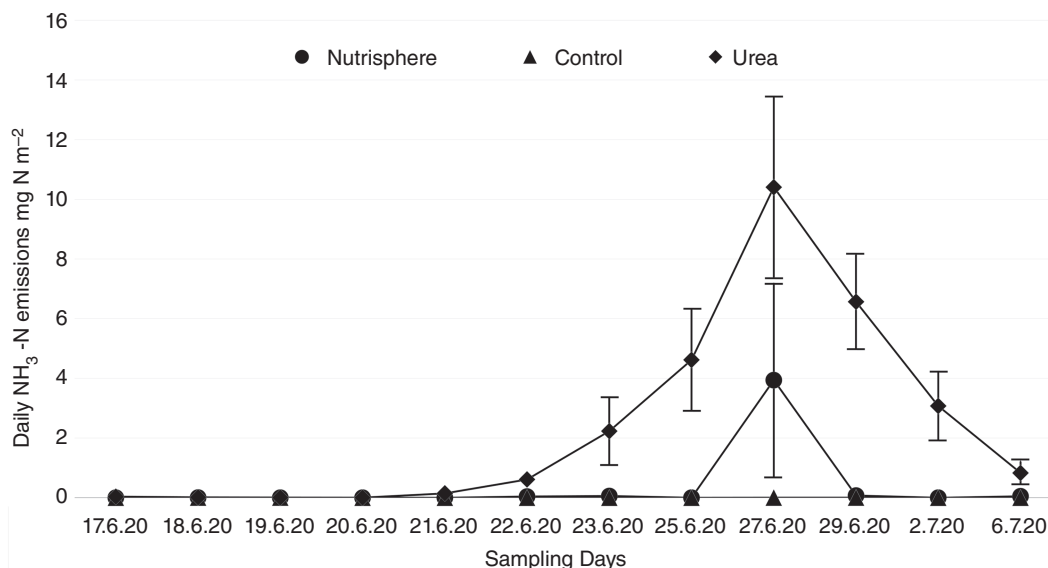
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FIGURE 3 Daily Flux of NH_3-N ($mg\,N\,m^{-2}\,d^{-1}$) over the study period. $N = 6$, Error Bars = SE.
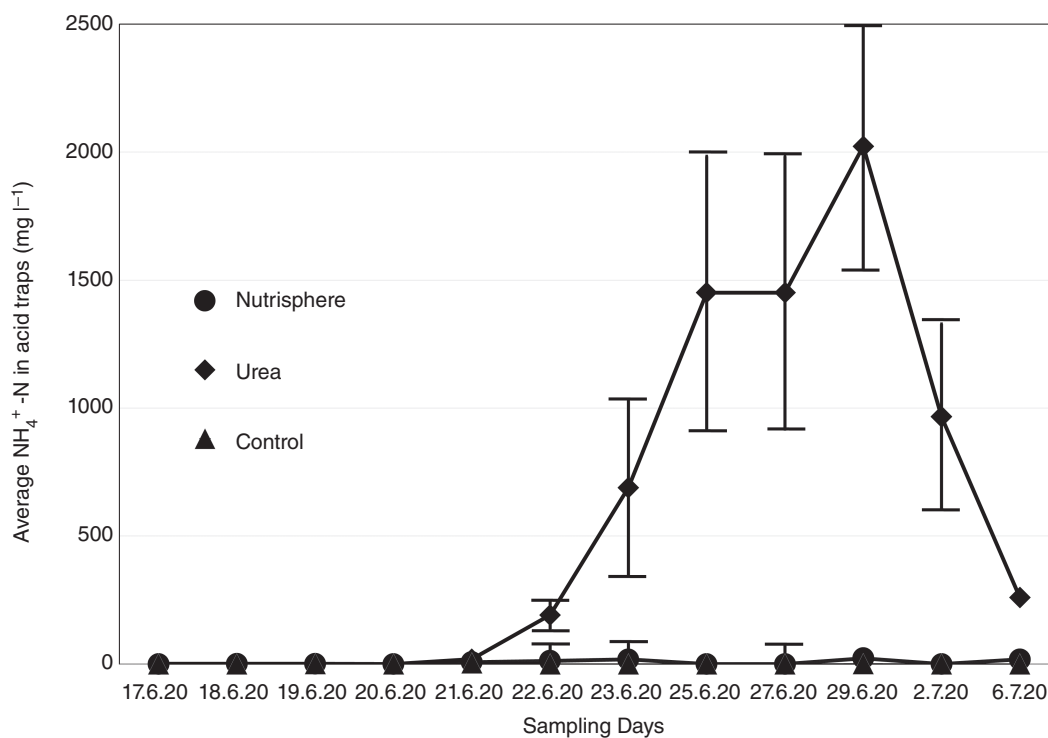

FIGURE 4 Concentration of NH_4^+-N in the acid traps. Sampling periods 1–7 are sampled daily, 8–10 are sampled every 2 days and 11–12 every 3 days. $N = 6$, Error Bars = SE.

and 12 samples were taken every 3 days, at sample period 11 urea had reduced to 25.35 mgN and NutriSphere-N® to 6.34 by sample period 12 urea concentration had returned to 4.73 mgN and NutriSphere-N® to 0.39 mgN. The control treatment remained close to zero with the highest average value of 0.26 mgN at sample period 10.

In relating the chamber air flow rate (Table 1) to the emissions peak (Figure 3), the airflow for the 4 days coming up to and including the emissions peak, was the second highest

of these four (167 cm^3 min^{-1}) on day 6, when the urea emissions rate is starting to increase significantly, the average flow rate in the chamber is highest on day 7 (265 cm^3 min^{-1}) as the urea emissions rate remains similar to the previous day. The flow rate is lowest of the 4 days on day 8 (115 cm^3 min^{-1}) as the Nutrisphere-N® emissions start to increase significantly and as the rate of increase in urea emissions is highest and the flow rate is second lowest on day 9 (122 cm^3 min^{-1}) when the rate of emissions start to reduce.

TABLE 2 Nutrisphere-N®Studies.

Author	Study	Crop	Rain/Irrig	Fertilizer	Soil texture	SOM	pH	Climate/weather	Yield effect	Volatilization effect	Conclusion
Barbieri et al. (2018)	Field	Corn (*Zea mays* L.)	Irrigated first 2 years, Rainfed third year	Urea	Loam, particle size distribution of 23% clay, 36% silt and 41% sand.	Year 1 OM 4.9%; Year 2 OM 5.4%; Year 3 OM 5.1%;	Year 1 ph 5.6; Year 2 pH 5.7; Year 3 pH 5.9;	130 m above sea level; 870 mm mean annual rainfall; 13.7°C mean annual temperature, water deficit -60 mm in year 1, 92 mm in year 2 and 122 mm in year 2 and 3	No effect	Reduction from 1.1% and 7.2% of N applied	Yield effect N.S; Volatilization loss $p < 0.05$
Cahill et al., (2010)	Field	Corn (*Zea mays* L.) and wheat (*Triticum aestivum* L.)	Rainfed	UAN	Pocalla series Corn (2008); Corn (2009); Cecil series Corn (2008); Corn (2009); Dillard series Corn (2008); Corn (2009); Statler series Corn (2009); Stallings series Wheat (2008); Wheat (2009); Portsmouth series Wheat (2008); Wheat (2009);	OM 0.22 to 7.45	2008 pH 4.8 to 6.5 pH; 2009 5.2 pH;	Temperatures were fairly similar to the 30-year normal Lower rainfall than the 30-year average	Yield 59% higher in 2008 and 21% higher in 2009 at Mountain Site, 15% higher 2009 in Coastal Plain		Stover yields both site years in mountain site $p < 0.05$, stover yields at coastal Plain 2009 $p < 0.05$. All other measure N.S.
Dunn and Wiatrak (2014)	Field	Rice (*Oryza Sativa* L.)	Rainfed	Urea	(A) Dewitt silt loam soil (fine, smectitic, thermic, Typic, Albaqualf). (B) Sharkey clay soil (very fine, smectitic, thermic Chromic Epiaquert).	Not reported	Not reported	For both years, ambient air temperatures of >26°C occurred from urea application through permanent flood all N applications were made to very dry surface soils in Year 1, to wet soils in year 2 at both locations	Agrotain rice yields than untreated urea at 78 kg N ha⁻¹ for location A. Nutrisphere-N rice yields better than Agrotain and untreated urea at location B in 2008. at the rate of 78 kg N ha⁻¹		Improved rice grain yields compared to untreated urea in location A and B, respectively, $p > 0.01$ All other measures N.S.
Edmeades and McBride (2012)	Meta-analysis	N/A	N/A	N/A	N/A	v	N/A	N/A	Yield responses from ranged from −8% to +12%		Average crop response of 0.05% N.S.

TABLE 2 (Continued)

Author	Study	Crop	Rain/Irrig	Fertilizer	Soil texture	SOM	pH	Climate/weather	Yield effect	Volatilization effect	Conclusion
Forrestal et al. (2016)	Field	Perennial Ryegras — Lolium perennae	Rainfed	Urea	Sandy loam	7.02% OM	pH 5.69;	Temperate Maritime Climate; Growing season rainfall (GSR) 441 mm; lower than 30-year average GSR 534mm	No effect	No effect	NH₃ emissions N.S.
Franzen et al. (2011)	Field	Spring wheat (*Triticum aestivum* L.); Durum wheat [*T. turgidum* L. *subsp durum* (Desf.) Husn.]	Rainfed	Urea UAN	1. Fine-loamy; 2. Fine-loamy; 3. Fine-loamy; 4. Coarse-loamy; 5. Fine-loamy; 6. Fine-silty; 7. Fine-loamy; 8. Fine-loamy	1. 3.6%; 2. 3.7%; 3. 2.4%; 4. 1.9%; 5. 5.1%; 6. 5.5% 7. 2.2%; 8. 2.2%;	Not reported	No weather data for North Dakota field experiment reported	No effect on yield no differences in grain protein except at the 101 kg N ha − 1	No effect	Yield difference N.S Differences in grain protein N.S except at the 101 kg N ha − 1 P<0.05
Franzen et al. (2011)	Lab	no crop	Not stated	liquid application	1. Overly clay loam (Pachic Hapludolls) derived from glacial lacustrine deposits 2. Renshaw sandy loam (Calcic Hapludolls) derived from glacial outwash.	1. 3.9% OM; 2. 2.1% OM	1. pH 6.3; 2. pH 6.4;	N/A		No effect	Urea hydrolysis reduction N.S.
Franzen et al. (2011)	Lab	no crop	Not stated	Urea	Renshaw sandy loam (Calcic Hapludolls) derived from glacial outwash.	2.1% OM	pH 6.4;	N/A		No reduction in ammonia volatilization	Ammonia volatilization difference N.S.
Franzen et al. (2011)	Lab	no crop	Not stated	Urea	Renshaw sandy loam (Calcic Hapludolls) derived from glacial outwash.	2.1% OM	pH 6.4;	N/A		No indication of inhibited nitrification	Nitrification inhibition N.S

(Continues)

TABLE 2 (Continued)

Author	Study	Crop	Rain/Irrig	Fertilizer	Soil texture	SOM	pH	Climate/weather	Yield effect	Volatilization effect	Conclusion
Franzen et al. (2011)	Field	Delayed-flood rice	Not stated	Urea	1. Sharkey clay (Vertic Haplaquepts); 2. Dewitt silt loam (Typic Albaqualfs); 3. Hillemann silt loam (Glossic Natraqualfs).	Not reported	1. pH 7.3; 2. pH 6.3; 3. pH 5.9;	No precipitation at the DREC in the 10 DBF (days before flooding) after the N sources were applied. Only a trace of precipitation between any of the N application times and flooding at LHRF and >5 cm of precipitation occurred the day after the 10 DBF N application at RREC	No effect		Yield effect of N fertilizer source N.S.
Goorahoo et al. (2015)	Field	Cotton-(Gossypium hirsutum)	Irrigated	UAN 32	Ramona Sandy Loam	Not reported	Not reported	Mediterranean climate weather data not reported		At rates of N 50, 100 and 150 lbs N/ac Reduced N_2O emissions by 19%, 54% and 52%, respectively	N_2O emissions reduction $P<05$
Goos (2008)	Lab	No crop	Controlled	UAN & Urea	Renshaw sandy loam or Overly clay loam	Not reported	Not reported	N/A		No effect on urease or nitrification rates	Reduction of urease or nitrification rates N.S
Goos (2013)	Lab	No crop	Controlled	UAN	Sandy loam; sandy clay loam; clay;	OM 1.8%; 2.8% 5.9%	pH 7.3; pH 8.1; pH 6.5;	N/A		Cumulative reduction in ammonia loss 11%	11% reduction in ammonia loss N.S.
Goos (2018)	Lab	No crop	Controlled	Urea	Loam; Loam; Loam;	OM 4.1%; 2.3%; 4.5%	pH 4.5, 5.2 and 5.7	N/A		Reduction of −1 and −4% for 5 and 50 $\mu g\,g^{-1}$ of NSN	Reduction in urea hydrolysis N.S.
Gordon (2009)	Field	Corn (Zea mays L.)	irrigated	urea UAN	Crete silt loam soil	OM 2.8%;	pH 7.0;	Weather data from Kansas Not Reported	20% increase in yield, 72% increase in grain leaf ear N, 19% increase in grain N%		Increased yields, $p < 0.05$.

T A B L E   2   (Continued)

Author	Study	Crop	Rain/Irrig	Fertilizer	Soil texture	SOM	pH	Climate/weather	Yield effect	Volatilization effect	Conclusion
Gordon (2014)	Field	(no-tillage) Corn (*Zea mays* L.)	Irrigated	UAN and Urea	Crete silt loam soil (fine, montmorillonitic, mesic Pachic Arquistoll	OM 2.00%	pH 6.8	Weather data from Kansas Not Reported	Increased yield 8%, uptake 17%		Increased yield $p < 0.05$
Goos & Guertal, (2019)	Lab	No crop	N/A	Urea	Sandy loam; Sandy clay loam, -Clay; Sandy Loam	OM% 1.8%; 2.8%; 5.9%; 1.7%	ph 7.3; pH 8.1; pH 6.5; pH 6.7;	Not relevant		No effect	Reduction of urea hydrolysis, ammonia volatilization and nitrification N.S.
Harty et al., (2017)	Field	Perennial Ryegrass — *Lolium perennae*	Rainfed	Urea	Sandy loam	OM 1. 7.9%; 2. 7.02%;	1. pH 5.5; 2. 5.7	Temperate Maritime climate Growing season rainfall (GSR) lower than 30 year average by 93 and 53mm, respectively.	No effect		Yield and uptake differences N.S.
Heiniger et al., (2014)	Field	Corn (*Zea mays* L.)	Rainfed	30% UAN	1. Fine-loamy; 2. Coarse-silty; 3. Fine; 4. Coarse-loamy; 5. Fine-loamy; 6. Fine-loamy; 7. Fine; 8. Fine-loamy, f	Not reported	Not reported	North Carolina weather data not reported	Increased yield by 0.74 Mgha^{-1}		Increased yield ($p < 0.1$)
Hopkins et al. (2008)	Field	Potato (*Solanum tuberos'm'*Russet Burba''''')	Not reported	Urea	Not reported	Not reported	Not reported	Idaho weather data Not reported	Increased standard yield (39 cwt/acre) and the full (42 cwt/acre) and reduced (38 cwt/acre) rates		Increased yield $p < 0.05$.
Lemus et al. (2013)	Field	Perennial Ryegras—*Lolium perennae*	Rainfed	Urea	Marietta fine sandy loam (Fine-loamy, siliceous, active, thermic Fluvaquentic Eutrudepts).	Not Reported	Not Reported	Precipitation below normal for growing season except Nov 2010 and April 2011 Average temperature colder in Dec and Jan, but above normal from the rest of the growing season.	No effect		Effect on forage production, N removal or forage quality N.S.

(Continues)

TABLE 2 (Continued)

Author	Study	Crop	Rain/Irrig	Fertilizer	Soil texture	SOM	pH	Climate/weather	Yield effect	Volatilization effect	Conclusion
Liu et al. (2019)	Field	Corn (*Zea mays* L.)	Rainfed	Urea	2013 1. Loring/ Henry silt loam 2. Hamblen silt loam; 2014 1. Memphis/ Loring silt loam and 2. Staser silt loam and 2015 1. Memphis silt loam and 2. Hamblen silt loam	Milan 2013 OM 1.55%; Jackson 2014 1.61%; 2015 1.21%; Springfeld 2013 ND; 2014 ND;	Milan 2013 pH 6.7; Jackson 2014 pH 6.5; 2015 pH 6.8; Springfeld 2013 pH 6.2; 2014 pH 6.4; 2015 pH 6.8	Tennessee weather relative to average Not Reported	No effect	No effect	Effects on reducing ammonia volatilization loss improving N nutrition, grain yield and N agronomic use efficiency N.S.
Maharjan et al. (2017)	Field	Corn (*Zea mays* L.)	Irrigated	UAN	Loamy Sand. 2009 and 2011 – mixed, mesic oxyaquic Ustipsamments; 2010 mixed,superactive, mesic oxyaquic Haplustolls;	2009 OM 1.1%; 2010 OM 1.6%; 2011 OM 1.1%	2009 pH 7.1; 2010 pH 6.8; 2011 pH 7.6;	Total seasonal water inputs (precipitation and irrigation) were 550, 718 and 823 mm in 2009, 2010 and 2011,	Increased yield in normal weather year not in extreme weather years.		Effects on GY, GNU, or TNU $p < 0.05$ in normal year, N.S. In extreme weather
Mazzei et al. (2018)	Lab	No crop	N/A	N/A	N/A	N/A	pH 7.5 and pH 5.0	N/A	No effect		Urease completely inactivated at pH 5.0 $p < 0.05$ but at pH 7.5 N.S.
Moyer and Kelley (2008)	Field -	Bermuda Grass (*Cynodon dactylon* (L.) Pers) 'Midland 99'	Rainfed	Urea	Not reported	Not Reported	Not Reported	Average weather in Kansas not reported, however, rainfall in 2008 growing season 155% of 30-year average.	No effect		Increase in yield N.S.
Norman et al. (2008)	Field	Rice (*Oryza sativa* L.)	Flooded	Urea	Not reported	Not Reported	Not Reported	Not Reported	No effect	No effect	Reduction of ammonia volatilization N.S. Yield increase N.S.
Connell et al. (2011)	Field	Bermuda Grass (*Cynodon dactylon* (L.) Pers)	Rainfed	Urea	1. Shellbluff silt loam (fine-silty, mixed, active, thermic Oxyaquic Dystrudepts) and 2. Davidson loam (fine, kaolinitic, thermic Rhodic Kandiudults).	Not reported	2008 1. pH 6.2; 2. pH 6.6; 2009 1. pH 6.9; 2. 6.9;	In 2008 rainfall lower than 30-year mean In 2009, rainfall at or above the 30-year mean.	No effect	No effect	Ammonia volatilization reduction N.S. yield increase N.S.

TABLE 2 (Continued)

Author	Study	Crop	Rain/Irrig	Fertilizer	Soil texture	SOM	pH	Climate/weather	Yield effect	Volatilization effect	Conclusion
Peng et al. (2015)	Lab	No crop	N/A	UAN	Ipage fine sandy loam (mixed, mesic Oxyaquic Ustipsamment).	1.40%	pH 7.1	N/A		Reduced N loss by 41%	N loss reduced $p<0.05$
Pereira et al. (2009)	Field	Corn (*Zea mays* L.)	Rainfed	Urea	Oxisol or Rhodic Hapludox soil (Dystroferric Red Latosol) (low cation exchange capacity).	2.09%	pH 6.43;	Recorded		Reduced volatilization in side-dressing fertilization.	Reduced volatilization $p<0.05$
Tubbs et al. (2009)	Field	Corn (*Zea mays* L.)	Rainfed	UAN 32	Sandy Soils	Not Reported	Not Reported	Not Reported	No impact		Improvement in plant performance N.S.
Wiatrak (2014a)	Field Study-	Corn (*Zea mays* L.)	Rainfed	Liquid 25-S (25N and 3.5% S)	Dothan loamy sand (fine loamy, kaolinitic, thermic Plinthic Kandiudult)	Not reported	pH 6.2.	Precipitation greater in 2012 and lower in 2010 and 2011 than 30-year average		Soil NO3-N content increased by 26.2%, 36.1%, 28.0% and 17.3% at 45 kg, 90 kg, 135 kg and 180 kg N ha^{-1}	Reductions soil NO$_3$-N losses $p<0.05$.
Wiatrak (2014b)	Field	Corn (*Zea mays* L.)	Rainfed	25-S (25N and 3.5% S)	Dothan loamy sand (fine loamy, kaolinitic, thermic Plinthic Kandiudult	Not reported	pH 6.2.	Precipitation greater in 2012 and lower in 2010 and 2011 than 30-year average	Increased grain yield by 33.3 and 29.5% at 90 and 135 kg N ha^{-1} at planting and 12.1%, 12.9%, 22.0% and 31.2% at 45, 90, 135 and 180 kg N ha^{-1}.		Improved corn grain yield $p<0.05$
Wiatrak and Gordon (2014)	Field	Corn (*Zea mays* L. cv. 'DeKalb DKC60-19')	Irrigated	Urea	Crete silt loam soil (Fine, smectitic, mesic Pachic Udertic Argiustolls)	OM 2.8%	pH 7	Not reported	Improved grain yields by 18.3% with apps of 180 kg N ha^{-1}.		Improved N content in leaves and grain and grain yields $p<0.05$

4 | DISCUSSION

This experiment was conducted in a temperature and light-controlled lean in chamber environment using a closed system designed to quantify the NH_3 losses from N fertilizers and frequent acid trap sampling also enabled comparisons of emissions profiles from the fertilizer treatments. The experiment was conducted for a 3-week period under simulated summer temperatures in a temperate maritime region. The chamber airflow ran non-stop between sampling periods (to simulate windy conditions), moisture levels were supplemented at the sampling time and the soil was allowed to dry out in between sampling to simulate rainfed systems. These environmental conditions combined with surface fertilizer application provided the conditions conducive for NH_3 volatilization.

In an incubation study (using four types of soil, five nitrogen sources, three incubation temperatures and two soil moisture regimes), based on a PCA analysis, the influence of various factors on NH_3 emission levels was identified in a descending importance as follows: soil type, nitrogen source, pH of the soil, soil temperature and moisture regime (Liu et al., 2011). The soil type and environmental effects relative to the experimental conditions including soil moisture, precipitation, temperature, windspeed, rainfed studies were examined in the context of the literature (Table 2).

4.1 | Soil type

According to Fenn et al. (1982) losses of NH_3 from soils are controlled by the soil cation exchange capacity (CEC) which can be related back to the soil texture and soil organic matter (OM) status. Coarse textured soils have a greater sand content, and as sand does not have many functional groups that can bind NH_4^+ ions, these soils have lower potential to retain NH_4^+ ions and are at increased risk for NH_3 loss (Liu et al., 2011). In contrast, clay and silt particles have much greater surface areas and more functional groups than sand with greater capacity to retain NH_4^+ ions and NH_3 emission rates tend to be lower in fine-textured soils (Liu et al., 2007). This present experiment considered only the surface application of a single mineral N source—urea in granular form. Urea hydrolysis, especially in surface applications of urea on moist soil, causes a temporary spike in pH around the granule as it disintegrates, this increase in pH alters the ratio of NH_4^+ and NH_3 present: above pH 9.75 NH_3 predominates while below pH 8.75, NH_4^+ predominates (Hem, 1985). Because of the direct impact of pH on the balance of NH_4^+ and NH_3, soil properties that buffer or resist pH changes will be important in reducing

NH_3 volatilization levels, so fine-textured soils should be at lower risk for volatilization. Although as urea granule is hydrolysed, the increase in pH is temporary, it can result in substantial volatilization loss from soils with an initial pH as low as 5.5 (Engel et al., 2011). Rochette et al. (2013) found that cumulative NH_3 emissions were closely related ($R^2 \geq .85$) to two factors, maximum increases in soil NH_3 concentration and soil pH. Nutrisphere-N® along with other products, designed to reduce NH_3 volatilization from urea, will be more effective in the environmental conditions conducive to NH_3 volatilization loss. Overall, soil texture alone is one factor of many which will contribute to NH_3 volatilization risk. Others include starting choice of N type, soil moisture conditions, the timing of precipitation, the soil pH, temperature and windspeed. Because so many other factors influence volatilization risk, there is no direct link between soil texture and Nutrisphere-N® effectiveness in reducing NH_3 emissions. For example, soil texture in studies where Nutrisphere-N® was reported to be effective ranged from loamy sand (Maharjan et al., 2017; Wiatrak, 2014a, 2014b), sandy loam (Goorahoo et al., 2015; Peng et al., 2015), silt loam (Dunn & Wiatrak, 2014; Gordon, 2014; Wiatrak & Gordon, 2014); loam (present study) and clay (Dunn & Wiatrak, 2014). While soil texture in studies that report Nutrisphere-N® as ineffective in reducing NH_3 emissions also range from sandy loam (Goos, 2008; Tubbs et al., 2009; Franzen et al., 2011; Lemus et al., 2013; Forrestal et al., 2016; Harty et al., 2017; Goos & Guertal, 2019), sandy clay loam (Goos & Guertal, 2019), silt loam (Connell et al., 2011; Franzen et al., 2011), loam (Connell et al., 2011; Norton, 2011), clay loam (Goos, 2008; Franzen et al., 2011), clay (Franzen et al., 2011; Goos & Guertal, 2019).

4.2 | Soil moisture and precipitation

The results from the temporal emissions from this experiment show a typical urea NH_3 emissions profile with a single peak. Soil moisture was a key contributor to this peak which occurred when the fertilizer granule had sufficiently disintegrated on the moist soil and at the point in the experiment at which the sampling frequency had increased from daily sampling to sampling every 2 days (between sampling period 7 and 8). Up to this point, soil moisture levels were replenished at daily sampling with a standard aliquot (10 mL) of water. The daily aliquot of water was doubled (20 mL) on day 8 to account for sampling frequency moving to every 2 days. It is likely that the rate of granule disintegration was increased by doubling the aliquot of water and this was followed by enhanced evaporation of soil moisture because of the longer time between sampling. Soil water, which contained appreciable

quantities of NH_3 and NH_4^+ dissolved, as it evaporated would also have contributed to the emissions peak. Both urea and Nutrisphere-N® treated urea fertilizer treatments in this experiment followed a similar emissions profile.

Literature also supports that urea-N is at greater volatilization risk following surface applications of urea at higher soil moisture (Pelster et al., 2019). A study by Engel et al. (2011) found the largest losses (30%–44% of applied N) occurred after urea was applied to high water content soil surfaces, followed by a period of slow drying with little or no precipitation. This is also in agreement with Forrestal et al. (2016) who identified the main contributing factor driving maximum urea volatilization (53%) was the starting level of soil moisture and the timing and duration of precipitation events. There is evidence of varying effectiveness of Nutrisphere-N® in improving NUE under different moisture conditions, Maharjan et al. (2017) found Nutrisphere-N® improved yield performance in normal weather years, but no effect on yield in extreme wet years or dry years. There was no yield effect of Nutrisphere-N® in a growing season where rainfall was 155% of the 30-year average (Moyer & Kelley, 2008) nor in extreme dry year when growing season rainfall deficit of 17% of 30-year average. (Harty et al., 2017). In contrast to these findings, Pereira et al. (2009) showed Nutrisphere-N® treated urea reduced urea N volatilization in side-dressing fertilization following high rainfall and Nutrisphere-N® reduced N losses with both urea and UAN and increased grain yield when soil moisture content was at 55%, 56% and 53% of field capacity when fertilizer was applied (Gordon, 2014).

However, in these studies, the detail of the starting soil conditions and the timing or precipitation is not presented which are essential in creating, enhancing or minimizing the conditions for volatilization. Soil moisture influenced volatilization levels in the study by Dunn and Wiatrak (2014) where urea treated with Nutrisphere-N® did not produce higher yields than urea alone when fertilizer was applied at low soil moisture, while Nutrisphere-N® improved rice grain yields compared to untreated urea when N applied at higher soil moisture. It is clear that Nutrisphere-N® as well as other products, designed to reduce NH_3 volatilization from urea, will be more effective in the environmental conditions conducive to NH_3 volatilization loss.

4.3 | Windspeed and temperature

Ammonia is also at a greater risk of volatilization at high temperatures, high windspeed and low humidity (Sommer et al., 2009). Kissel (1986), found that a temperature rise from 7.0°C to 26°C increased the transformation of urea to NH_4^+ by a factor of four and the proportion present as NH_3 also increased. The present study temperature was chosen to simulate summer temperatures in Ireland. The airflow was on continuously throughout the study to simulate windy conditions apart from short breaks during sampling. Humidity was not controlled. These temperature and wind conditions combined with the surface applied fertilizer would have been conducive to volatilization loss. In field studies where the combined temperature and windspeed conditions are conducive to NH_3 volatilization, Nutrisphere-N® consistently reduced N loss. For example, Nutrisphere-N® treated urea (applied as KimCoat©) reduced urea N volatilization when applied at air temperatures greater than 30°C in Brazil (Pereira et al., 2009). Nutrisphere-N® helped to reduce soil NO_3-N losses Wiatrak (2014a) and improve growth parameters and yield of corn (Wiatrak, 2014b), where the growing season average temperature exceeded the 30-year average. Nutrisphere-N® reduced N losses with both urea and UAN in no till corn (*Zea mays* L.) and increased grain yield in conditions favourable for NH_3 volatilization (Gordon, 2014). Peng et al., 2015 in a laboratory study incubated at a daytime temperature of 25°C, and a night-time temperature of 18°C found UAN-with Nutrisphere-N® significantly limited N loss compared to UAN alone. Goorahoo et al., 2015 found Nutrisphere-N® reduced N_2O fluxes in cotton (*Gossypium hirsutum*) by as much as 50%, with reduced efficacy at highest fertilizer rate. Dunn and Wiatrak found rice yields (*Oryza satvia* L.) were improved by both Agrotain and Nutrisphere-N® compared to untreated urea at the rate of 78 kg N ha^{-1} and only in the year when both the soil and environmental conditions were conducive to N loss.

Windspeed is also a factor influencing the NH_3 volatilization rate. For the present study, the 4 days leading up to and after the peak, there was a lack of linear relationship between the average flow rate and the rate of emissions, with the lowest windspeed coinciding with the fastest rate of increase of emissions. This suggests windspeed, while it may contribute to volatilization, was not the critical factor in driving NH_3 emissions in this study. This is supported by research which shows that while NH_3 loss rate increased when wind speeds increased up to 2·5 m s^{-1}, no consistent increase in NH_3 volatilization was found when the wind speed increased from 2·5 to 4 m s^{-1} (Sommer & Olesen, 1991). This is in agreement with Thompson et al. (1990) who found while wind speed had a positive effect on NH_3 volatilization, the effect was small in relation to the total loss; increasing the wind speed from 0.5 to 3.0 m s^{-1} increased the total 5 day loss by a factor of 0.29.

4.4 | Inhibitor efficacy at Rainfed sites

Smith et al. (2014) suggest greater yield advantages will be found when Nutrisphere™ is used under conditions

where yield is not limited by lack of rainfall. For example, under irrigated conditions, Nutrisphere-N® treated urea and/or UAN consistently reduced total NH_3 volatilization losses (Barbieri et al., 2018), increased yield in grain (Gordon, 2014; Wiatrak, 2014b) and rice (Dunn & Wiatrak, 2014) and improved yield and N uptake in corn (Maharjan et al., 2017; Wiatrak & Gordon, 2014). This is in contrast to more variable results using Nutrisphere-N® under rainfed conditions where Nutrisphere-N® increased yield of corn (Smith et al., 2014) and potatoes (Hopkins et al., 2008); Nutrisphere-N® did not reduce emissions in temperate grassland (Forrestal et al., 2016), forage bermudagrass (Connell et al., 2011), spring wheat, durum wheat (Franzen et al., 2011) and corn (Liu et al., 2019). Nutrisphere-N® did also not increase yield in temperate grassland (Harty et al., 2017), bermudagrass (Moyer & Kelley, 2008; Connell et al., 2011), Spring wheat and durum wheat (Franzen et al., 2011), corn (Liu et al., 2019; Tubbs et al., 2009), sugar beet (Norton, 2011) and perennial ryegrass (Lemus et al., 2013). In the present study, the temperature and continuous airflow conditions in the chamber meant soil moisture levels in this experiment were allowed to reduce before an aliquot of water was applied during daily sampling. This soil drying was enhanced further when sampling and aliquot addition moved to every 2 days. This simulated the soil conditions at rainfed field sites where the drying soil may have contributed to enhanced volatilization levels.

4.5 | Other sources of variability

A potential source of variability in these trials is the source, age and viability of the inhibitor. The effectiveness of inhibitor products can be reduced if the product is not stored properly or the product is carried over from year to year. NutriSphere-N® has a shelf life of 2 years, while granular urea treated with NutriSphere-N has a shelf life of 12 months (Verdesian, 2022). The product format can also vary; it can also be purchased already mixed from a merchant or the product can be mixed/coated ahead of the experiment. Lack of consistent protocol for storage or mixing can impact the lifespan and effectiveness of the product. Future studies should identify format and source of product as well as the length and conditions of storage ahead of the trials. This will ensure consistent and like for like comparisons in experimental trials.

4.6 | Study shortcomings

Because of the controlled environmental conditions, this study does not account for weather differentials including diurnal, seasonal and spatial differences in meteorology, soil heterogeneity or soil deposition of ammonium (Sutton et al., 2013). It also used bare-sieved arable soil and so did not include the effect of soil structure or the presence of a crop. It was conducted on a single soil type under controlled temperature and moisture conditions. The experiment also included only one single application rate of N fertilizer and the maximum sampling frequency was daily which reduced the resolution of the data. For that reason, this experiment should be supplemented with further field experimentation and incorporate multiple soil types at differing N rates, multiple N sources and high sampling frequency.

4.7 | Implications of this study

The present laboratory incubation study found an 86% reduction in NH_3 emissions from Nutrisphere® amended urea compared to unamended urea. Previous field studies in Ireland found no emissions reductions from Nutrisphere® on grassland but comparable reductions of 78.5% compared to urea applied at a rate of $200 \, kg \, N \, ha^{-1}$ in five $40 \, kg \, N \, ha^{-1}$ applications (Forrestal et al., 2016). While an arable study on Spring barley also found no emissions reductions from Nutrisphere® but an average 20% reduction from NBPT (Roche et al., 2016). Studies have also found rapid hydrolysis of urea in Irish temperate grassland, Watson and Miller (1996) reported that 1.3% of N remained in the urea form in the soil 1.75 days after application. This is in contrast to the incubation study where the emissions peak occurred 10 days after fertilizer application. It is likely that the grass cover in the field site in addition to the higher humidity present contributed to the faster hydrolysis in the field site.

Fertilizer prices (urea) have increased steadily for decades, linked to the price of energy used in the manufacture, rising from €178 tonne^{-1} in 1990, €201 in 2000, €329.97 in 2010, €335.94 in 2020 (CSO, 2021). However, the current energy crisis has meant fertilizer prices have reached an all-time high with retail prices for urea fertilizer in Ireland reached €1200 tonne^{-1} in April 2022 (Farmers Journal, 2022a) and €1500 tonne^{-1} by August 2022 (Farmers Journal, 2022b). Urea is the most concentrated solid N fertilizer (46% N), cheaper to manufacture, more economical to transport and less expensive than other forms of granular fertilizer N. However, because of its high volatilization potential, it has not been used widely historically in Western Europe. Results from early experiments showed that urea was less effective than other straight forms of N (Smil, 2001). Lower urea performance was often because of (a) loss of N efficiency as a result of NH_3 volatilization, driven by both

soil conditions and climatic factors post-fertilizer application (Watson, 2000) and (b) the lower density of urea compared to AN/CAN impacting on uniform field spreading (Dampney et al., 2003). Granulation now supersedes prilling as the method of choice for urea solidification (Kroschwitz & Howe-Grant, 1995). Recent Irish research showed that using protected urea (combining urea with NBPT) reduced N_2O emissions compared to CAN (Harty et al., 2016), offered similar yield and uptake potential to CAN (Harty et al., 2017) and reduced NH_3 emissions compared to urea (Forrestal et al., 2016). The present prohibitive cost of fertilizer means that farmers must use all means necessary to maximize the nutrient retention by minimizing losses from any fertilizer applied. Farmers who may not have previously considered the inclusion of inhibitors with their fertilizer, such as Nutrisphere®, used in the current study, may now be more open to their use.

While Nutrisphere-N® successfully reduced NH_3 emissions compared to urea, in controlled conditions in the present experiment, it is important that a field assessment of the NH_3 emissions from urea, Nutrisphere-N® and other N inhibitors compared to urea be conducted to assess the relative performance under field conditions.

5 | CONCLUSION

This experiment was conducted in a temperature and light-controlled lean in chamber environment using a closed system designed to quantify the NH_3 losses from N fertilizers and to compare the emissions profiles from different fertilizer treatments. The temporal emissions from this experiment show a typical urea NH_3 emissions profile with a single peak. This was driven by increasing NH_3 volatilization which occurred as the fertilizer granule began to break down and peaked once the granule had sufficiently disintegrated. Both urea and Nutrisphere-N® treated urea fertilizer treatments in this experiment followed a similar profile of emissions. The cumulative NH_3 emissions over the experimental period were significantly higher for untreated urea than both the NutriSphere-N® treated urea (86%) and the untreated control, while the emissions from the NutriSphere-N® treated urea were significantly (86%) lower than the untreated urea and were not significantly different from the untreated control. It will be important that consistent storage protocols and coating of the fertilizer with Nutrisphere-N® for use in experiments should be ensured for like by like comparisons. In controlled conditions, Nutrisphere-N® successfully reduced NH_3 emissions compared to urea, and a field assessment of the NH_3 emissions from urea, Nutrisphere-N® and other N inhibitors compared to urea is recommended.

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