



# Oil-based polyurethane-coated urea reduces nitrous oxide emissions in a corn field in a Maryland loamy sand soil

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## ABSTRACT

Urea is the most widely used N fertilizer due to its high N concentration (46%), cost effectiveness and ease of handling. However, urea is susceptible to loss as N<sub>2</sub>O, a greenhouse gas and catalyst of stratospheric ozone decline. Polymer-coated fertilizers may be effective in reducing such losses but the appropriate coating thickness for effective field performance is unknown. We prepared urea granules with polyurethane coating (PCU) based on castor oil at 2%–8% by weight. We tested the fertilizer value of these materials for maize (*Zea mays* L.) and measured field loss of N<sub>2</sub>O. Maize grain yield and N uptake were similar in treatments fertilized with urea (uncoated) and each of the coated materials. Cumulative N<sub>2</sub>O–N per unit of grain yield, however, was reduced by 80% with PCU8% compared with uncoated urea. Results indicate that polyurethane-coated urea performs similarly to uncoated urea for maize production while reducing soil N<sub>2</sub>O emissions up to 60–80%, with an efficiency factor twice as high as that suggested by the Intergovernmental Panel on Climate Change (IPCC) for N fertilizers. Our results indicate that urea with a polyurethane coating of 8% (PCU8%) had the best combined agronomic and environmental performance in a field study.

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## 1. Introduction

Fertilizers, including those containing nitrogen (N), have been fundamental to increasing agricultural productivity per unit of land. However, fertilizer N can be lost from agricultural soils due to many N transformation processes occurring in soil (Robertson and Vitousek, 2009; Trenkel, 2010; Silva et al., 2017; Mariano et al., 2019). Fertilizer N losses reflect asynchrony between N application and/or release and crop N uptake. Important loss mechanisms include nitrate leaching, runoff and erosion, ammonia (NH<sub>3</sub>) volatilization, and gas emissions such as dinitrogen (N<sub>2</sub>), nitric oxide

(NO) and nitrous oxide (N<sub>2</sub>O) (Ruser et al., 2006; Firestone and Davidson, 1989; Raymond et al., 2016; Cancellier et al., 2016; Mariano et al., 2019). Notably, N<sub>2</sub>O, which is produced largely during nitrification and denitrification in agricultural soils, has a direct influence on the greenhouse effect, since it has a global warming potential 298 times higher than that of CO<sub>2</sub> (Forster et al., 2007; Hyatt et al., 2010; Díaz-Rojas et al., 2014). It also serves as a catalyst of stratospheric ozone degradation and its atmospheric concentration is increasing (Ravishankara et al., 2009; Parkin and Hatfield, 2014). Agricultural soils are the primary source of N<sub>2</sub>O and in the United States account for about 79% of anthropogenic N<sub>2</sub>O emissions (USEPA, 2014).

Since N losses from agricultural soils impart substantial economic and environmental costs, scientists have long sought ways to reduce the rate of N release from urea to better match crop N uptake patterns (Azzem et al., 2014; Burton et al., 2008). While urea is not taken up by crops, urea readily mineralizes to HCO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> in soils. Ammonium is then readily nitrified to NO<sub>3</sub><sup>-</sup> by soil nitrifying

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bacteria. Since plants take up N from soil in the form of  $\text{NH}_4^+$  and  $\text{NO}_3^-$ , the release of N in these forms is a critical step following application of urea to soil. Ammonium and  $\text{NO}_3^-$ , however, also serve as substrates for  $\text{N}_2\text{O}$  production by soil nitrifying and denitrifying bacteria, respectively. Thus, the temporal pattern of urea release is critical to many subsequent N transformations in soil.

One common approach to reducing the rate of N release from urea is to apply N fertilizers as close to the time of high crop N demand as possible. For maize, this involves applying some N fertilizer at planting with the bulk applied when maize is about 30 cm tall, just prior to peak demand. This approach, "sidedressing," has been shown to improve maize N use efficiency (Keeney, 1982; Phillips et al., 2009; Zebarth et al., 2008; Eagle et al., 2017) but it requires a second application of fertilizer during a relatively narrow window of opportunity, which increases application costs while increasing risk that timely application could be jeopardized if soil conditions are not conducive to application at the optimal time. Another approach to better N synchronicity is to modify urea diffusion kinetics with surface barriers, i.e., coatings, allowing a single fertilizer application at planting. Polymer-coated urea, in particular, has received considerable attention, reflected by the significant number of available products (Azzem et al., 2014; Shaviv, 2000; Detrick and Hargrove, 2002; Whittington, 2005; Coogan and Damery, 2003; Ogle and Sims, 2010; Chen et al. 2011, 2018; Halvorson et al., 2010).

However, few of these products are stable in warm environments, since most of them (especially those based on polyacrylate polymers) control urea release via slow solubilization of the polymer in water in a very uncontrolled manner, resulting in release that is often not different than for uncoated fertilizers. In addition, many coated urea granules, including commercial products, are reported to have a typical N content of 35–36%, which indicates a material containing about 20% coating by weight (Trenkel, 2010). Due to these limitations, we have developed a bio-based hydrophobic polyurethane (PU) coating from vegetable oils that is biodegradable and mechanically resistant. Coated granules with 7–9.5% by weight (wt%) PU show urea release below 50% in water after 60 days (Bortoletto-Santos et al., 2016). Despite the promising laboratory results, the effectiveness of these materials in improving nitrogen use efficiency (NUE) and decreasing N losses in the field has not been tested.

Therefore, we evaluated these PU coated materials in the field to evaluate their impact on maize N uptake and soil  $\text{N}_2\text{O}$  emissions. Our hypothesis is that urea coated with bio-based polyurethane (PU) derived from vegetable oils will substantially reduce  $\text{N}_2\text{O}$  emissions while maintaining maize grain yield since N release from the coated urea applied at planting will be more temporally synchronous with maize N demand than uncoated urea applied at planting.

## 2. Materials and methods

### 2.1. Preparation of fertilizer materials

Urea granules (ranging between 2.8 and 3.2 mm in diameter) were coated with a polyurethane resin system based on castor oil (referred to here as polyurethane coated urea, PCU). The polyurethane formation consisted of a condensation reaction between castor oil (generously provided by A. Azevedo Óleos, São Paulo, Brazil) and 4,4'-diphenylmethane diisocyanate (MDI – Desmodur, Bayer). Castor oil was mixed with elemental sulfur (8.0% by weight) and then it was reacted with MDI in a ratio of 40:60 by mass (MDI:oil). The use of elemental sulfur (Synth) in the polymer formation improved the coating's filmogenic capacity and provided better adhesiveness and flexibility to the coating.

The coating process was prepared from the dispersion of castor oil + elemental sulfur and MDI over the granules, using a metal turntable coater rotating at 30 rpm, with 25 cm side shields and air flow heated at 70–80 °C. Urea granules were prepared with polymer coatings at mass ratios of 2–8% by weight (in increments of 2 wt%), which did not alter N concentrations substantially (Table 1). For example, 20 g of polyurethane were applied to 1 kg of urea, in the process employing 2% of polymer.

### 2.2. Physical and chemical characteristics of the coated urea materials

#### 2.2.1. Elemental analysis (CHN)

Total nitrogen content of the materials (uncoated and coated granules) was determined by elemental analysis using the CHNS/O 2400 Series II Elemental Analyzer (PerkinElmer).

#### 2.2.2. X-ray microtomography

Analysis of the morphology of the urea and the coatings was performed by X-ray microtomography (SkyScan 1172, Bruker). The images were acquired using the following conditions: 3.94  $\mu\text{m}$  spatial resolution (voxel size), 0.2° rotation step, 180° rotation, and averaging of 10 frames. The reconstruction of the tomographic images was performed using NRecon SkyScan software.

#### 2.2.3. Water-release assay

A water-release assay was used to evaluate the efficacy of the coating system, quantifying the urea release rate as a function of time at room temperature. The assay consisted of immersing 0.5 g of urea (coated and uncoated) in a 250 mL beaker, under constant stirring to promote homogeneous release of urea. In addition, 0.5 mL aliquots were taken periodically: every 24 h over 10 days, then every 48 h until day 20, and every 120 h until day 50. These aliquots were used to determine the concentration of urea released as described in section 2.2.4. Uncoated urea was included as a control treatment. All assays were conducted simultaneously to ensure identical laboratory conditions.

#### 2.2.4. Urea determination

Urea concentration in water was determined with a Shimadzu UV-1601 PC using an adaptation of the methodology of With et al. (1961) and Bortoletto-Santos et al. (2016). A sample (0.5 mL) of the solution was mixed with 2.5 mL of a 10% trichloroacetic acid solution (Sigma-Aldrich) and 0.5 mL of Ehrlich reagent (0.36 mol  $\text{L}^{-1}$  dimethylbenzaldehyde in 2.4 mol  $\text{L}^{-1}$  hydrochloric acid) and absorbance was obtained in the 400–500 nm range.

### 2.3. Field experiment

#### 2.3.1. Experimental site

A field experiment was established to evaluate PCU effects on maize N uptake and soil  $\text{N}_2\text{O}$  emissions at the Beltsville Agricultural Research Center (BARC), a campus of the United States Department of Agriculture Agricultural Research Service (USDA-ARS) in

**Table 1**

Material, code, percentage of PU coating by weight and total nitrogen content of the coated and uncoated urea granules.

Material	Code	PU coating (wt%)	Total N (%)
Urea (uncoated)	Urea	–	47.4 ± 0.2
Urea + PU 2%	PCU2%	2.1 ± 0.1	46.8 ± 0.2
Urea + PU 4%	PCU4%	4.2 ± 0.2	45.9 ± 0.2
Urea + PU 6%	PCU6%	6.0 ± 0.2	45.1 ± 0.3
Urea + PU 8%	PCU8%	8.1 ± 0.2	44.6 ± 0.3

Beltsville, Maryland (39° 01' 54.4" N, 76° 56' 11.6" W). Properties of the soil, a Downer loamy sand (Coarse-loamy, siliceous, semiactive, mesic Typic Hapludults), are provided in the Supplementary Information (Table S1).

### 2.3.2. Field management

The field was chisel plowed to a depth of 20 cm followed by one pass of a disk, a field cultivator and a packer. Maize (Pioneer P9675AMXT) was planted 15 July, 2017 using a John Deere 7200 planter at 69,160 plants ha<sup>-1</sup> in rows spaced 76 cm apart. Before planting, potassium fertilizer was applied at a rate of 168 kg K<sub>2</sub>O ha<sup>-1</sup> (based on soil test results for soil samples collected February 2017). A combination of pre-emergent herbicides typical for the region was applied just prior to planting at the following rates: atrazine (0.34 kg a.i. ha<sup>-1</sup>; 6-chloro-*N*-ethyl-*N'*-(1-methylethyl)-1,3,5-triazine-2,4-diamine), simazine (1.22 kg a.i. ha<sup>-1</sup>; 6-chloro-*N*, *N'*-diethyl-1,3,5-triazine-2,4-diamine), S-metolachlor (1.42 kg a.i. ha<sup>-1</sup>; 2-chloro-*N*-(2-ethyl-6-methylphenyl)-*N*-(2-methoxy-1-methylethyl) acetamide) and mesotrione (0.186 kg ha<sup>-1</sup>; 2-(4-Mesyl-2-nitrobenzoyl)-1,3-cyclohexanedione).

Each fertilizer treatment was randomly assigned to one plot in each of four blocks. Nitrogen fertilizer application rate (160 kg-N ha<sup>-1</sup>) was typical for the region to achieve economically optimum grain yield (Coale, 2010). The amount of material applied for each fertilizer type was calculated based on the total N content of each material (Table 1). Fertilizer materials were applied 18 July by hand in trenches (10 cm wide x 2 cm deep) dug using hand hoes; trenches were parallel to and about 38 cm from each of two adjacent maize rows in each plot. Fertilizers were distributed evenly along the entire 3 m of each of three trenches per plot and then immediately covered with the disturbed soil to minimize any potential volatilization of ammonia. In the no fertilizer control treatment, trenches were dug and then covered with soil but no fertilizer materials were applied. In addition, another treatment (V6) was evaluated where uncoated urea was applied using the same procedure described above 33 days after planting (18 July) when the maize was at the V6 growth stage. After maize harvest (Nov. 21), a cereal rye (*Secale cereale* L.) cover crop was planted in rows spaced 19 cm apart at 125 kg seed ha<sup>-1</sup> using a no-till drill.

### 2.3.3. Nitrous oxide measurements

Nitrous oxide measurements were based on the methodology described by Parkin and Venterea (2010). Rectangular aluminum anchors (internal dimension 0.640 m × 0.328 m; 0.210 m<sup>2</sup> each) were installed about 1 m from the end of each plot between the two middle rows of maize, with the long side perpendicular to the maize rows, as shown in Fig. 1a. Anchors were hammered into the soil to a depth of about 10 cm on 18 July, 2017.

Each anchor (illustrated in Fig. 1b) was fitted with a gutter along its outer perimeter. At the time of sampling, the gutters were filled with water and a stainless-steel lid, fitted with a sampling port and a vent, was seated in the gutter. The water formed a gas tight seal during sampling. Prior to placing the lids on the anchors, a soil thermometer was placed on the soil surface inside the chamber and the air temperature was recorded. Gas samples were taken through the sampling port using a 10 mL syringe fitted with a 22 g, 2.54 cm needle. Samples were injected into pre-labeled 12 mL vials (Labco Exetainer, Lampeter, UK) with butyl rubber septa that had previously been flushed with 99.9% N<sub>2</sub>. Ten mL gas samples were withdrawn from each chamber at 0, 7, 14 and 21 min. Lids were removed immediately after sampling and the chamber internal air temperature was recorded using the previously placed thermometer. Gas samples were taken after each rainfall event of approximately 10 mm or more, usually for three consecutive days (46 total sampling events during the 106 day maize growing season).

Samples were usually taken between 9 and 11 in the morning when soil and air temperature are near mean daily values (Alves et al., 2012).

The concentration of N<sub>2</sub>O in each gas sample was determined by gas chromatography (VARIAN 450 gas chromatograph equipped with an electron capture detector - temperature 300 °C), with split/splitless injector (temperature 120 °C) and silica capillary Fused Poropak QS column. An auto sampler (Combi PAL System) injected 5 mL samples from each vial into the GC. Nitrogen was used as the carrier gas and CH<sub>4</sub>/Ar as auxiliary gas, both with 30 mL min<sup>-1</sup> flow rates.

Nitrous oxide concentrations in the vials were converted to N<sub>2</sub>O concentrations in the anchor headspace using standard curves and the ideal gas law, corrected for mean temperature in the anchor at sampling time (mean of temperature after sampling and temperature prior to sampling) and for the dilution effect of injecting headspace samples into a preflushed vial. Standard curves were constructed by preparing, in duplicate, vials with at least five different N<sub>2</sub>O concentrations in the same types of vials used for samples by adding known volumes of N<sub>2</sub>O from a Certified Standard tank (2.295 ppm N<sub>2</sub>O) to vials previously flushed with UHP N<sub>2</sub>. Ten standards vials were analyzed on the GC for every 40 samples analyzed to ensure that concentrations of the standards bracketed the concentrations of the samples. Anchor volumes were calculated using the mean of ten measured values of the height above the soil surface for each anchor. Chamber volumes were calculated as the sum of the volume defined by the lid and that of the anchor.

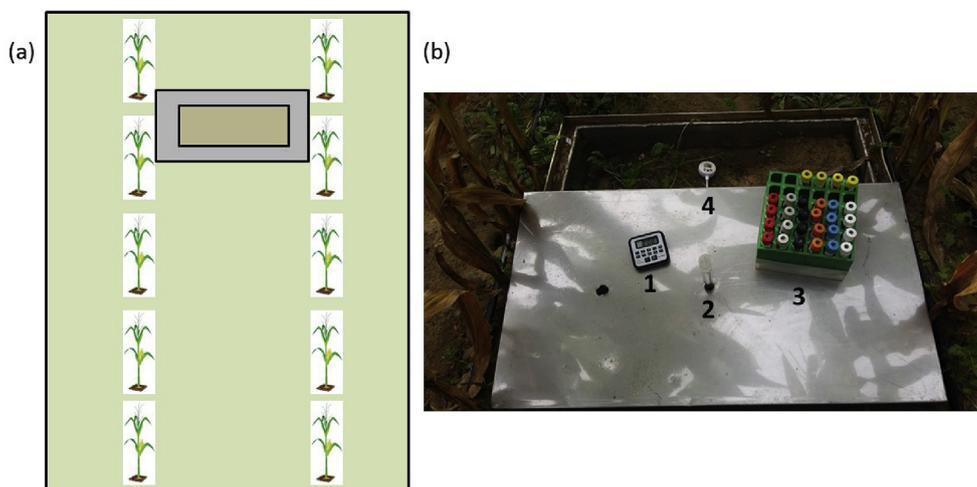
Linear regression of N<sub>2</sub>O concentration over time (assessed using the coefficient of determination, R<sup>2</sup>) was used to calculate the emission rate for each chamber for each sampling day. In addition, linear interpolation between N<sub>2</sub>O emissions values on subsequent sampling days was used to calculate N<sub>2</sub>O emissions for dates when samples were not collected. Daily emissions (measured and interpolated) were summed for the 106 d sampling period.

Volumetric soil water content (m<sup>3</sup><sub>H<sub>2</sub>O</sub> m<sup>-3</sup><sub>soil</sub>) and soil temperature (°C) were measured within 1 m of each gas sampling anchor for the 0–12 cm depth using Campbell Scientific CS655 sensors (Campbell Scientific, Inc., Logan, UT) installed vertically in the soil. The CS655 is a quasi-TDR sensor that generates and transmits an electromagnetic pulse along two 12 cm long stainless-steel rods (wave guides) into the soil. The time required for the wave to return to the probe oscillator correlates to the surrounding medium's dielectric permittivity. The permittivity is calculated from the travel time and inserted into Topp's equation to calculate volumetric water content (Topp et al., 1980; Campbell Scientific, 2015). Data were collected using a Campbell Scientific CR1000 data logger. Sensor measurements were made every 5 min and averaged every 10 min to provide detailed information about changes in soil water content. Data were periodically downloaded directly from the data logger. Soil moisture and temperature data were used to help interpret soil N<sub>2</sub>O emissions.

### 2.3.4. Determination of ammonium (NH<sub>4</sub><sup>+</sup>-N) and nitrate (NO<sub>3</sub><sup>-</sup>-N) in soil

Release of urea in soil was estimated by analyzing soil extracts for NH<sub>4</sub><sup>+</sup>-N, the product of urea mineralization, and NO<sub>3</sub><sup>-</sup>-N, the product of NH<sub>4</sub><sup>+</sup> nitrification. These processes occur rapidly in warm soils and plants take up N as NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup>. Soil samples were taken in each plot at two different depths (0–15 cm and 15–30 cm), using a 19 cm diameter probe. Four cores were taken at each depth within about 15 cm of the maize row in each plot. The four cores at a given depth were combined to form one sample on each of nine sampling days (2, 10, 17, 24, 30 August; 11, 25 September; and 13 and 27 October).

The soil samples were air-dried, ground to pass a 2-mm sieve



**Fig. 1.** (a) Schematic diagram showing placement of gas sampling chamber anchors relative to maize rows in a maize plot and (b) photo of an anchor (background) with the lid in the foreground as well as the materials used during gas sampling (1 - stopwatch, 2 - syringe (inserted into sampling port), 3 - sample vials and 4 - thermometer, placed on soil surface).

and stored in pre-labeled bags. After drying, 3 g soil were weighed and 30 mL of 1 M KCl were added. The samples were shaken for 1 h at 200 rpm and allowed to settle for 30 min. Then the extracts were filtered using a Millipore Filter where a blank (KCl only) and a standard containing QAQC soil were also prepared. Filtrate of the KCl extraction was analyzed for inorganic N ( $\text{NO}_3^- + \text{NH}_4^+$ )-N colorimetrically using a SEAL Auto-Analyzer 3 (Mequon, WI). Concentration of inorganic N in extracts was adjusted to reflect the weight of soil. Soil inorganic N results are presented in the supplementary materials.

### 2.3.5. Statistical analyses

Response variables were analyzed using R (R Core Team, 2018). The variables were first Box-Cox transformed to stabilize variances across each variable's range. For all variables except Yield ( $\lambda = 1.6$ ),  $\text{N}_2\text{O}$  emissions factor ( $\lambda = 0.3$ ), and N uptake ( $\lambda = 0.1$ ), the log ( $\lambda = 0$ ) transformation was chosen. Because of the physical layout of treatments in contiguous blocks, where treatments in two different blocks could be physically closer than two treatments from the same block, we decided that an analysis using spatial position and soil characteristics was more appropriate than that commonly used for a randomized complete block. We thus started with the transformed data and a full model (treatment, linear and quadratic spatial trends and their interaction, and soil composition (proportion clay and proportion sand)). A step-wise selection on all explanatory variables other than treatment resulted in a final model for each variable. For each variable, p-values for pairwise comparisons of treatments were adjusted using Tukey's HSD, with  $\alpha = 0.02$  (since a repeated measures adjustment [six dependent variables] also needs to be made, setting  $\alpha = 0.02$  gives the false discovery adjustment).

## 3. Results and discussion

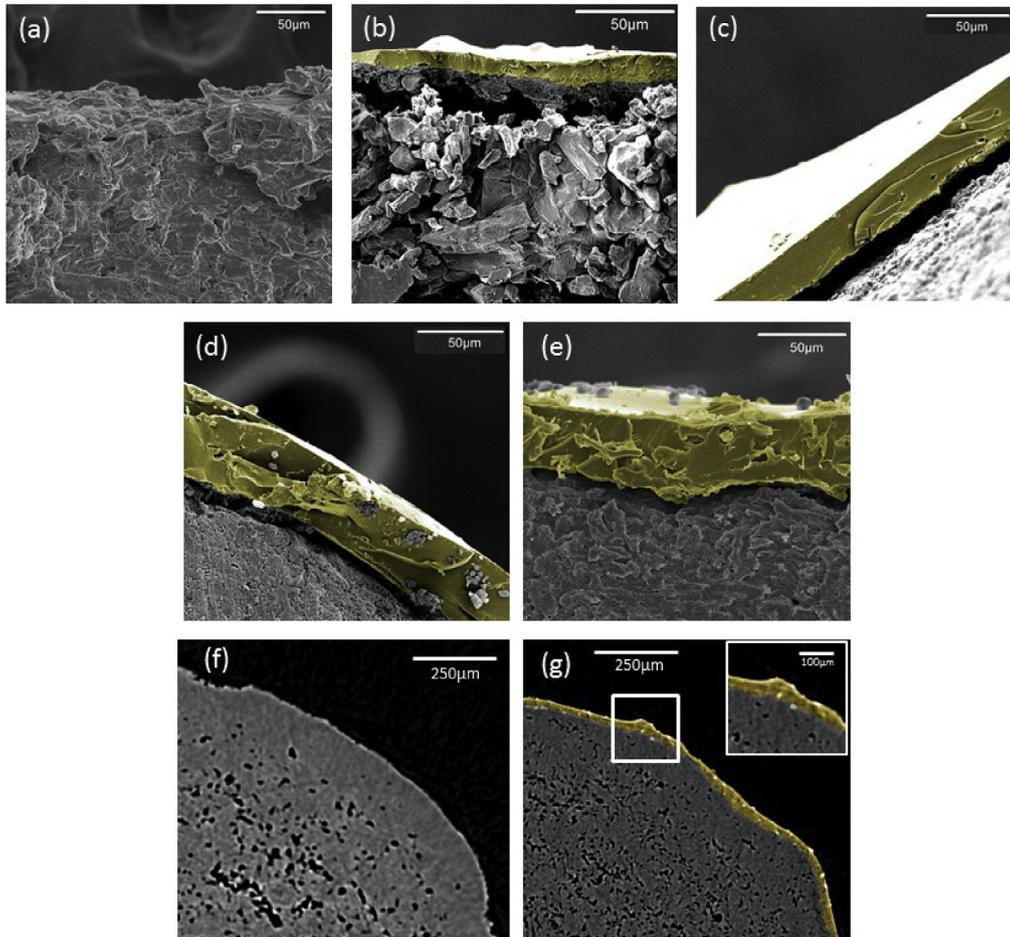
Fig. 2 shows that the polymeric coating exhibits good cohesion and uniformity on the surface of the urea granule. Also, the contact region between the coating and the fertilizer shows good adhesion (or interaction) between the materials. The SEM images (Fig. 2a to e) reveal that the coating has a variable thickness between 25  $\mu\text{m}$  (PCU2% and PCU4%) and 50  $\mu\text{m}$  (PCU6% and PCU8%).

Fig. 3 shows the urea release curves in water for the various PCUs and the uncoated urea. It is evident that the coating thickness

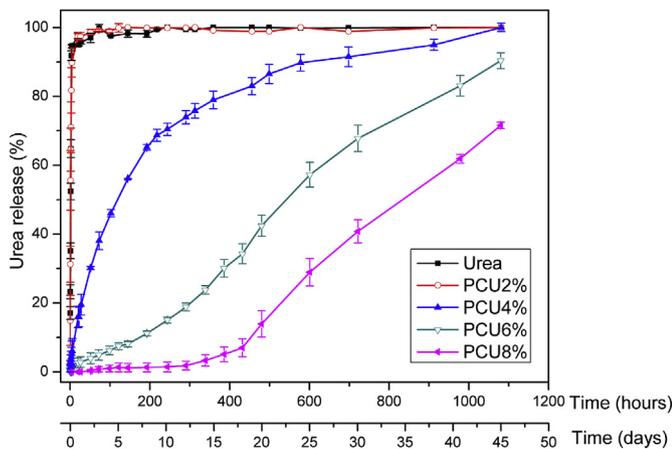
is directly correlated to the release profile (the release rate of the fertilizer) in that there is a positive relationship between coating thickness and urea release times. While materials with thicker coatings released less than 100% of urea after 40 days (e.g. 80% urea released in 42.5 d for PCU6%), urea release for PCU2% was similar to that for uncoated urea, reaching ~90% release in less than 2 days. This indicates that a thin polymer coating is deficient, resulting in poor controlled release performance.

Under field conditions, temporal  $\text{N}_2\text{O}$  emissions patterns, shown in Fig. 4, were also impacted by the thickness of the polyurethane coating. Higher  $\text{N}_2\text{O}$  emissions were observed for U, PCU2% and PCU4% compared to the other materials soon after the application of the fertilizers in the soil (0–~40 days after planting). For example,  $\text{N}_2\text{O}$  emissions from 8 to 18 d after fertilizer materials were applied (18–28 July) were  $680 \pm 101$ ;  $620 \pm 78$  and  $466 \pm 44 \text{ g ha}^{-1}$ , respectively, for U, PCU2% and PCU4% (Table 2). Nitrous oxide emissions in the PCU6% and PCU8% treatments were substantially lower ( $266 \pm 61$  and  $177 \pm 8 \text{ g ha}^{-1}$ , respectively; Table 2) and not different than the two control treatments (SC and V6, Table 2 and Fig. 4).

Since soil moisture patterns were very similar among all treatments, we present mean values for all plots in Fig. 5. Figs. 4 and 5 together clearly illustrate that highest  $\text{N}_2\text{O}$  emissions coincide with periods of high soil moisture during the early maize growing season (i.e. following rainfall events).  $\text{N}_2\text{O}$  is produced by both nitrifying and denitrifying bacteria under low oxygen conditions (Davidson et al., 1991), which occur during periods with high soil moisture because the rate of oxygen consumption by soil organisms is greater than the rate of oxygen diffusion into soil from the atmosphere (Davidson et al., 1991). However, it is also evident from Figs. 4 and 5 that soil moisture alone is not a sufficient condition leading to  $\text{N}_2\text{O}$  emissions as emissions are very low in all treatments (except V6) between 45 and 75 days after planting, when soil moisture was relatively high on numerous occasions. Both nitrifying and denitrifying bacteria also require the presence of N substrates —  $\text{NH}_4^+$  for nitrification and  $\text{NO}_3^-$  for denitrification (Davidson et al., 1991). Conditions of low soil oxygen and high mineral N occurred in the Urea, PCU2% and PCU4% treatments during the early growing season. However, maize N uptake rates increase considerably about 30 days after planting (Hanway, 1966) such that soil mineral N is usually very low for a number of months, which results in low  $\text{N}_2\text{O}$  emissions regardless of soil moisture



**Fig. 2.** SEM images of (a) uncoated urea and (b–e) the interface between urea and castor oil polyurethane at 2, 4, 6, or 8 wt%, respectively. In addition, microtomography image of (f) an uncoated urea granule and (g) a urea granule coated with 8 wt% polyurethane, which is highlighted in yellow. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



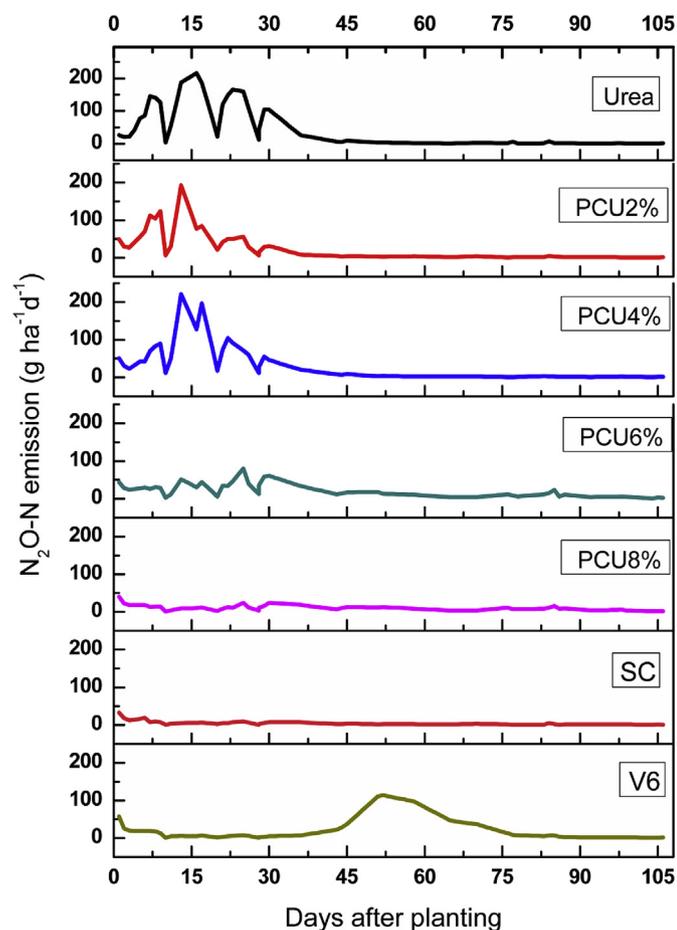
**Fig. 3.** Average curves of urea release in a water immersion. Vertical bars are standard deviations.

conditions. The V6 treatment, however, shows a substantially different N<sub>2</sub>O emission pattern with no substantial peaks until the relatively wet period beginning 01 September when mineral N would have been substantially greater than in the other treatments since urea in this treatment was applied on 17 August. Although sidedressing is a strategy to increase temporal synchrony between

N application timing and crop N uptake, N<sub>2</sub>O emissions can still occur when soils are wetted soon after urea application when much of the mineral N released from urea is not yet taken up by the crop. In general, it is interesting to note that high N<sub>2</sub>O emissions continued after each wetting event in almost all treatments even as soil moisture declined rapidly in this sandy soil. The reason for this pattern is unclear.

To compare N<sub>2</sub>O emissions results statistically, we divided the 106 d experimental period into six time periods defined by both soil moisture and N<sub>2</sub>O emissions patterns, as illustrated in Fig. 5 and defined in Table 2. Days that represent the beginning and end of each period had low soil moisture and N<sub>2</sub>O emissions. Table 2 shows that during both the first and second periods N<sub>2</sub>O emissions were greatest in the Urea, PCU2% and PCU4% treatments, intermediate in the PCU6% treatment and lowest in the PCU8%, SC and V6 treatments. These results reflect patterns described above in that the materials with the fastest urea release rates produced the most N<sub>2</sub>O early in the season, suggesting that N release occurred before maize N uptake was substantial. The more thinly coated urea products (PCU2%, PCU4%) did, however, have significantly or near significantly lower N<sub>2</sub>O emissions than uncoated urea during the third time period.

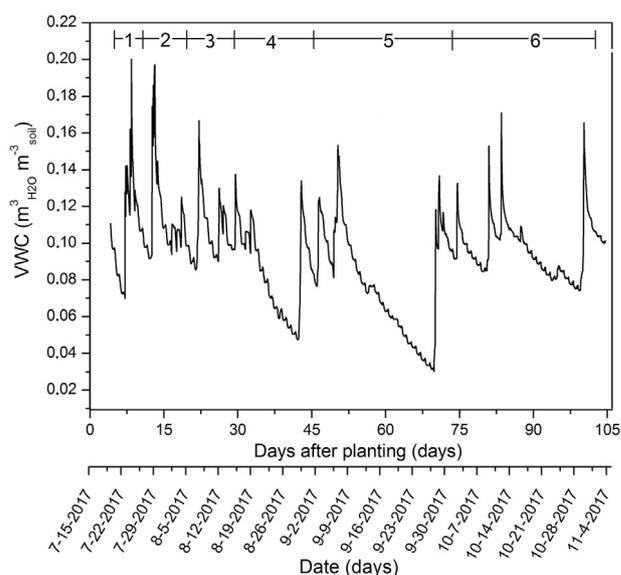
N<sub>2</sub>O emissions in the PCU6% and PCU8% treatments were substantially lower than for Urea through the third sampling period, suggesting that N release was substantially reduced prior to maize taking up substantial N. N<sub>2</sub>O emissions for PCU6% were similar to



**Fig. 4.** N<sub>2</sub>O emissions from soil planted to maize and fertilized at planting with urea, urea coated with polymer at 2, 4, 6, or 8 wt% (PCU2% to PCU8%), a soil control (SC) treatment with no fertilizer applied, and a treatment in which urea was applied at sidedressing when the maize was at the V6 growth stage (V6). N application rate was 160 kg N ha<sup>-1</sup> for all but the SC treatment.

that for Urea during period 4 and N<sub>2</sub>O emissions were greater for both PCU6% and PCU8% than all treatments other than V6 during periods 5 and 6; however, absolute values of emissions during these two periods were relatively low.

Cumulative N<sub>2</sub>O emissions during the maize growing season show a general pattern of reduced N<sub>2</sub>O emissions with increasing thickness of the polyurethane coating. Emissions for PCU2% and PCU6% were reduced by almost 50% while emissions for PCU8% were reduced by about 70% compared to uncoated urea. The N<sub>2</sub>O



**Fig. 5.** Mean volumetric water content (m<sup>3</sup><sub>H<sub>2</sub>O</sub> m<sup>-3</sup><sub>soil</sub>) for all plots measured during the experiment. Numerical values above the soil moisture curves indicate six different time periods during which N<sub>2</sub>O emissions data were summed to facilitate statistical comparisons, as presented in Table 2.

emission factor (EF) for Urea, which was calculated after subtracting N<sub>2</sub>O–N emissions from the SC treatment from all other treatments was 2.2, indicating that 2.2% of the N applied in the fertilizer was emitted as N<sub>2</sub>O–N. This is an EF twice as high as that suggested by the Intergovernmental Panel on Climate Change (IPCC) for N fertilizers but within the IPCC uncertainty range of 0.3–3% (Eggleston et al., 2006). PCU2% and PCU6% reduced the EF by about half while PCU4% reduced the EF by only 29%. PCU8%, however, reduced the EF by 82%. Thus, all PCU products except PCU4% reduced the N<sub>2</sub>O EF by more than the V6 treatment, which reduced the EF by 35%. These results are consistent with the water release curves presented earlier in that a thicker coating resulted in slower release of urea which would limit excess soil mineral N and thereby decrease transformation to N<sub>2</sub>O. The incongruous results for PCU4% might reflect an artifact created during the coating process; nonetheless, the overall impact of coating thickness delaying and reducing N<sub>2</sub>O emissions is consistent.

While these PCU materials, particularly PCU8%, were very effective at reducing soil N<sub>2</sub>O emissions, this is a benefit only if they are also effective N fertilizers. Our maize yield, N uptake and N recovery data show that all four PCU products were as effective as Urea in supplying N. Mean maize grain yield, N uptake and N

**Table 2**

Cumulative soil N<sub>2</sub>O emissions over six sampling periods (see Fig. 5) for a field planted to maize and fertilized with urea and urea coated with polymers<sup>a</sup>.

Sampling time period	Dates	N <sub>2</sub> O–N emissions (g ha <sup>-1</sup> )						
		Urea	PCU2%	PCU4%	PCU6%	PCU8%	SC <sup>b</sup>	V6 <sup>c</sup>
1	18 July - 28 July	680 a <sup>d</sup>	620 a	466 ab	266 bc	177 d	142 d	222 cd
2	28 July - 07 Aug	1402 a	900 a	1323 a	308 b	76 c	50 c	51 c
3	07 Aug - 15 Aug	1003 a	343 b	575 ab	376 b	108 d	52 e	45 e
4	15 Aug - 01 Sept	682 a	213 cd	380 ac	528 ab	233 bc	84 e	97 de
5	01 Sept - 04 Oct	165 c	127 c	156 c	410 b	316 b	93 c	2175 a
6	04 Oct - 03 Nov	54 c	52 b	54 b	208 a	177 a	48 b	106 a
Cumulative	106 d	3986 a	2254 b	2954 ab	2096 b	1087 c	469 d	2696 ab

<sup>a</sup> PCU2% to PCU8% indicates polymer concentration at 2, 4, 6, or 8 wt%.

<sup>b</sup> SC is the control with no fertilizer applied.

<sup>c</sup> V6 is urea applied at sidedressing when the maize was at the V6 growth stage.

<sup>d</sup> Values followed by the same letter within a row are not statistically different at P = 0.05.

**Table 3**

Maize N uptake and recovery, maize grain yield and N<sub>2</sub>O emissions factor following maize harvest in a field fertilized at maize planting with urea and urea coated with polymers<sup>a</sup>.

Treatment	N uptake (kg N ha <sup>-1</sup> )	N recovery (%)	Maize grain yield (Mg ha <sup>-1</sup> )	Cum. N <sub>2</sub> O–N (g ha <sup>-1</sup> )/Grain yield (kg ha <sup>-1</sup> )
Urea	139 ± 19 a <sup>b</sup>	52.8 ± 12.3 ns	8.52 ± 0.92 a	0.47 ± 0.15 a
PCU2%	135 ± 11 a	50.1 ± 6.9 ns	8.54 ± 0.49 a	0.26 ± 0.04 ab
PCU4%	145 ± 15 a	56.3 ± 9.5 ns	8.79 ± 0.90 a	0.34 ± 0.07 ab
PCU6%	155 ± 14 a	62.7 ± 9.2 ns	8.90 ± 0.93 a	0.24 ± 0.05 bc
PCU8%	148 ± 12 a	58.7 ± 7.5 ns	8.21 ± 0.72 a	0.14 ± 0.04 c
SC	66 ± 4 b	–	3.89 ± 0.46 b	0.13 ± 0.03 c
V6	133 ± 33 a	49.2 ± 20.7 ns	6.56 ± 0.62 ab	0.42 ± 0.08 ab

<sup>a</sup> Treatment designations as in Table 2.

<sup>b</sup> Values followed by the same letter within a column are not statistically different at P = 0.05.

recovery were the same for all PCU materials as for Urea (Table 3). This indicates that the slower release of N from the coated ureas compared to uncoated urea suggested by the N<sub>2</sub>O data did not hamper N uptake by maize, i.e. the N release by these materials was at least as synchronous with maize N uptake as urea. The substantially reduced N<sub>2</sub>O emissions and similar maize performance for PCU8% treatment indicate substantially improved synchrony between N release and maize N uptake. This relationship can be quantified by expressing N<sub>2</sub>O emission relative to grain yield as presented in Table 3. While Urea produced almost 0.5 g N<sub>2</sub>O–N per kg maize grain yield, PCU6% and PCU8% reduced this value by about 50% and 70%, respectively. The value for PCU8% was no different than that for the SC treatment, indicating that its N<sub>2</sub>O emission from fertilizer is probably negligible. The PCU2%, PCU4% and V6 treatments were not significantly different than the Urea treatment, but the lower values suggest a trend confirmed by PCU6% and PCU8%.

Although sidedress N application can improve maize N use efficiency (Keeney, 1982) and reduce the production of N<sub>2</sub>O per kg of grain, according to an hierarchical model meta-analysis of studies comparing sidedress and preplant application of nitrogen fertilizers (Eagle et al., 2017), we did not find this to be the case. Other individual studies have also shown no consistent effect of sidedressing N on N<sub>2</sub>O emissions (Phillips et al., 2009; Zebarth et al., 2008). In our study, the use of coated fertilizers outperformed sidedressing urea, providing an alternative management option that could eliminate the need for two N applications in one year for maize, thereby reducing fuel use and farmer labor. However, these results, from a year with relatively high precipitation, need to be corroborated with data collected during additional years.

One concern about slow release fertilizers is that N release might occur after N uptake by the cash crop, thus leading to potential N losses after the maize growing season. To test the availability of soil N after maize harvest and into the spring of 2018, we planted rye after maize harvest to assess soil N availability. Biomass of rye + weeds was lowest in SC and similar in all other treatments except PCU8%, which had at least 40% more biomass than the other treatments (data not shown). Nitrogen uptake by rye + weeds, however, showed no statistical differences among any treatments. These results suggest that N availability was similar in all treatments after the maize growing season. However, since we were not able to quantify N<sub>2</sub>O emissions during this period, it is uncertain whether any potential delayed release of urea from the coated materials may have contributed to N<sub>2</sub>O emissions during the winter and spring. In addition, an important caveat to our conclusions is that we did not measure NO<sub>3</sub><sup>-</sup>-N leaching in this experiment. It is possible that leaching differed among treatments; that information will provide a more complete picture of the sustainability of these materials. In addition, our promising results indicate a need to broaden the conditions under which these PCUs are tested. Additional work is needed under different soil types, climates and

weather conditions. In addition, since NH<sub>3</sub> volatilization following urea application is not eliminated by subsurface application of urea (Rochette et al., 2013), further studies investigating the effects of these PCUs on ammonia volatilization are warranted.

#### 4. Conclusion

Our results clearly show that these PCU materials can substantially reduce soil N<sub>2</sub>O emissions without impacting maize grain yield, N uptake and N recovery. The importance of these results is reflected in the widespread production of maize, a crop with high N demand. While these results are specific to sandy soils in the mid-Atlantic region of the USA, additional research is needed to test these materials on different soil types and climate regimes and over longer time periods.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jclepro.2019.119329>.

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