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Evaluating novel biodegradable polymer matrix fertilizers for nitrogen-efficient agriculture

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Abstract

Enhanced efficiency fertilizers (EEFs) can reduce nitrogen (N) losses in temperate agriculture but are less effective in the tropics. We aimed to design a new EEF and evaluate their performance in simple-to-complex tests with tropical soils and crops. We melt-extruded urea at different loadings into biodegradable polymer matrix composites using biodegradable polyhydroxyalkanoate (PHA) or polybutylene adipate-*co*-terephthalate (PBAT) polymers with urea distributed throughout the pellet. These contrast with commercially coated EEF that have a polymer-coated urea core. We hypothesized that matrix fertilizers would have an intermediate N release rate compared to fast release from urea or slow release from coated EEF. Nitrogen release rates in water and sand–soil columns confirmed that the matrix fertilizer formulations had a more progressive N release than a coated EEF. A more complex picture emerged from testing sorghum [*Sorghum bicolor* (L.) Moench] grown to maturity in large soil pots, as the different formulations resulted in minor differences in plant N accumulation and grain production. This confirms the need to consider soil interactions, microbial processes, crop physiology, and phenology for evaluating fertilizer performance. Promisingly, crop δ^{15}N signatures emerged as an integrated measure of efficacy, tracking likely N conversions and losses. The three complementary evaluations combine the advantages of standardized high-throughput screening and more resource-intensive and realistic testing in a plant-soil system. We conclude that melt-blended biodegradable polymer matrix fertilizers show promise as EEF because they can be designed toward more abiotically or more microbially driven N release by selecting biopolymer type and N loading rate.

Abbreviations: EEF, enhanced efficiency fertilizer; PBAT, polybutylene adipate-*co*-terephthalate; PHA, polyhydroxyalkanoate.

1 | INTRODUCTION

The sustainable intensification of agriculture is an essential component of the global food security strategy to generate high crop yields with minimum environmental impact (Garnett et al., 2013; United Nations, 2015). Future food systems need to conserve or improve soil health and fertility, which is underpinned by efficient nutrient management to minimize nutrient losses from soil that cause off-site pollution (Foley et al., 2011; Steffen et al., 2015; United Nations, 2019). Nitrogen (N) is in the spotlight as N losses from soils cause profound environmental problems, with a roadmap proposed to improve the efficiency of N use in cropping (Udvardi et al., 2021). In the tropics, soil and climate conditions exacerbate the challenge of efficient fertilizer use, as soils can be highly weathered and fertilizer nutrients are less well retained (Baligar & Bennett, 1986), warm temperatures accelerate the loss of soil organic matter and microbial nutrient conversions (Stanford et al., 1973), and high-intensity rainfall events force nutrient losses from soil (Bouwman, 1998; Seyfried & Rao, 1987).

There is consensus on the need for improved fertilizer formulations and delivery methods that synchronize nutrient release with crop nutrient demand (Bindraban et al., 2020; Chen et al., 2006; Snyder, 2017; Timilsena et al., 2015). This has stimulated efforts to develop enhanced efficiency fertilizers (EEFs) (Trenkel, 2010) that primarily center on three modes of action: (i) stabilized soluble fertilizers that contain N transformation inhibitors (e.g., urease and nitrification inhibitors) (Vilas et al., 2019), (ii) coated fertilizers (e.g., polyethylene-coated urea) with slow solubilization rates, and (iii) matrix-encapsulated fertilizer formulations with delayed nutrient release that may require microbial degradation (Dimpka et al., 2020). While EEFs offer promise, multiple challenges need to be overcome, including variable efficacy (Li et al., 2018; Snyder, 2017), economic viability (Rose et al., 2018), and undesirable by-products such as microplastics and enzyme inhibitors (Bindraban et al., 2020; Ng et al., 2018).

These challenges could be overcome by selecting appropriate biodegradable polymer-based N formulations that are generated with commercially relevant production techniques (Levett et al., 2019). There is rapid progress in the development of biodegradable polymeric systems for the sustained release of chemicals, peptides, proteins, and enzymes in agricultural applications (Mishra et al., 2019). We focus here on two biodegradable polymers: polyhydroxyalkanoate (PHA) and polybutylene adipate-*co*-terephthalate (PBAT). PHAs are a family of fully biodegradable polymers that bacteria naturally synthesize and metabolize. PHAs can serve as a matrix or as a coating for slow-release agrichemical formulations, including urea fertilizers (Costa et al., 2013; Harmaen et al., 2016; Volova et al., 2016). Offering a different suite of mechanical and thermal properties, PBAT is a polymer derived from petrochemicals that has relatively good biodegradability and potential for blending (Jian et al., 2020).

Core Ideas

- Polymer matrix fertilizers are novel slow-release fertilizers.
- Polymer matrix fertilizers release N via multiple routes, including biodegradation.
- Short-term N release rates were intermediate compared to polymer-coated or pure urea.
- N release and plant availability were modulated by soil and microbe interactions.
- δ^{15}N emerged as a signal integrating N release and plant bioavailability.

Matrix-based formulations are produced via a range of processes including cold-pressing pellets, solvent casting of films and granules, and polymer-coating of pellets. Despite rapid progress in material development, there has been limited systematic evaluation of matrix-encapsulated fertilizer formulations in realistic broad-acre or horticultural production environments. This is unsurprising because the interactions between crop N uptake, climatic factors, and N transformation processes and loss pathways, combined with diverse fertilizer N release mechanisms, complicate the systematic evaluation of fertilizer formulations. Effective evaluation of novel fertilizer formulations throughout the design phase requires complementary approaches, from initially screening many formulations in high-throughput controlled settings to evaluating selected formulations over several cropping seasons in agronomically relevant situations that, ideally, also track the N inputs and losses. The many factors that impact fertilizer performance include microbial degradation of fertilizer formulations, which depends on microbial community composition and activity, overall nutrient availability, and the material properties of the formulations. Any screening process must therefore be sensitive to these parameters and encompass the intricate interactions of N release from biodegradable matrix formulations that are influenced by soil type, water content, temperature, the rate of microbial degradation, interaction of the released N with soil physical and chemical properties, as well as the speed and timing of crop N uptake (Fan & Li, 2010; Nardi et al., 2018). Test systems have inherent benefits and drawbacks. For example, testing at high temperatures allows faster evaluation of formulations (Carson et al., 2014), but may be unrealistic for assessing sensitive microbiological processes. We chose a multi-stage process to (i) advance matrix-based EEF as a potential alternative to existing fertilizers, (ii) evaluate the strengths and limitations of different test systems, and (iii) consider future avenues for EEF design and efficient N use in tropical cropping systems.

To address the aims, we designed and manufactured novel EEF with urea encapsulated in a matrix of PHA or PBAT using extrusion processing at relatively high urea loadings in line with commercial EEF applications. Nitrogen release from these formulations was compared to commercial water-soluble pelleted urea and polymer-coated commercial urea fertilizer in systems of increasing complexity: (1) short-term (hours) release in water, (2) medium-term (days) mobilization and leaching from sand:soil columns, and (3) longer term (months) growth of sorghum [*Sorghum bicolor* (L.) Moench] plants to grain maturity in a glasshouse.

2 | MATERIALS AND METHODS

2.1 | Production of novel polymer matrix fertilizers

Two polymers were used to manufacture three novel composite urea fertilizers. PHA (poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate)) with 1 mol% 3HV content and weight-average molecular weight ($\overline{M_w}$) of 590 kDa was supplied by TianAn Biopolymer under the trade name ofENMAT Y1000. PBAT was supplied by BASF under the trade name of Ecoflex FBX 7011, with a weight-average molecular weight ($\overline{M_w}$) of 142 kDa. The polymers and urea (Chemsupply) were dried overnight at 60°C prior to extrusion. All extrusion material was produced at a rate of 15 g min^{-1}. For PBAT, pellets of polymer and urea were added to create two formulations comprising 20 and 37.5 wt.% urea, respectively. PHA–urea was similarly produced, except PHA was added as a powder to produce 15 wt.% urea. The extruded material was cut into ∼3-mm-sized pellets using a strand pelletizer. Approximately 3 kg of each material was produced for testing. Urea pellets (∼3 mm, Chemsupply) and a commercially available polymer-coated product Agromaster (3-month release period, 3–4 mm, ICL Speciality Fertilizers) were used as control and reference materials, respectively.

The N contents of fertilizer samples were analyzed (CNS 928 elemental analyzer, LECO) at the start, middle, and end of the production process for each formulation. We detected no differences in N contents across the production run, and all material was pooled for later use. Measured N contents were converted into the percentage of urea and the formulations referred according to their urea content, namely, PHA 12% urea (PHA12), PBAT 20% urea (PBAT20), and PBAT 33% urea (PBAT33).

2.2 | Screening nitrogen release in water

Three pellets of each formulation were immersed in 50 mL of Milli-Q water in a 100-mL screw-top plastic vial, and 5 mL samples were withdrawn at time intervals of 0, 0.083, 0.25, 0.5, 1, 2, 4, 8, 24, and 48 h. The system was homogenized with gentle manual agitation prior to sampling, and the volume was kept constant by adding 5 mL of Milli-Q water immediately after sampling. The containers were closed after each sample was taken to avoid evaporation loss. Each experiment was performed in triplicate. Concentrations of urea, ammonium (NH_4^+), nitrate (NO_3^-), and nitrite (NO_2^-) were determined with colorimetric assays (Greenan et al., 1995; Kempers, 1974; Miranda et al., 2001) measured with a microplate reader (Omega, BMG Labtech), and the cumulative grams of N released were calculated. The released urea was reported in percentage N released based on the theoretical total mass of urea in the three pellets that were analyzed. No conversion of urea into NH_4^+, NO_3^-, or NO_2^- was detected.

2.3 | Leached sand–soil column nitrogen release

Microcosms were made from 50-mL centrifuge tubes, with an open top (27 mm internal diameter) and open base (21 mm internal diameter) inset with two mesh layers, 0.2 mm thick, mesh size 37 μm on top of 1 mm thick, mesh size 1 mm (Inselsbacher et al., 2009). The medium was composed of 4:1 v/v sand (Crystalline Silica, Richgro washed play sand) and 2 mm sieved clay loam dermosol soil (Isbell, 2002). Soil characteristics were as follows: pH ($1{:}5_{H2O}$) 5.9, EC 0.04 dS m^{-1}, CEC 5.3 cmol kg^{-1}, total C 0.5%, NH_4^+–N 1 mg N kg^{-1}, NO_3^-–N 2 mg N kg^{-1}, P Colwell 12 mg kg^{-1}, K 0.07 cmol kg^{-1}, Mg 1.1 cmol kg^{-1}, and Ca 3.9 cmol kg^{-1}. The sand–soil medium (50 g) was added to achieve a bulk density of 1.15 g cm^{-3}. Microcosms were irrigated with artificial soil solution (Cornelis et al., 2012; 6 mM $MgSO_4$, 6 mM $CaCl_2$, and 5 mM K_2SO_4) to 0.4 m^3 m^{-3} water-filled pore space and kept at 22°C for 3 days. Following the 3-day incubation, microcosms were flushed with 30 mL of soil solution, left for 24 h, before two pellets of fertilizer formulations were buried at 2-cm depth. Average N loads with the addition of two pellets for each treatment were as follows: control (0 mg N), PHA12 (3 mg N), PBAT20 (7 mg N), PBAT33 (8.5 mg N), urea (28 mg N), and commercially coated EEF Agromaster (31 mg N).

Six replicate microcosms for each fertilizer formulation were arranged in a blocked design. For the duration of the incubation, microcosms were kept at 22°C and water content maintained at 0.4 m^3 m^{-3} water-filled pore space by irrigating with distilled water to weight every second day. Microcosms were flushed with 25 mL soil solution (∼1.25 times pore volume) at intervals (1, 3, 8, 11, 21, and 50 days after fertilizer application). Leachate was collected, and the volume was quantified. Concentrations of urea, NH_4^+, NO_3^-, and NO_2^- were determined with colorimetric assays (Greenan et al., 1995; Kempers, 1974; Miranda et al., 2001). The soluble N

in the leachate with no fertilizer addition was 0.01–0.03 mg N and was subtracted to calculate soluble N released from fertilizer formulations for each leaching event.

2.4 | Sorghum grown with fertilizer formulations

The sorghum experiment was conducted at The Environmental Research Complex (James Cook University, Cairns, Australia) from December 2019 to May 2020, and comprised 72 × 20-L pots with one sorghum plant per pot (HAT 150843 sorghum seeds; Pacific Seeds). Sorghum was chosen as a model species to evaluate impacts of varied N supply as it is a commonly grown tropical crop with a growth period of 115–140 days with increasing N demand ~20 days after sowing (van Oosterum et al., 2010). Pots were filled with 18.5 kg air-dried clay loam soil (as used in 2.3 sand:soil columns) mixed with 20% perlite to facilitate draining. Fertilizer treatments included no fertilizer addition (control), PHA12, PBAT20, PBAT33, Agromaster, and urea. Two grams of N (~150–1200 pellets) were added per pot at the time of seed sowing, corresponding to 100 kg N ha^{-1}. The soil was wetted to 70% gravimetric field capacity and maintained near this target throughout the experiment.

Treatments were randomly located within a glasshouse that tracked outside air temperature. There was a reflective shade cloth under the glasshouse roof that reduced incoming solar radiation by 50% and spread transmitted light more evenly throughout the glasshouse. Average air temperature and relative humidity inside the glasshouse over the course of the experiment were 25.6°C and 87.6%, respectively.

To measure the potential for N losses due to leaching from the fertilized soils, half the pots (36) were randomly selected for the leaching treatment. Leaching events were administered 1, 3, and 14 weeks after sowing. In each leaching event, 10.5 L (~1.5 times pore volume) of tap water was added to each pot. Leachate was collected from each pot and 200 mL subsampled from the total volume when drainage was complete. The subsample was frozen (−20°C) and submitted for analysis of dissolved NH_4^+, total Kjeldahl N, NO_3^-, and NO_2^- (SGS Australia). Organic N (including urea) was calculated from Kjeldahl N minus NH_4^+.

Plant physiological parameters, chlorophyll concentration (μmol m^{-2}), and stomatal conductance (mol H_2O m^{-2} s^{-1}), were measured on the youngest fully expanded leaf multiple times throughout the experiment. Chlorophyll concentration was measured on days 59 and 86 after sowing with a chlorophyll meter (Apogee Instruments), and stomatal conductance was measured on days 59, 62, 83, 84, and 85 after sowing using a porometer (SC-1 Leaf Porometer; Decagon Devices). Plants were grown until grain reached physiological maturity between 93 and 139 days after sowing. When this growth stage was achieved, above-ground dimensions (height and diameter) were measured, and plants were destructively harvested. Above-ground plant biomass was removed, and roots were extracted carefully from pots under running water after submerging each pot with soil in a larger water container overnight. Leaves, stems, grains, and roots were weighed after oven drying at 60°C for 3 days. The youngest, fully expanded leaf from each plant was ground to a fine powder for elemental and isotopic analyses. Foliar dry matter and fertilizer formulations were analyzed at the Advanced Analytical Centre (JCU) for natural abundance stable isotopes of carbon ($\delta^{13}C$), nitrogen ($\delta^{15}N$), and total C and N with a Costech Elemental Analyser coupled via a ConFloIV interface to a ThermoFinnigan Delta V PLUS Continuous-Flow Isotope Ratio Mass Spectrometer (ThermoFischer, Scientific). To estimate whole-plant N contents at harvest, N concentrations in the dry mass of all plant components (leaves, stems, grains, and roots) of the third largest plant from each treatment were analyzed. We used multiple regression to develop a predictive model of whole-plant N content for this subset of the experimental plants from N concentrations measured in the youngest, fully expanded leaf and the total plant dry mass. The fitted regression equation was whole-plant N (g) = 0.0066 × DM + 0.4194 × %N − 0.4153, where DM is whole-plant dry mass (g) and %N is percentage of N in the young, expanded leaf. Plotting the observed versus predicted values for the equation gave $R^2 = 0.95$. Plant leaf $\delta^{15}N$ was compared between treatments after subtracting the major N source $\delta^{15}N$, for the control soil and the fertilizer formulations. Measured $\delta^{15}N$ of soil and fertilizers were soil 6.3‰, PHA12 −1.9‰, PBAT20 −1.9‰, PBAT33 −2.1‰, urea −0.7‰, Agromaster −0.2‰.

Parameters were compared between treatments using two-way analysis of variance (ANOVA) and post-hoc Tukey tests, with fertilizer type and leaching as factors. Data were transformed to meet ANOVA assumptions where required. Statistical analyses were performed in Statistica (Statistica version 13, TIBCO Software Inc.) and R using the FactoMineR package.

3 | RESULTS AND DISCUSSION

3.1 | Nitrogen release in water and sand:soil columns

The five urea formulations displayed contrasting N release rates in water (Figure 1A). Full N release from conventional urea occurred within hours, while Agromaster and PHA12 released 10% and 12% of urea after 24 h, respectively. Intermediate N release profiles occurred with PBAT20 (20% urea released after 24 h) and PBAT33 (80% urea released after 24 h) compared to commercial urea or coated urea.

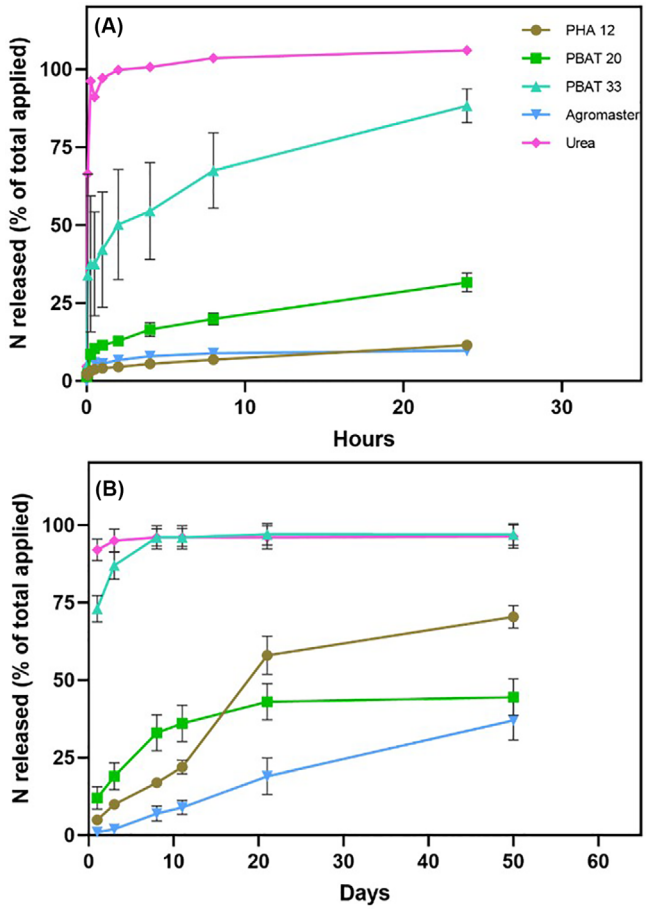

FIGURE 1 Nitrogen released (percentage of total N applied) from fertilizer formulations (polyhydroxyalkanoate [PHA 12], polybutylene adipate-co-terephthalate [PBAT 20], PBAT 33, Agromaster, urea) in water ($n = 3$) (A) and leached sand–soil columns ($n = 6$) (B). Data are averages with error bars indicating 95% confidence intervals.

Nitrogen release was more rapid from the composite with a higher N loading (PBAT33) compared to those with lower loadings (PBAT20, PHA12), consistent with previous controlled release studies from extruded biopolymer/active agent materials (Levett et al., 2020). This is due to more urea being exposed at the pellet surface and thus available for immediate dissolution, as well as the dissolution of soluble additives in the bulk of the pellets through co-continuous pathways and cracks from local stresses (Levett et al., 2021).

To further evaluate mechanisms of N release, we measured N losses from leaching columns with inert silica sand and microbially active soil maintained at water contents within the predicted range for maximum carbon and N mineralization rates (Franzluebbers, 1999). Nitrogen leached after 24 h in the first leaching event was strongly related to the N release in water after 24 h (sand:soil N release = 0.94 × water release − 10, $R^2 = 0.98$, $p < 0.0005$). The N release rates from the fertilizer formulations in sand–soil columns were slower and required between 3 and 8 days to reach approximately the same proportional N release as observed in water (Figure 1B). While urea released N within a day, PBAT33 released ~100% only at the second leaching event on day 3. After 21 days, Agromaster, PHA12, and PBAT20 had released 20%, 30%, and 50% of their N content, respectively. The presence of urea in the leachate of Agromaster after 8 days of incubation contrasts with the minimal presence of urea in the leachate of all other fertilizer types (Figure S1) and is indicative of a so-called "catastrophic release" of polymer-coated fertilizer when the coating bursts (Fertahi et al., 2021). The three main N forms, urea, NH_4^+, and NO_3^- shifted toward NO_3^- over time of incubation, confirming that ammonifying and nitrifying microbes were present in the soil.

The release from PHA12 between days 11 and 21 increased from 20% to 60% N and is consistent with biodegradation of the fertilizer pellets, which allows a greater reservoir of urea to be accessed with pellet attrition (Levett et al., 2019). This was not observed in the other fertilizer formulations and indicates that biodegradation plays a lesser role for N release from PBAT and Agromaster pellets. This is expected as PHA has a higher microbial degradability than PBAT (Muller et al., 2001). Further, we expect biodegradation of PHA to be faster in more microbially active soil (Boyandin et al., 2013; Levett et al., 2019) than the sand-dominated matrix used here. PBAT can be degraded by bacterial and fungal serine hydrolases (Perz et al., 2016), and it is possible that biodegradability of PBAT would be accelerated in soil with greater microbial activity.

The pronounced difference between PBAT formulations with 33% and 20% urea demonstrates that a larger ratio of polymer to urea alters N release. This is promising as it provides flexibility for the design of fertilizers with different N release patterns, oriented toward more immediate dissolution in the soil solution or, on the other hand, a slower N release via microbial degradation. We did not analyze the microbial communities associated with each of the N formations, but the presence of bioavailable carbon in the polymers would attract microbes and increase their activity (Redding et al., 2022). For example, supplying biochar-urea formulations stimulated the bacterial activity compared to pure urea, especially the growth of nitrifying copiotrophic Proteobacteria, while denitrifier activity decreased, benefiting N efficiency and yield of rapeseed grown in pots (Liao et al., 2020). The biodegradation of polymer matrix EEF and associated N transformations in the soil-plant interface will impact EEF performance, including the dynamics of rhizosphere microbial communities integral for N relations (Yeoh et al., 2016) and affecting N delivery to crops. A further consideration is the environmental impacts of by-products of polymer degradation. While PHA is a naturally occurring bacterial product that produces CO_2 and water in aerobic conditions, PBAT degradation produces terephthalic acid, adipic acid, and butanediol, which alter the chemical properties and microbial community of the local environment

and have been identified as having negative impacts on plant growth (Liu et al., 2022). Hence, PHA is a preferred option for further development due to its renewable source, N release rates, and breakdown intermediates.

3.2 | Nitrogen losses from sorghum grown with the fertilizer formulations

The main N forms, NO_3^-, NH_4^+, and organic N (sum of urea and proteinaceous N) quantified in leachate after three forced leaching events in pot-grown sorghum are presented in Figure 2. Nitrogen losses in tropical systems are often skewed toward the early crop establishment phase when high-intensity rainfall events coincide with a phase of low crop N demand (Robinson et al., 2011). In the pot experiment, the first two leaching events in weeks 1 and 3 during a period of low sorghum N demand (van Oosterom et al., 2010) are representative of this period in tropical crop systems. The third and final leaching event in week 14 coincided with grain filling and maturation and estimated the surplus soluble N in the soil.

In the first leaching event, leachate of the unfertilized control and the fertilized soils contained 300–500 mg NO_3^--N, ~20–30 mg organic N, and <3 mg NH_4^+-N, indicating that considerable NO_3^- was present in the soil at the start of the experiment. Subsequent leaching events had a baseline of ~15–20 mg organic N and negligible amounts of inorganic N released from the unfertilized control. The second leaching event had a larger range of NO_3^- loss in the order PHA12 > PBAT > urea > Agromaster. Like the first leaching event, PHA12 lost more organic N and NH_4^+-N than the other formulation treatments. The final leaching event showed limited inorganic N loss from all soils.

Total N detected in the combined leachates (weeks 1, 3, and 14) ranked N loss via leaching as PHA12 930 mg N > PBAT, urea, and Agromaster 860–530 mg N > unfertilized control 410 mg N (Figure S2). The high N loss from PHA12 was likely caused by microbial N mobilization early in the experiment. Several lines of evidence support this notion. PHA is a readily available carbon source that can stimulate microbial degradation of the pellet. In the short-term (water) test, where microbial degradation would be insignificant, PHA12 had a slow N release comparable to Agromaster. In the medium-term (sand–soil column) test, PHA12 had an intermediate N release between Agromaster and PBAT33. Lastly, previous research detected around a 30-fold increase in nitrous oxide emission and 100-fold increase in carbon dioxide emission from PHA12-fertilized soil compared to urea-fertilized soil after 9 days of incubation (Redding et al., 2022). Together, this points to biodegradation as the primary N release mechanism for PHA12.

Overall, N leaching losses did not differentiate the urea formulations in the same manner as observed in water release and column testing. Because urea and PBAT33 showed fast N release in sand–soil columns, we expected strong N solubilization over the first week and relatively high N levels in the first leachate compared with other formulations. No significant correlations between leaching events or total leachate and sand–soil release were found for any time point. This may be due to the soil's high cation-binding capacity. We calculated that if all urea in the formulations was to be converted to NH_4^+, it would occupy only 14% of the soil binding sites in the pot experiment, compared to 39% and up to 400% of the binding sites for two pellets of PHA12 and Agromaster in the sand–soil column, respectively. This excess in cation binding capacity in the pot experiment could result in a plant-available N store that is protected from leaching and a source for future plant uptake, but also nitrification. Indeed, NO_3^- was the main N form released from pots in line with its high mobility in soil. Field evaluations of EEF in temperate wheat systems have also demonstrated that high availability of ammonium and nitrate in soil also moderates the yield and reduced nitrous oxide emission benefits of polymer-coated urea EEFs (Thilakarathna et al., 2020).

In addition to leaching from pots, gaseous losses could have occurred in the form of ammonia, N_2, and NO_x. We did not directly quantify gaseous losses but instead, aiming to integrate N transformations, determined $\delta^{15}N$ signatures (the natural abundance of stable isotopes ^{15}N and ^{14}N). Nitrogen loss from a system generally causes a relative enrichment of ^{15}N in plant tissues, as loss occurs preferentially from the lighter isotope (^{14}N), with ^{15}N enrichment of the remaining N. The relative accumulation of ^{15}N in systems with greater loss results in a larger difference between the $\delta^{15}N$ of the original N source and the plant (Austin & Vitousek, 1998; Amundson et al., 2003; Handley & Raven, 1992; Högberg, 1997). We compared the differences in foliar $\delta^{15}N$ at harvest and fertilizer $\delta^{15}N$ with N release from sand:soil columns (Figure 3). Pots without leaching showed a nonlinear increase in the difference of $\delta^{15}N$ between plant and fertilizer and N release, and this trend was exacerbated in pots with forced N leaching. Three broad responses were observed: the least difference in $\delta^{15}N$ between plant and N source, indicative of least N lost from pots, occurred in unfertilized control and Agromaster. An increase by ~1 delta unit in leached compared to unleached pots indicates slightly elevated N losses in the former. The foliar signature from PHA12 and PBAT20 had a pronounced ~4–5 and 9–10 increase in delta units in $\delta^{15}N$ in non-leached and leached pots, respectively, indicative of medium and higher N losses from both systems, respectively. The highest increase was observed in PBAT33 and urea, with 6–8 and 8–10 units difference in foliar and fertilizer $\delta^{15}N$ in unleached and leached pots, respectively. Broadly, the three categories match the N release measured in the short to medium term with a low N loss (unfertilized control,

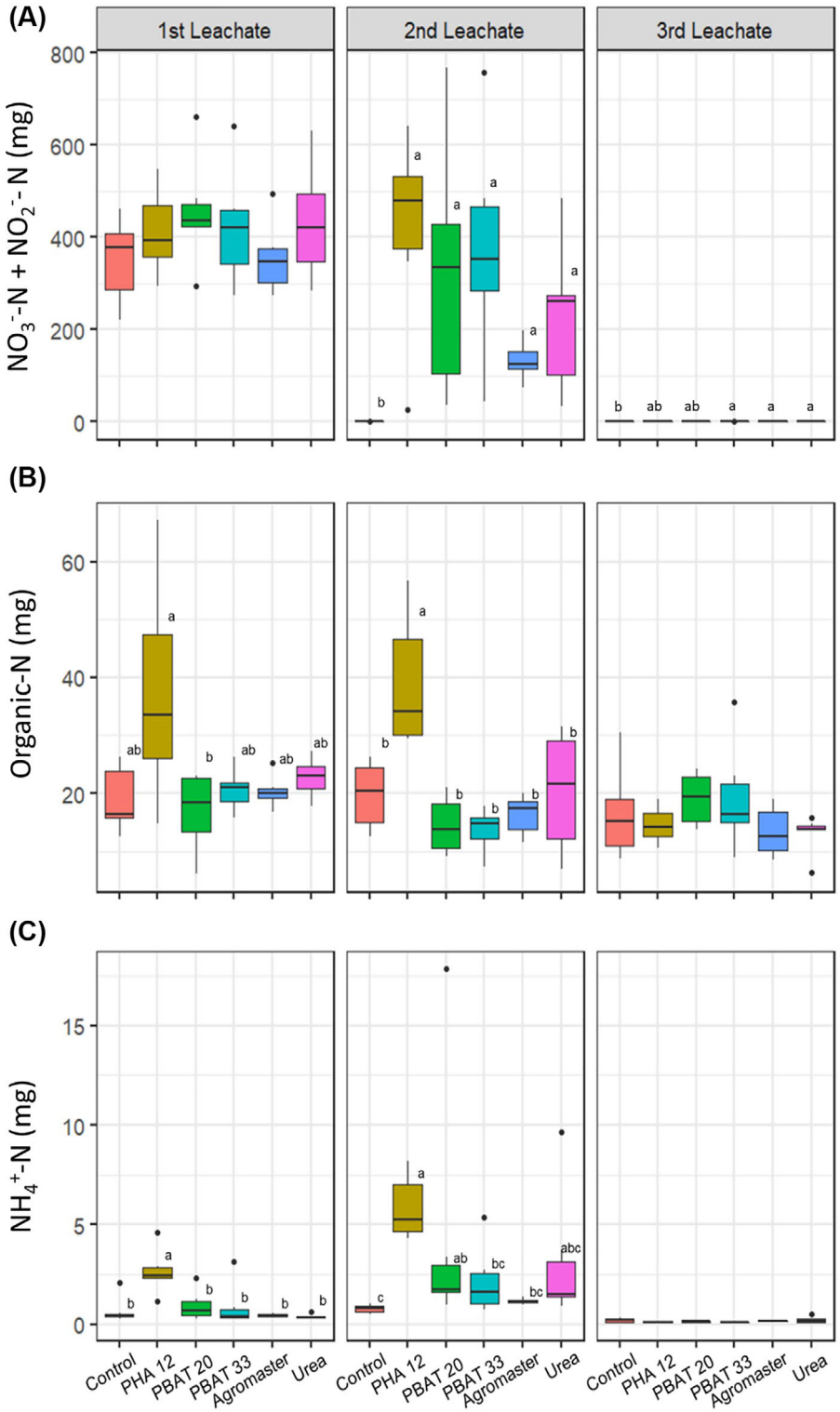

FIGURE 2 Boxplots of NO_3^-/NO_2^--N (A), organic N (B), and NH_4^+-N (C) (mg) in leachate (10.5 L applied) at each of three events (1, 3, and 14 weeks) from pots with sorghum grown with no applied fertilizer (control) and fertilizer formulations polyhydroxyalkanoate [PHA 12], polybutylene adipate-co-terephthalate [PBAT 20], PBAT 33, Agromaster, and urea. Different letters indicate significant differences in leached N forms between fertilizer formulations within each event (Table S1, Tukey's post-hoc $p < 0.05$, $n = 6$).

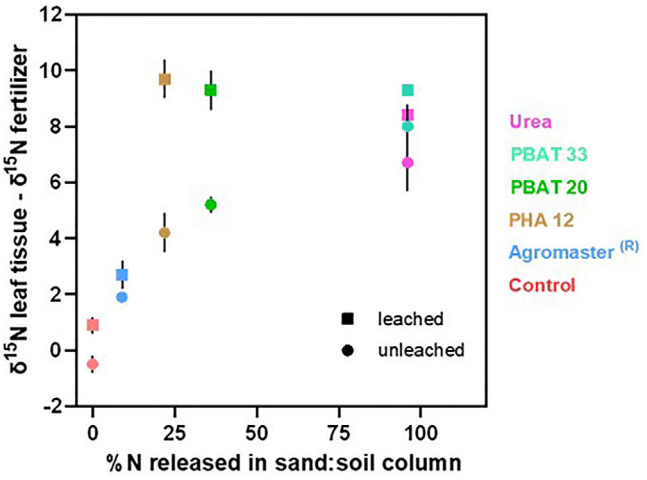

FIGURE 3 The difference between the δ^{15}N of sorghum leaf tissue at harvest (~120 days) and that of the fertilizer at the beginning of the pot trial plotted against the N release rate after 11 days in the sand/soil column experiment. For the control treatment, the δ^{15}N difference was calculated as the difference between plant tissue and the δ^{15}N of the soil. The data represent the average with standard error ($n = 6$).

Agromaster), an intermediate loss (PHA12, PBAT20), and a high loss (PBAT33, urea). We conclude that δ^{15}N has much potential to quantify the efficacy of fertilizers in complex systems, including plants with longer N accumulation phases, integrating the interactions between crop, fertilizer, microbes, and soil. The experimental systems and screening tools presented here can provide information prior to the evaluation of the impact of matrix formulations on major N loss pathways in target production systems. Loss pathways and agronomic efficiency of N fertilizer are dependent on specific site characteristics and environmental and seasonal variation in climate, particularly rainfall. It is essential to evaluate matrix formulations in appropriate contexts given the increasing awareness that management of a loss pathway, for example, leaching, can lead to increases in others, such as nitrous oxide emissions (Preza-Fontes et al., 2023).

3.3 | Sorghum biomass and physiological response to fertilizer N availability

Total plant biomass increased significantly with fertilizer addition with up to three- and sevenfold greater biomass in unleached and leached N treatments, respectively (Figure 4A,B). Plant N accumulation followed a similar trend as biomass allocation (Figure 4C,D), except that a greater relative reduction of plant N accumulation occurred in PHA12-leached pots compared to other fertilized treatments. Compared across all formulations, plant N accumulation was not related to N release at any timepoint in either leached or unleached systems. The response of grain production in response to leaching and fertilizer differed to that of total biomass and N accumulation (Figure 4E,F). The higher grain yield in leached treatments was associated with an additional 15–20 days to reach grain maturity (Figure 4G,H). In unleached pots, we observed contrasting relative grain and biomass responses, with PBAT33 producing the lowest grain yield of all fertilized treatments (Figure 4E). Overall, this indicates that residual soil NO_3^- present in the early part of the experiment combined with different N availability of the fertilizer formulations impacts plant physiology and yield. It is known that the temporal aspect of N supply impacts plant phenology. For example, removing N limitation pre-anthesis in sorghum plants recovered grain yield with increased grain size rather than grain number (Worland et al., 2017). Thus, the response of all yield components (grain number, grain size, grain quality, and protein content) should be considered in the evaluation of N fertilizer formulations. The specificity of the fertilizer response by different plant species and the significance of the plant organ comprising yield are illustrated by the different responses of pak choi and sorghum, where pak choi biomass increased when grown with PBAT33 compared to urea (Redding et al., 2022).

Physiological plant traits are influenced by N supply, including biomass allocation to different plant parts, leaf N content, leaf stomatal conductance, and chlorophyll content (Sinclair & Vadaz, 2002). We aimed to distinguish the responses of sorghum to the different fertilizers to help identify useful screening tools for evaluating fertilizer N release and availability. We used principal component analysis to assess plant trait responses to fertilizer formulations in unleached and leached systems. The first three dimensions explained 67% and 65% of the total variation in the unleached and leached environments (Figure 5, Tables S3 and S4). The greatest differences in fertilizer treatments occurred in the unleached system (Figure 5A), where the first and second dimensions are compared; here, Agromaster is separated from the other fertilizers and positively correlated with leaf N and chlorophyll content and negatively correlated with the δ^{15}N signature (Figure 5A, Table S3). These strong positive correlations between leaf N and chlorophyll content and their negative correlation with δ^{15}N show that in the unleached system, N losses from fertilizer influenced leaf N status but were not correlated with other plant traits. The leached system showed less separation of the fertilizers based on the plant trait response, despite between 540 and 930 mg N removed from the system through leaching. The low loading of δ^{15}N in the leached system and non-correlation of leaf chlorophyll measurements at days 59 and 86 indicate that the rapid loss of N due to leaching has influenced plant N uptake and allocation. Together, this further highlights the impact of timing of leaching events relative to the N release from fertilizer formulations and measured plant traits.

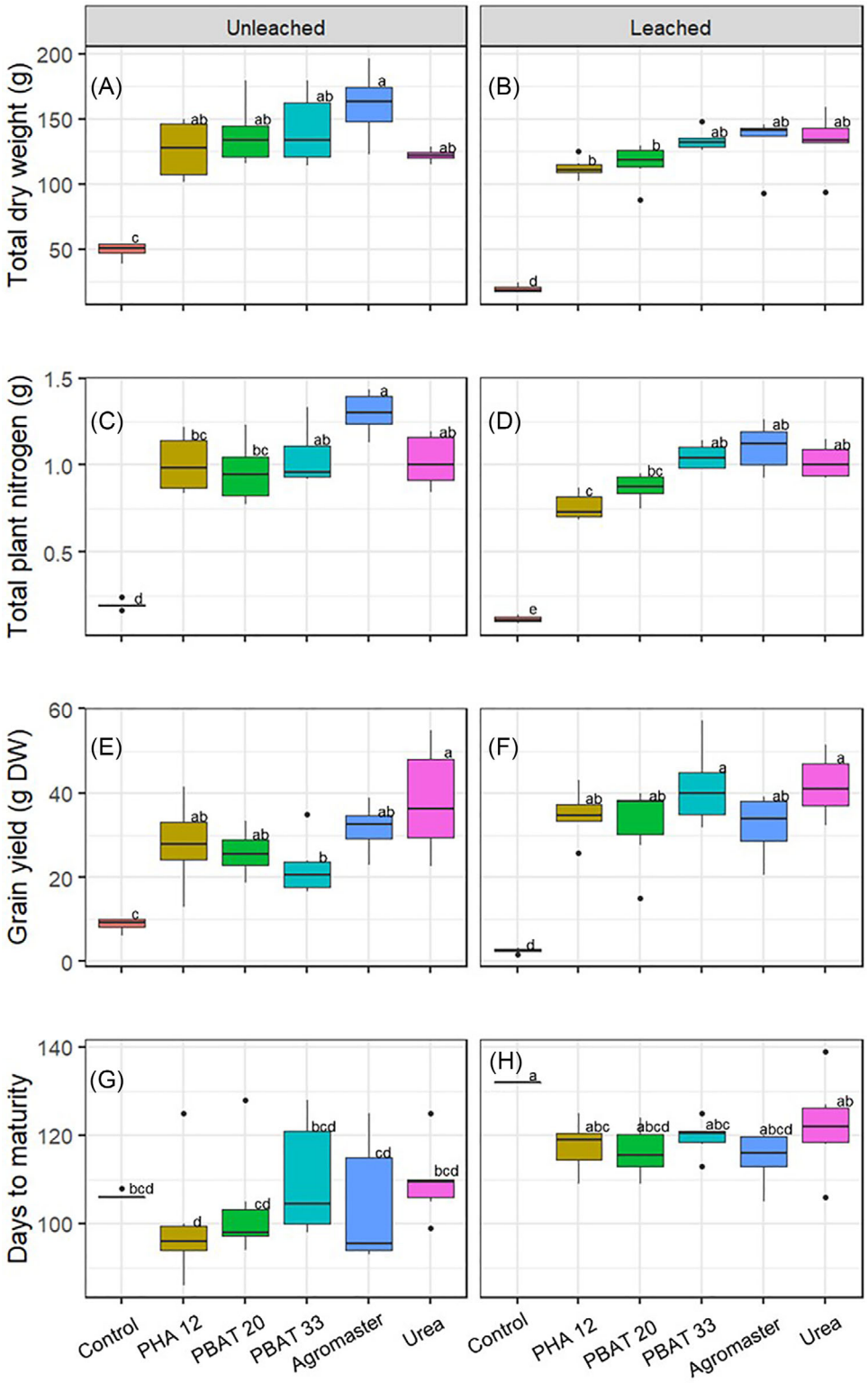

FIGURE 4 Total biomass (g DW) (A), total plant nitrogen (g N) (B), grain yield (g DW) (C), and days to grain maturity (D) produced by each fertilizer treatment when unleached and leached. Different letters indicate significant differences in plant traits between fertilizer formulations across both leached and unleached treatments (Table S2, Tukey's post-hoc, $p < 0.05$, $n = 6$).

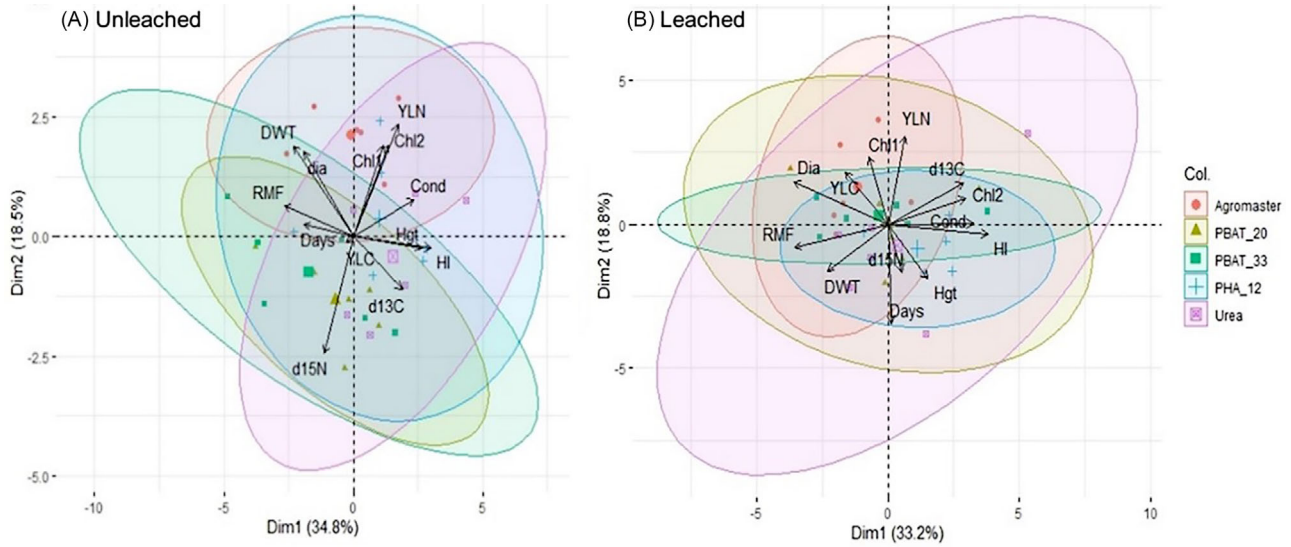

FIGURE 5 PCA dimensions 1 and 2 based on plant traits for six replicates for fertilizer formulations in unleached (A) and leached pot experiments (B). The ellipses are a 95% confidence interval of all individuals of the fertilizer treatment groups. Traits are given as follows: Chl1, chlorophyll content of youngest fully expanded leaf at day 59; Chl2, chlorophyll content of youngest fully expanded leaf at day 86; Cond, leaf conductance; d13C, (δ^{13}C) leaf delta 13C; d15N leaf, fertilizer d15N (δ^{15}N); Dia, stem diameter; DWT, total dry biomass; Hgt, plant height; HI, harvest index; RMF, root mass fraction; YLC, youngest fully expanded leaf %C; YLN, youngest fully expanded leaf %N.

4 | CONCLUSION

Testing the efficacy of fertilizer formulations is inherently challenging, with abiotic and biotic factors affecting how N becomes available to crops. The tested fertilizer formulations displayed considerable differences in N release in laboratory-based experiments, but these did not predict agronomic performance based on yield, plant N accumulation, or leached N in the pot experiment. Rather, the three testing systems provided distinct information relevant for the design and evaluation of fertilizer formulations. The longer term pot experiment highlights that the efficacy of EEF is not only influenced by N release profiles but also by soil physical, chemical, and biological properties. These properties are likely to have a stronger effect on the fate of N than the initial release, particularly in slower growing crops and in crops with longer N accumulation. Leached columns comprised of varied substrates can evaluate integrated biotic and abiotic interactions on N release, while longer term plant growth testing should vary the timing and intensity of leaching events to emulate the targeted production system. Evaluating plant tissue δ^{15}N signatures and the temporal variation in plant traits, such as leaf N content, offers insight into N availability and plant uptake. The three testing systems provided a complementary regime to evaluate novel fertilizers. We conclude that biodegradable matrix-encapsulated fertilizer could fill the gap in existing commercial products that have faster and slower N release, and that essential information of N release should be obtained as a first screen before field experimentation to evaluate agronomic efficiency and potential for reduced environmental losses.

AUTHOR CONTRIBUTIONS

Torsten Witt: Conceptualization; data curation; formal analysis; investigation; methodology; writing—original draft; writing—review and editing. **Nicole Robinson**: Conceptualization; data curation; formal analysis; investigation; methodology; writing—original draft; writing—review and editing. **Ana C. Palma**: Conceptualization; data curation; formal analysis; investigation; methodology. **Lucas Cernusak**: Conceptualization; formal analysis; methodology; writing—original draft; writing—review and editing. **Steven Pratt**: Conceptualization; methodology; writing—review and editing. **Matthew Redding**: Conceptualization; methodology; writing—review and editing. **Damien J. Batstone**: Conceptualization; Methodology; Writing—review and editing. **Susanne Schmidt**: Conceptualization; funding acquisition; writing—original draft; writing—review and editing. **Bronwyn Laycock**: Conceptualization; funding acquisition; methodology; project administration; resources; supervision; writing—review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

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SUPPORTING INFORMATION

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