Journal of Sustainable Agriculture and Environment
WILEY
Global Initiative of Sustainable Agriculture and Environment
Harnessing Natural Resources

RESEARCH ARTICLE OPEN ACCESS

Nanocomposite Reduces Volatile and Aqueous Reactive Nitrogen Losses From Soil Compared to Conventional and Alternative Fertilisers

Jessica Chadwick[1,2] | Jingyi Shi[2] | Megan L. Purchase[2] | Peng Zhang[1] | Iseult Lynch[1] | Sami Ullah[1] | Deying Wang[2] | Ryan M. Mushinski[2]

[1]School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham, UK | [2]School of Life Sciences, University of Warwick, Coventry, UK

Correspondence: Ryan M. Mushinski (Ryan.Mushinski@warwick.ac.uk)

Received: 19 November 2025 | **Revised:** 20 January 2026 | **Accepted:** 22 January 2026

Funding: Biotechnology and Biological Sciences Research Council (BBSRC), Grant/Award Numbers: BB/T00746X/1, BB/X002187/1; Natural Environment Research Council (NERC), Grant/Award Numbers: NE/S007350/1, UKRI1284

Keywords: controlled release fertiliser | environmental sustainability | nanocomposite | nitrogen | soil

ABSTRACT

Reactive nitrogen losses from agriculture contribute substantially to greenhouse gas emissions, water pollution and ecosystem degradation. Controlled-release fertiliser technologies offer potential solutions, yet few comprehensively evaluate performance across multiple nitrogen loss pathways and soil types. This study evaluated the environmental performance and agronomic efficacy of urea-doped amorphous calcium phosphate (U-ACP) nanoparticles compared to conventional urea across three contrasting soil types (sandy, sandy loam, clay loam) using lettuce (*Lactuca sativa*) as a model crop. U-ACP nanoparticles (20–100 nm) were synthesised and characterised for dissolution kinetics in simulated soil environments. Controlled glasshouse experiments (8 weeks, 100 kg N ha^{-1} application rate) quantified gaseous emissions (ammonia, nitrous oxide, nitric oxide), aqueous leaching losses, soil biochemical properties, plant nitrogen uptake and functional gene abundances for nitrogen cycling processes. U-ACP demonstrated significantly reduced reactive nitrogen losses across all pathways and soil types. Cumulative ammonia volatilisation decreased by 53%–57% in sandy and sandy loam soils compared to conventional urea ($p < 0.001$), whilst nitrous oxide emissions declined by 19%–27% across all soil types ($p < 0.001$). Total nitrogen leaching concentrations were 44% lower in sandy soils where losses are typically highest ($p < 0.001$), with ammonium leaching reduced by 71%–85% across soil types. Cumulative gaseous nitrogen losses decreased by 20%–48% depending on soil type. Despite these substantial reductions in nitrogen losses, U-ACP maintained comparable plant biomass whilst achieving 52%–89% higher nitrogen uptake index across soil types ($p < 0.001$). U-ACP also supported enhanced soil microbial functionality, with significantly elevated complete ammonia oxidiser (comammox) and alkaline phosphatase (*phoD*) gene abundances ($p < 0.05$). Calcium phosphate-based nanocomposite fertilisers offer a viable pathway towards sustainable intensification of agriculture by simultaneously reducing environmental nitrogen pollution whilst maintaining or improving crop productivity across diverse soil conditions.

1 | Introduction

The global challenge of feeding an ever-growing population while maintaining environmental sustainability has reached a critical juncture. With the world's population projected to peak at 11 billion around 2100, agricultural production must increase by 60% by 2050 to meet demand (FAO 2023). This challenge is compounded by widespread soil degradation, creating a vicious cycle where deteriorating soil quality necessitates ever-increasing fertiliser inputs (Beretta-Blanco et al. 2019). Synthetic nitrogen fertilisers have become essential for modern agriculture, yet current systems operate at only 30%–50% efficiency (Ladha et al. 2016; Omara et al. 2019), meaning that most applied nitrogen is lost to the environment rather than taken up by crops.

These nitrogen losses occur through multiple pathways, including volatilisation as ammonia, denitrification to nitrous oxide and leaching as ammonium and nitrate. This creates what Galloway et al. (2003) termed the nitrogen cascade, where a single nitrogen atom contributes sequentially to multiple environmental problems as it moves through ecosystems. Recent estimates indicate that 2.95 million tonnes of nitrogen were lost as nitric oxide from global maize and wheat cultivation alone in 2020 (Wang et al. 2024), while leaching losses from urea application average 35.4 kg N ha^{-1} annually (Hina 2024). This cascade amplifies reactive nitrogen's environmental burden across atmospheric, terrestrial and aquatic systems (Gong et al. 2024). Excess nitrogen drives eutrophication of water bodies, with fertiliser-sourced nitrogen being more mobile than naturally occurring sources (Bijay-Singh and Craswell 2021). Reactive nitrogen emissions, including ammonia, nitric oxide, nitrogen dioxide, nitrous oxide and other volatile species, contribute to tropospheric ozone formation, induce global warming, degrade air quality and pose risks to human respiratory health (Tang et al. 2018). Additionally, soil acidification from excessive fertiliser application promotes the losses of soil inorganic carbon via CO_2 emissions and carbonate leaching (Raza et al. 2021), inhibits beneficial microbial communities and creates conditions that favour nitrogen losses over plant uptake, including emissions of nitrous oxide, a greenhouse gas with 298 times the global warming potential of CO_2 (IPCC 2021). The interconnected nature of these impacts necessitates fertiliser technologies that address multiple loss pathways simultaneously rather than targeting individual mechanisms in isolation.

Soil microbial communities play a critical role in determining whether applied nitrogen is efficiently used by plants or lost to the environment (Xun et al. 2024). Under optimal conditions, soil microorganisms facilitate an equilibrated nitrogen cycle where ammonia is oxidised to plant-available nitrate by nitrifying bacteria, while excess nitrate can be safely denitrified to dinitrogen gas under anaerobic conditions (Kuypers et al. 2018). However, conventional fertiliser application disrupts this balance through rapid chemical changes that create suboptimal conditions for beneficial microbial processes, favouring nitrogen losses over retention and plant uptake.

Nanotechnology offers promising solutions to these challenges by enabling controlled nutrient release that better matches plant demand while supporting stable soil conditions (Li and Li 2024). Nanomaterials possess unique properties, including high surface area to volume ratios and enhanced reactivity, that make them suitable for controlled-release fertiliser systems (Liu and Lal 2015). Engineered nanoparticles can enhance nutrient use efficiency through controlled dissolution kinetics, targeted delivery mechanisms and enhanced plant uptake pathways (Fraceto et al. 2016). Among nanofertiliser approaches, calcium phosphate-based systems are particularly promising due to their biocompatibility and natural occurrence in soils (Ditta and Arshad 2016). Urea-doped amorphous calcium phosphate (U-ACP) nanoparticles represent a multinutrient delivery system that has demonstrated the ability to maintain crop yields while reducing nitrogen requirements. Studies with wheat showed faster root uptake of U-ACP compared to conventional urea (Ramírez-Rodríguez et al. 2020), while similar calcium phosphate-based nanofertilisers have demonstrated sustained nutrient release characteristics, reduced leaching losses and enhanced crop performance in controlled experiments (Kottegoda et al. 2017). Benefits have been observed across diverse crop systems, including viticulture and hydroponics (Pérez-Álvarez et al. 2021; Gaiotti et al. 2021; Carmona et al. 2021). However, comprehensive nitrogen-focused evaluation of U-ACP's environmental performance, particularly regarding gaseous emissions, leaching dynamics and soil microbial community effects, remains limited.

This study aimed to comprehensively evaluate the environmental performance of U-ACP compared to conventional urea fertilisation, focusing on nitrogen cycling processes, emissions, leaching losses and soil microbial community effects. We hypothesised that U-ACP would demonstrate improved environmental performance through reduced nitrogen losses and better soil biological function while achieving comparable plant growth, relative to urea. Specifically, we predicted that controlled release characteristics would result in lower volatile and aqueous reactive nitrogen losses, altered soil microbial community structure favouring nitrogen use efficiency, and reduced soil acidification due to the calcium phosphate buffer capacity.

2 | Methods and Materials

2.1 | U-ACP Synthesis and Characterisation

U-ACP was synthesised following Ramírez-Rodríguez et al. (2020) by mixing calcium-citrate-urea and phosphate solutions, incubating at 37°C for 24 h, washing with pure water and air-drying (detailed protocol in Supporting Information: Method 1). Transmission electron microscopy (TEM; JEOL 1400 TEM at 120 kV) and dynamic light scattering (DLS; Zetasizer Nano ZS) determined particle morphology and hydrodynamic size. Thermogravimetric analysis (TGA; Mettler Toledo TGA/DSC 1, 25°C–600°C at 10°C min^{-1} under nitrogen) confirmed urea incorporation. Dissolution behaviour was assessed by dispersing U-ACP at 100 mg L^{-1} in deionised water, 0.01 M $CaCl_2$ and artificial rhizosphere solution at 25°C over 72 h. The rhizosphere solution contained glucose (3.5 g L^{-1}), organic acids (citric, malic, oxalic) and amino acids to simulate root exudates (complete composition in Supporting Information: Method 2). Released nitrogen, phosphorus and calcium were analysed with sampling at 1, 2, 4, 8, 24, 48 and 72 h.

2.2 | Soil Characterisation and Experimental Design

Three soils were collected from University of Warwick sites, including sandy loam (pH 6.9 ± 0.4), clay loam (pH 7.4 ± 0.3) and

sandy soil (pH 7.2 ± 0.3). Characterisation included particle size distribution (pipette method), pH (0.01 M $CaCl_2$, 1:2.5), organic matter (loss-on-ignition at 550°C), total C and N (dry combustion), exchangeable cations (atomic absorption spectrophotometry) and available phosphorus (Olsen method). Baseline enzyme activities were measured for urease, dehydrogenase and acid phosphatase (detailed protocol in Supporting Information: Method 3). The factorial experiment included five nitrogen sources (control, conventional urea, U-ACP, ammonium nitrate, nitrification-inhibited [ENTEC] urea) across three soil types. All treatments were applied on an equal nitrogen basis, ensuring equivalent nitrogen input across fertiliser types. Urea and U-ACP were tested at 50, 75, 100 and 125 kg N ha^{-1}, other fertilisers at 100 kg N ha^{-1} only, with three replicates each. Mesocosm pots (18 cm diameter, 15 cm height) used to quantify gas flux and plant growth, comparing only urea versus U-ACP, contained 1.5–1.6 kg soil at 1.5 g cm^{-3} bulk density. Falcon tube (50 mL) microcosms were used for analysing the soil biochemical, leachate and microbial response to different fertiliser amendments. Water-soluble fertilisers were applied in 300 mL solutions; U-ACP was incorporated as a solid before watering. Lettuce (*Lactuca sativa* cv. Buttercrunch) was grown under controlled conditions (16:8 h photoperiod, 400 μmol m^{-2} s^{-1} PPFD, 20/18°C day/night, 65% RH) with irrigation maintained at 50%–60% field capacity. Complete experimental design details are provided in Supporting Information: Method 4.

2.3 | Gas Flux and Leachate Measurements

Gaseous emissions were measured by placing 160 cm^3 polyvinyl chloride chamber tops onto the mesocosm pot, connected to a Teledyne T200U-NOy analyser (nitric oxide [NO]) and Protea FTIR Gas Analyser (nitrous oxide [N_2O], ammonia [NH_3]). Control, urea and U-ACP treatments (100 kg N ha^{-1}) were measured for 2 h per chamber with 20-min automated switching. Method modified from Purchase et al. (2023). Gas flux measurements were performed on three replicates each for control and U-ACP treatments, while urea treatments included six replicates, with three additional replicates originating from a concurrent study conducted under identical experimental conditions, measurement protocols and timing. Measurements were taken daily during Week 1, twice weekly for Weeks 2–4, then weekly until Week 8 (detailed protocol in Supporting Information: Method 5). Falcon tube microcosms (50 mL) contained 35 ± 2 g soil placed over cotton wool. Tubes had drainage holes and were positioned over collection vials. Soil moisture maintained at 50%–60% field capacity with 15–20 mL water every 2–3 days, with total water added over the 8-week experiment was 460 ± 40 mL per tube. Leachate was collected by gravity at 10 timepoints, with total volume collected was 130 ± 25 mL per tube (~ 28% of applied water). Leachates was filtered (0.45 μm), stored at 4°C, and analysed within 48 h for ammonium and nitrate (SEAL AutoAnalyzer 3 HR), total dissolved nitrogen (Shimadzu TOC/TN-L) and phosphorus. Soil sampling occurred at Weeks 0, 1, 2, 4, 6 and 8 for pH, extractable nitrogen (2 M KCl) and enzyme activities. Analytical protocols detailed in Supporting Information: Method 6. Quality control parameters for all analytical methods are provided in Supporting Information: Table S1.

2.4 | Plant Analysis

Plants were harvested at Week 8. Fresh weights, growth measurements and tissue nutrient concentrations were determined. Nitrogen uptake index (NUI) was calculated to assess the relative effectiveness of fertiliser treatments in promoting plant nitrogen acquisition. NUI was expressed as plant nitrogen uptake per unit of applied nitrogen, calculated as nitrogen uptake (mg $plant^{-1}$) divided by the field-equivalent application rate (100 kg N ha^{-1}) multiplied by 10. This normalisation provides a dimensionless comparative index representing mg N uptake per 10 kg N ha^{-1} applied, facilitating comparison across treatments and soil types while accounting for differences in plant biomass production. Higher NUI values indicate more efficient nitrogen acquisition per unit of fertiliser applied. This metric differs from traditional nitrogen use efficiency definitions, such as agronomic efficiency or apparent recovery efficiency (Congreves et al. 2021), by providing a direct comparative index at identical application rates without requiring control subtraction for each replicate. Plant tissue preparation and analysis protocols are detailed in Supporting Information: Method 7.

2.5 | Soil Microbial Analysis

Soil DNA was extracted using the DNeasy PowerLyzer PowerSoil Kit from 0.25 g frozen soil samples taken from Falcon tube microcosms. Quantitative polymerase chain reaction (qPCR) (Bio-Rad CFX96 Touch) with SYBR Green chemistry targeted nitrogen and phosphorus cycling genes, including bacterial and archaeal *amoA*, comammox, *nxrB*, *nirK*, *nirS*, *norB*, *nosZ* clades I and II, *nifH* and *phoD*. Universal 16S rRNA gene primers targeting bacteria and archaea quantified total prokaryotic abundance. Gene abundances were normalised to 16S rRNA gene abundance by subtracting $\log_{10}$ 16S gene abundance from target gene abundance, which is mathematically equivalent to $\log_{10}$(target/16S) and represents the log-ratio of target gene to total prokaryotic abundance (Fierer et al. 2005). This yields relative abundances representing the proportion of the prokaryotic community harbouring each functional gene. Area under curve (AUC) analysis integrated gene responses using trapezoidal integration between consecutive sampling points (Weeks 0, 1, 2, 4, 6, 8). To assess integrated microbial community responses over the experimental period, AUC analysis was performed on qPCR data. Gene abundances at each time point were first normalised to 16S rRNA gene abundance ($\log_{10}$ gene copies-$\log_{10}$ 16S copies) to account for total bacterial biomass variation. For each replicate, AUC values were calculated using the trapezoidal rule,

$$\mathrm{AUC} = \sum_{i=1}^{n-1} \frac{(y_i + y_{i+1})}{2} \times (t_{i+1} + t_i),$$

where y_i represents the normalised gene abundance ($\log_{10}$ gene copies—$\log_{10}$ 16S copies) at timepoint i, t_i represents time in weeks, and $n = 6$ sampling timepoints (Weeks 0, 1, 2, 4, 6, 8). This calculation integrates gene abundance over the five consecutive time intervals spanning the 8-week experimental period. To enable cross-gene statistical comparisons, AUC values for each gene were standardised to z-scores by subtracting

the gene-specific mean and dividing by the standard deviation across all samples. Final values represent mean standardised AUC averaged across all soil types ($n = 9$ replicates per treatment, 3 soil types × 3 field replicates). Statistical significance was determined by one-way ANOVA on standardised AUC values for each gene, followed by Tukey's honest significant difference (HSD) test for pairwise comparisons ($\alpha = 0.05$). Further details are noted in Supporting Information: Method 8. Primer sequences for all gene targets are provided in Supporting Information: Table S2, with thermal cycling conditions in Supporting Information: Table S3 and gBlock standard details in Supporting Information: Table S4.

2.6 | Statistical Analysis

Data analysis used R software version 4.3.0 (complete statistical procedures in Supporting Information: Method 9 and Supporting Information: Table 5). Normality and homogeneity of variance were assessed using Shapiro–Wilk and Levene's tests. Linear mixed-effects models analysed normally distributed data with treatment as fixed effects and pot/tube as random effects. Post-hoc comparisons used Tukey's HSD test. Standardised AUC values were analysed by one-way ANOVA followed by Tukey's HSD for pairwise comparisons. Statistical significance was set at $p < 0.05$.

3 | Results

3.1 | U-ACP Characterisation

TEM revealed spherical to subspherical U-ACP nanoparticles (20–100 nm, most 30–60 nm) with smooth, well-defined boundaries (Figure 1A). DLS analysis showed hydrodynamic size of 154 ± 31.2 nm with polydispersity index of 0.49 ± 0.1 and zeta potential of -20.0 ± 0.9 mV, indicating reasonable colloidal stability. Thermogravimetric analysis demonstrated three-stage thermal decomposition with $25.4\% \pm 3.2\%$ total mass loss to 589°C, indicating approximately 15% (weight) urea incorporation and 75% inorganic calcium phosphate content (Figure 1B and Supporting Information: Result 1). Complete characterisation parameters including BET surface area, pore volume and elemental composition are summarised in Supporting Information: Table S6. BET analysis revealed high specific surface area ($127.3 \pm 8.4\ m^2\ g^{-1}$) with mesoporous structure characterised by pore volume of $0.234 \pm 0.019\ cm^3\ g^{-1}$ and average pore diameter of 7.36 ± 0.52 nm, consistent with the nanoparticle morphology observed by TEM. U-ACP demonstrated controlled release characteristics with biphasic kinetics across three dissolution media (Figure 1C–E). Nitrogen (urea) release was most rapid, achieving 85%, 68% and 80% cumulative release in deionised water, $CaCl_2$ and rhizosphere extract respectively after 72 h. The Higuchi kinetic model provided best fit ($R^2 > 0.95$), confirming diffusion-controlled sustained release. Detailed kinetics and modelling parameters are provided in

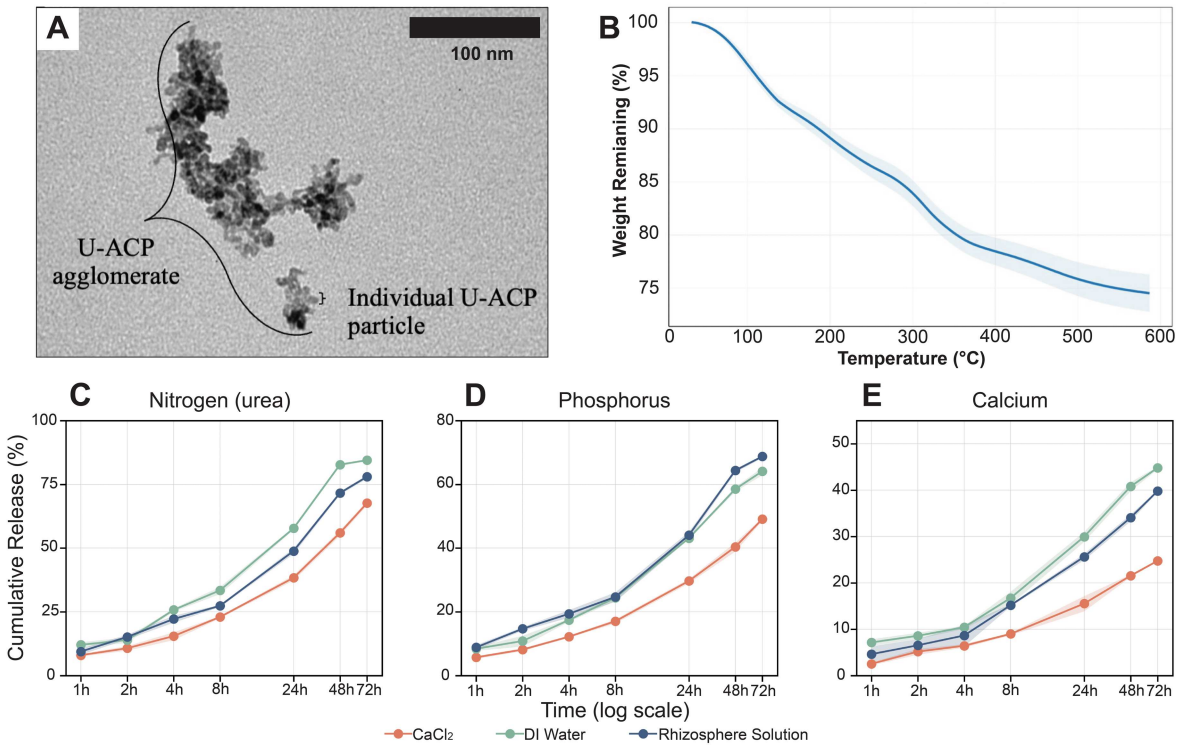

FIGURE 1 | U-ACP characterisation. (A) TEM-generated micrographs of pristine U-ACP nanocomposites. (B) Thermogravimetric analysis of U-ACP nanoparticles. Mean weight percentage (dark blue line) ± SD (shaded region) as a function of temperature ($n = 3$). Three-stage thermal decomposition profile shows $25.4 \pm 3.2\%$ total mass loss, corresponding to physiosorbed water (32°C–200°C), coordinated urea decomposition (200°C–350°C) and crystallisation to hydroxyapatite (350°C–600°C). (C–E) Cumulative release of nitrogen (urea), calcium and phosphorus from U-ACP nanoparticles in three dissolution media over 72 h. Deionised water (green line), $CaCl_2$ solution (red line) and artificial rhizosphere extract (blue line) are included. Shaded area represents standard error ($n = 3$).

Supporting Information: Results 2 and Supporting Information: Table S7.

3.2 | Soil Characterisation

The three soil types used in this study exhibited distinct physicochemical properties (Supporting Information: Table S8) and enzymatic activity (Supporting Information: Result 3). The sandy soil had a pH of 7.2 ± 0.33, while the clay loam and sandy loam soils were 7.4 ± 0.34 and 6.9 ± 0.39, respectively. Statistical analysis revealed no significant differences in pH between soil types ($F_{2,6} = 1.85$, $p > 0.05$). Organic matter content was highest in the clay loam soil ($4.2 \pm 0.2\%$) compared to sandy loam ($2.9 \pm 0.2\%$) and sandy soil ($1.9 \pm 0.4\%$). Total nitrogen followed a similar pattern, with clay loam containing $0.17 \pm 0.01\%$ N, sandy loam $0.12 \pm 0.01\%$ N and sandy soil $0.08 \pm 0.01\%$ N. These differences between soil types were statistically significant for both organic matter ($F_{2,6} = 52.19$, $p < 0.01$) and total nitrogen ($F_{2,6} = 53.82$, $p < 0.01$). Cation exchange capacity (CEC) varied significantly between soil types ($F_{2,6} = 84.59$, $p < 0.01$), with clay loam showing the highest values (17.9 ± 2.0 cmol kg^{-1}), followed by sandy loam (8.4 ± 1.0 cmol kg^{-1}) and sandy soil (4.2 ± 0.1 cmol kg^{-1}). Available phosphorus also differed significantly between soils ($F_{2,6} = 76.44$, $p < 0.01$), with clay loam having 30.2 ± 2.8 mg kg^{-1}, sandy loam 15.9 ± 1.6 mg kg^{-1} and sandy soil 9.6 ± 1.6 mg kg^{-1}. Baseline soil enzyme activities, without any added fertiliser or amendment, varied significantly between soil types, with the clay loam soil generally showing the highest baseline enzyme activities (Supporting Information: Result 3). Urease activity was highest in clay loam soil (26.8 ± 4.4 μg NH_4^+-N g^{-1} soil h^{-1}) compared to sandy loam (20.2 ± 2.6 μg NH_4^+-N g^{-1} soil h^{-1}) and sandy soil (11.3 ± 1.6 μg NH_4^+-N g^{-1} soil h^{-1}), with significant differences between soil types ($F_{2,6} = 18.99$, $p < 0.01$). Dehydrogenase activity showed similar trends ($F_{2,6} = 69.33$, $p < 0.01$), with clay loam (3.4 ± 0.4 μg TPF g^{-1} soil $24\,h^{-1}$) > sandy loam (1.8 ± 0.16 μg TPF g^{-1} soil $24\,h^{-1}$) > sandy soil (0.62 ± 0.25 μg TPF g^{-1} soil $24\,h^{-1}$). Phosphatase activity was also significantly different between soils ($F_{2,6} = 18.30$, $p < 0.01$), reflecting the generally higher biological activity in the clay loam soil.

3.3 | Soil Gas Flux Response to Fertiliser Additions

Temporal and soil-specific volatile reactive-N gas fluxes are shown in Figure 2. Nitric oxide (NO) emissions showed distinct temporal patterns following fertiliser application. Control treatments maintained consistently low fluxes throughout the experiment (0.31 ± 0.02 μg N m^{-2} h^{-1} across all soil types). Conventional urea application resulted in pronounced NO emission peaks within the first week, with maximum fluxes reaching 4.5 μg N m^{-2} h^{-1} in sandy loam soil. In contrast, U-ACP treatments demonstrated more sustained NO emission profiles with lower peak values of 1.3 μg N m^{-2} h^{-1} in the same soil type. Following the initial peaks, both fertiliser treatments showed gradual NO decline, with urea emissions declining more rapidly than U-ACP emissions. Nitrous oxide (N_2O) emissions exhibited similar temporal patterns to NO, with urea treatments producing sharp initial peaks followed by gradual decline. U-ACP treatments showed more sustained N_2O emission profiles with lower peak values, but extended duration compared to urea. Sandy loam soil showed the most pronounced differences between treatments, while clay loam and sandy soils showed more modest U-ACP effects. The smaller reduction in clay loam soil likely reflects its higher buffering capacity and water-holding characteristics, which reduce the relative advantage of U-ACP's controlled-release mechanism (see Section 4.2 for detailed mechanistic discussion). Ammonia (NH_3) volatilisation showed the most dramatic treatment differences, with urea producing characteristic sharp emission peaks within the first week, followed by rapid decline to near-background levels. U-ACP treatments maintained more moderate, sustained NH_3 emissions throughout the measurement period. Sandy soil showed the highest overall NH_3 emissions for both treatments, likely reflecting the influence of soil pH and texture on volatilisation processes.

Cumulative gaseous nitrogen losses of the discreet experimental periods revealed significant treatment and soil-specific effects (Supporting Information: Result 4). Total gaseous nitrogen losses were reduced by U-ACP compared to urea, with reductions of 45.7% in sandy loam, 48.3% in sandy soil and 20.0% in clay loam soil. The analysis of individual gas contributions showed that NH_3 losses constituted the largest component of total gaseous losses, particularly in sandy soils where NH_3 volatilisation was most pronounced. Cumulative NH_3 losses showed the greatest treatment differences, with U-ACP reducing losses by 53.1% in sandy loam (0.86 vs. 1.83 mg N m^{-2}), 57.1% in sandy soil (1.03 vs. 2.40 mg N m^{-2}) and 10.0% in clay loam soil (1.32 vs. 1.47 mg N m^{-2}). Cumulative N_2O losses showed moderate reductions across all soil types. Sandy loam showed a 26.5% reduction (0.86 vs. 1.17 mg N m^{-2}), sandy soil showed a 23.2% reduction (0.84 vs. 1.10 mg N m^{-2}) and clay loam soil showed a 19.1% reduction (0.80 vs. 0.99 mg N m^{-2}). NO losses were consistently and substantially reduced by U-ACP across all soil types, with reductions of 41.6% in clay loam, 52.6% in sandy loam and 55.9% in sandy soil.

3.4 | Soil Biochemical Response to Fertiliser Additions

Figure 3 illustrates significant changes in soil biochemical variable in response to urea, U-ACP, ammonium nitrate and ENTEC urea amendments (100 kg N ha^{-1}), which were dynamic over time. Soil pH dynamics differed markedly between treatments, with urea causing rapid acidification while U-ACP maintained stable pH values. At Week 2, urea treatments showed significant pH reduction ($-12.8 \pm 3.2\%$, $p < 0.001$) compared to minimal changes with U-ACP ($-2.1 \pm 1.8\%$, $p = 0.23$), attributed to calcium phosphate buffering. Soil enzyme activities showed sustained elevation with U-ACP compared to urea. Urease activity remained elevated at Week 8 in U-ACP treatments compared to both control ($p < 0.05$) and urea ($p < 0.05$). Dehydrogenase activity was consistently higher in U-ACP treatments at Weeks 4 and 8 (+ 23.7% and + 31.2% respectively, both $p < 0.01$). Phosphatase activity was significantly higher in U-ACP treatments across all time points (Week 2: $p < 0.05$; Week 4: $p < 0.05$; Week 8:

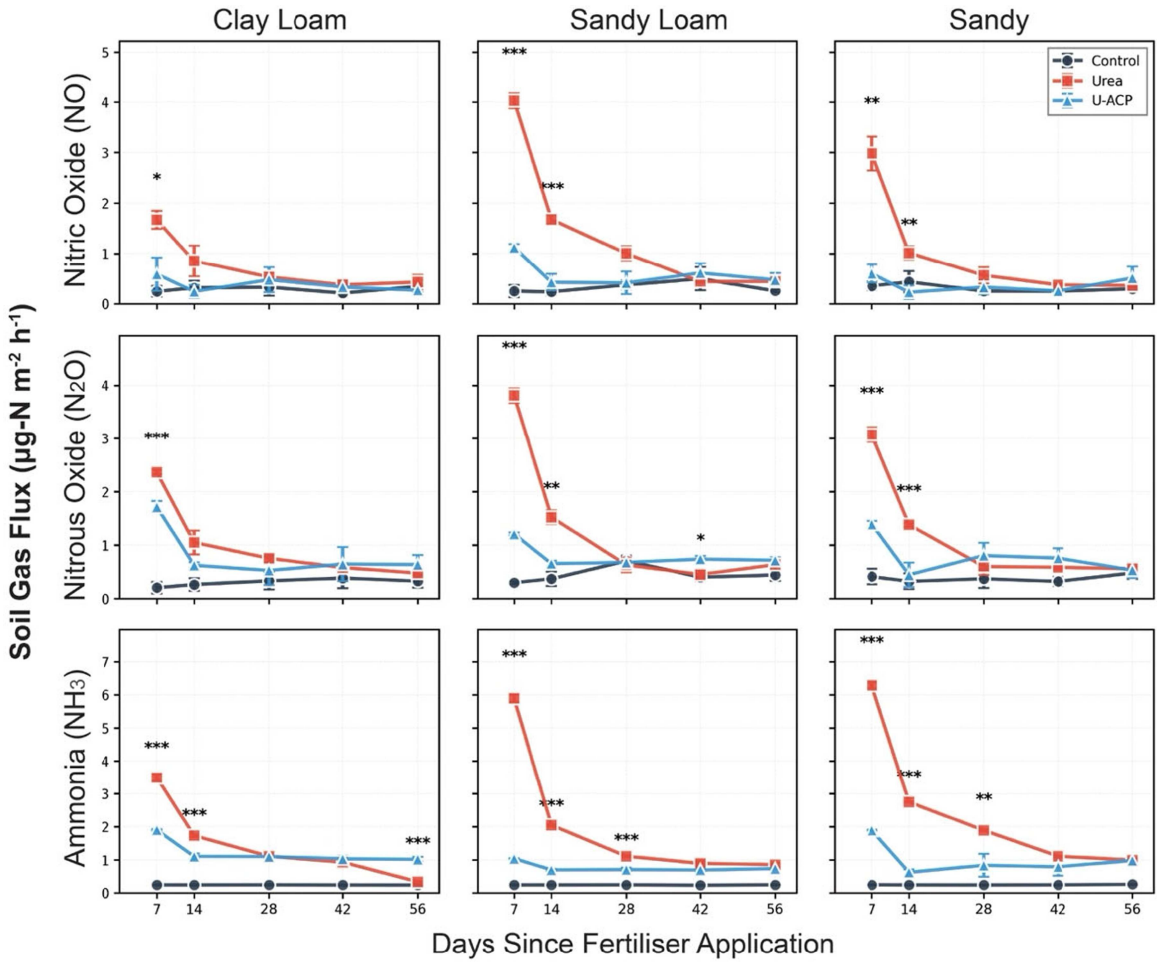

FIGURE 2 | Temporal patterns of gaseous nitrogen emissions following fertiliser application. Time series showing (A) nitric oxide (NO), nitrous oxide (N_2O) and ammonia (NH_3) emissions over the 8-week experimental period for three soil types. Control treatments (black circles), urea treatments (red squares) and U-ACP treatments (blue triangles) included. Error bars represent standard error ($n = 3$ for control and U-ACP, $n = 6$ for urea). Statistical differences between urea and U-ACP treatment at each time point are indicated by asterisks (*$p < 0.05$; **$p < 0.01$; ***$p < 0.05$).

$p < 0.01$). Extractable soil nitrogen demonstrated clear controlled-release characteristics. U-ACP maintained strong dose-response relationships at Week 8 ($R^2 = 0.79$), while urea showed minimal dose-response effects ($R^2 = 0.21$), representing 40% improved nitrogen retention. Complete dose-response analysis is provided in Supporting Information: Results 5.

3.5 | Leachate Analysis

As shown in Figure 4, leachate nitrogen concentrations varied significantly between treatments and soil types (Treatment: $F_{4,405} = 87.3$, $p < 0.001$; Soil: $F_{2,405} = 145.7$, $p < 0.001$; Time: $F_{9,405} = 23.8$, $p < 0.001$), with significant Treatment × Soil and Treatment × Time interactions (both $p < 0.001$). Ammonium leaching showed distinct patterns across treatments. Control treatments maintained low concentrations (≤ 1.7 mg N L^{-1}). Conventional urea produced the highest peaks (32.0, 16.6 and 8.5 mg N L^{-1} in sandy, sandy loam and clay loam soils, respectively), followed by ammonium nitrate (21.4, 13.2 and 6.5 mg N L^{-1}) and ENTEC urea (20.0, 13.3 and 6.3 mg N L^{-1}). U-ACP demonstrated substantially lower ammonium leaching across all soil types (4.9, 3.7 and 2.5 mg N L^{-1}), representing 85%, 78% and 71% reductions compared to conventional urea (all $p < 0.001$). One-way ANOVA confirmed significant treatment effects in sandy soil ($F_{4,10} = 78.9$, $p < 0.001$), with U-ACP significantly different from all other fertilisers (all $p < 0.001$). Nitrate leaching was highest with ammonium nitrate (39.7, 26.4 and 12.5 mg N L^{-1}) due to immediate nitrate availability. Conventional urea showed substantial peaks 2–4 weeks post-application (33.2, 19.8 and 11.5 mg N L^{-1}). ENTEC urea reduced nitrate peaks compared to urea (13.0, 9.7 and 7.5 mg N L^{-1}; $F_{1,18} = 23.7$, $p < 0.001$) but remained higher than U-ACP ($F_{1,18} = 15.2$, $p < 0.01$). U-ACP produced moderate nitrate concentrations (12.3, 9.5 and 6.9 mg N L^{-1}) with sustained, gradual release patterns rather than sharp spikes. Total nitrogen leaching averaged 10.4 ± 3.0 mg N L^{-1} for U-ACP, significantly lower than ammonium nitrate (15.7 ± 13.5 mg N L^{-1}), ENTEC urea (16.0 ± 5.3 mg N L^{-1}) and conventional urea (16.6 ± 12.1 mg N L^{-1}) ($F_{4,445} = 95.7$, $p < 0.001$; all pairwise comparisons $p < 0.001$). In sandy soil, where leaching risks are highest, U-ACP reduced total nitrogen by 44% versus urea ($t_{18} = 8.9$, $p < 0.001$), 41% versus ENTEC urea ($t_{18} = 12.3$, $p < 0.001$) and 37% versus ammonium nitrate ($t_{18} = 6.7$, $p < 0.001$). U-ACP also showed significantly lower temporal variability (coefficient of variation = 0.29) compared to urea (0.73), ammonium nitrate (0.86) and ENTEC urea (0.33) ($F_{4,445} = 47.8$, $p < 0.001$).

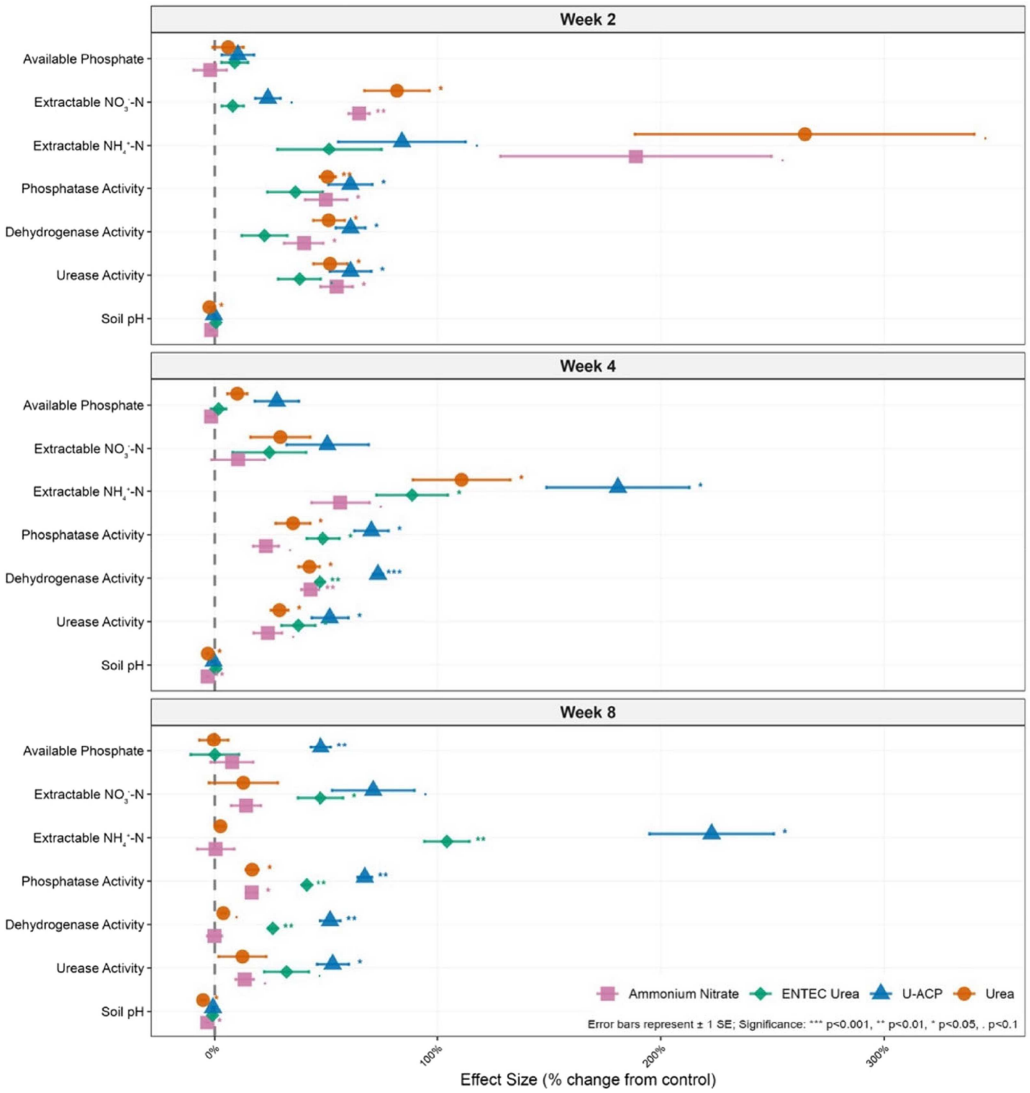

FIGURE 3 | Treatment effect sizes across soil biochemical parameters. Forest plot showing standardised effect sizes (% change from control) for key soil parameters at Weeks 2, 4 and 8 following different forms of nitrogen fertiliser application (100 kg-N ha^{-1}). Effect sizes are shown for available phosphorus, extractable NH_4^+, extractable NO_3^-, phosphatase activity, dehydrogenase activity, urease activity and soil pH across all soil types. Error bars show 95% confidence intervals.

3.6 | Plant Growth and Nitrogen Acquisition Response to Fertiliser Addition

U-ACP achieved comparable fresh biomass production relative to conventional urea across all soil types with significant improvements in NUI (Figure 5). Fresh shoot biomass showed no significant differences between treatments in sandy loam and sandy soils, but U-ACP was significantly higher in clay loam (6.55 ± 0.23 vs. 5.81 ± 0.50 g, $p < 0.05$). U-ACP and urea demonstrated similar coefficients of variation in biomass production (0.42 for both treatments). NUI was significantly higher for U-ACP across all soil types; 90% higher in clay loam, 75% higher in sandy soil and 52% higher in sandy loam (all $p < 0.001$). These reflect enhanced nitrogen acquisition per unit applied, with U-ACP-treated plants achieving NUI values of 12.84, 3.74 and 6.53 in clay loam, sandy and sandy loam soils, respectively, compared to 6.77, 2.14 and 4.30 for urea treatments. Detailed tissue analysis and nutrient dynamics are provided in Supporting Information: Results 6.

3.7 | Soil Microbial Dynamics

qPCR analysis of nitrogen and phosphorus cycling genes revealed treatment-specific cumulative responses over the 8-week experimental period. AUC analysis of 16S rRNA gene normalised abundances, expressed as standardised AUC values, showed distinct patterns across key biogeochemical processes (Figure 6). Nitrification genes showed mixed treatment responses. Bacterial ammonia oxidisers (*amoA* AOB) and archaeal ammonia oxidisers (*amoA* AOA) exhibited no significant treatment differences (*amoA* AOB: $F_{2,24} = 2.4$, $p = 0.111$). However, complete ammonia oxidisers (comammox) demonstrated significantly elevated cumulative response in U-ACP treatments compared to both control and urea applications ($p < 0.05$). Nitrite oxidisers (*nxrB*) showed treatment-specific patterns, with conventional urea differing from both control and U-ACP treatments.

Denitrification genes revealed variable responses across the pathway. Nitrite reductase genes (*nirK* and *nirS*) and nitric oxide reductase (*norB*) showed no significant treatment effects. Nitrous

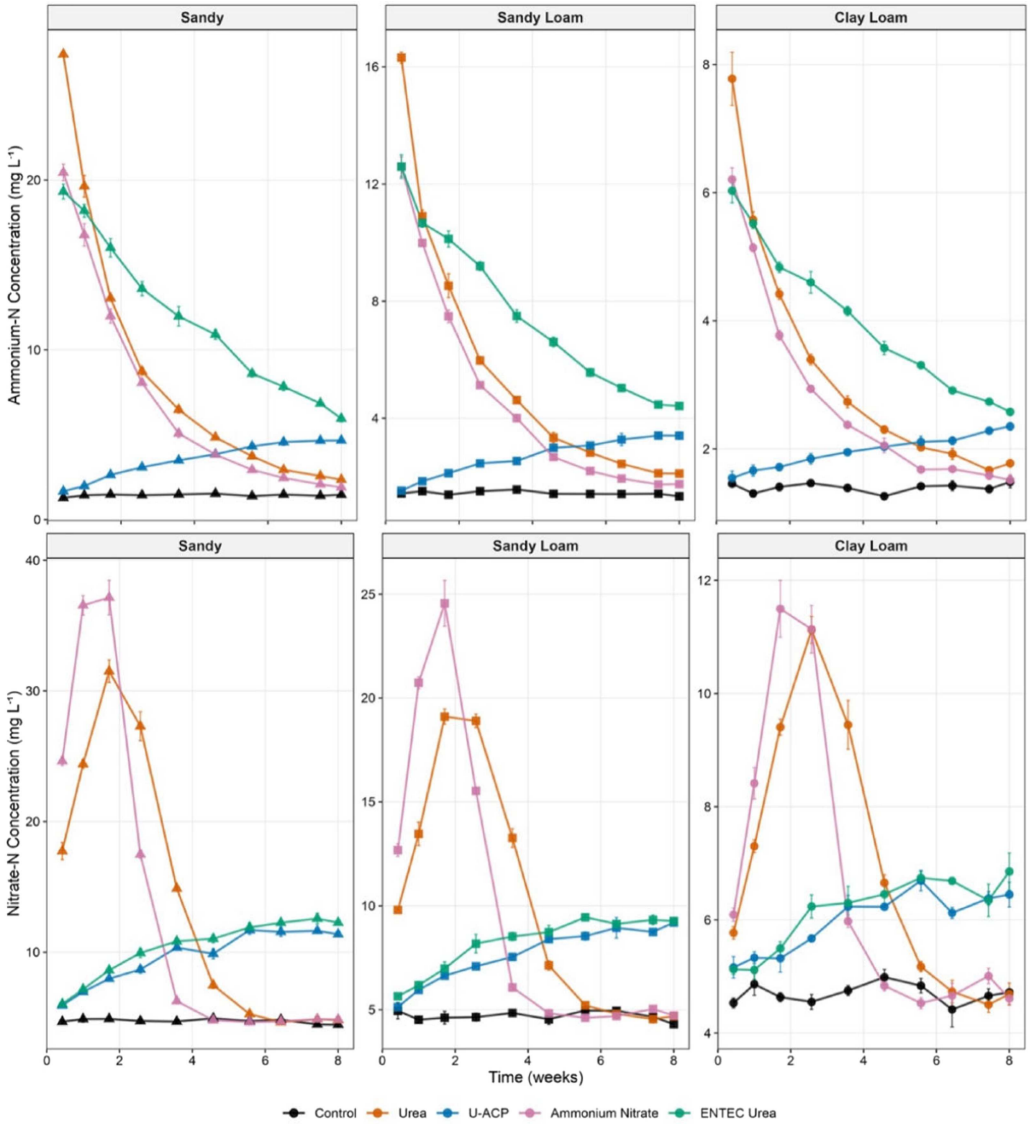

FIGURE 4 | Ammonium and nitrate leaching concentrations over time. Temporal patterns of inorganic *N* concentrations in leachate from three soil types over the eight-week experimental period with the different nitrogen fertiliser forms. Error bars represent standard error ($n = 3$).

oxide reductase genes (*nosZ* Clade I and Clade II) also exhibited no significant differences between treatments. The ratio of *nosZ* to *nirK* genes showed subtle differences, with U-ACP maintaining higher ratios that correlated negatively with cumulative N_2O emissions ($r = -0.47$, $p < 0.01$). Phosphorus cycling capacity, assessed through alkaline phosphatase (*phoD*) gene abundance, showed significant treatment effects ($F_{2,24} = 6.2$, $p < 0.01$). Both U-ACP and urea treatments maintained elevated cumulative responses compared to control, likely reflecting nutrient stimulation of microbial phosphorus cycling. Nitrogen fixation potential (*nifH*) exhibited no consistent significant differences comparing urea versus U-ACP treatments ($F_{2,24} = 1.8$, $p = 0.18$). Detailed temporal patterns are provided in Supporting Information: Result 7.

4 | Discussion

4.1 | Environmental Performance of U-ACP

Our evaluation of U-ACP nanofertiliser presented in this study provides evidence for its potential to address the dual challenges of maintaining agricultural productivity while reducing environmental impacts associated with conventional nitrogen fertilisation. Our results demonstrate that U-ACP achieves comparable *Lactuca* growth performance while reducing gaseous nitrogen emissions, leaching losses and maintaining more stable soil biological conditions compared to conventional urea and alternatives.

The controlled-release characteristics of U-ACP, confirmed through dissolution studies across multiple chemical environments, represent the fundamental mechanism underlying its environmental performance. The biphasic release kinetics observed in our dissolution experiments, characterised by initial rapid release followed by sustained, diffusion-controlled availability, align with optimal plant nitrogen demand patterns (Kottegoda et al. 2017; Wu et al. 2024; Maaz et al. 2025). The differential release rates of urea, calcium and phosphorus components create a time-dependent nutrient availability profile that distinguishes U-ACP from conventional fertilisers, providing nitrogen access while sustaining phosphorus and calcium supply through continued matrix dissolution. This sequential release pattern is advantageous compared to

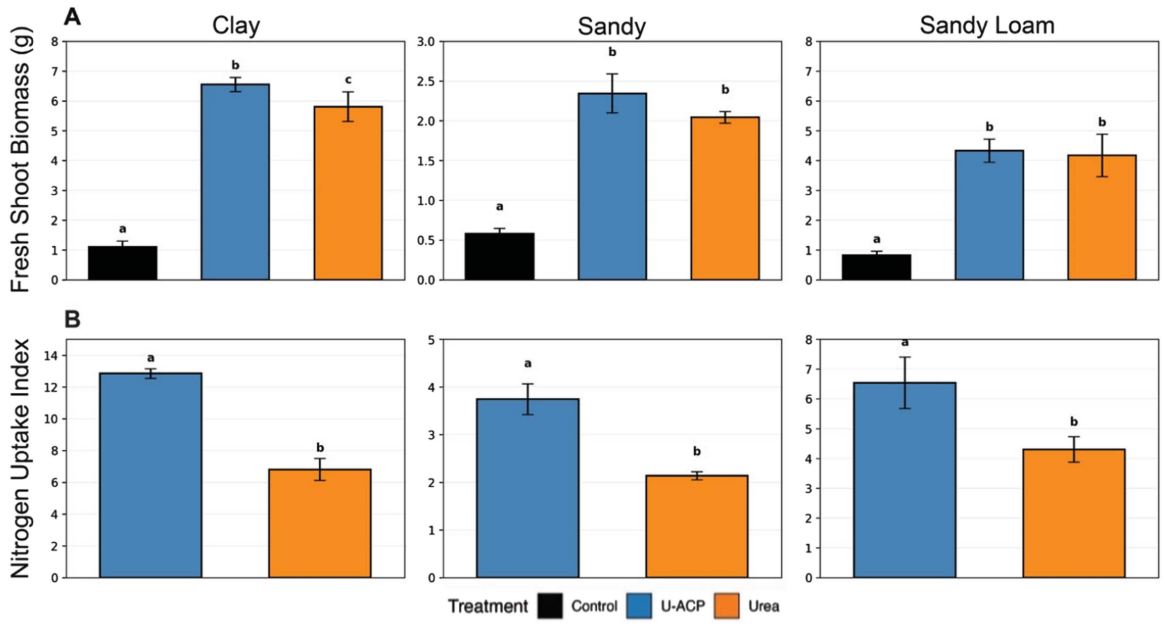

FIGURE 5 | Plant biomass production and NUI across fertiliser treatments and soil types. (A) Fresh shoot biomass at Week 8 for control (black bars), U-ACP (blue bars) and urea (orange bars) treatments. Letters above bars indicate significant differences within each soil type based on Tukey-adjusted post hoc comparisons ($\alpha = 0.05$). (B) NUI at Week 8 final harvest for U-ACP (blue bars) and urea (orange bars) treatments across three soil types. NUI was calculated as plant N uptake (mg plant^{-1}) divided by the application rate (100 kg N ha^{-1}) × 10, providing a dimensionless comparative index representing mg N uptake per 10 kg N ha^{-1} applied. Higher NUI values indicate more efficient nitrogen acquisition from applied fertiliser. Letters above bars indicate significant differences within each soil type based on Sidak-adjusted post hoc comparisons ($\alpha = 0.05$). Treatments sharing the same letter do not differ significantly. Error bars represent standard deviation ($n = 3$ biological replicates).

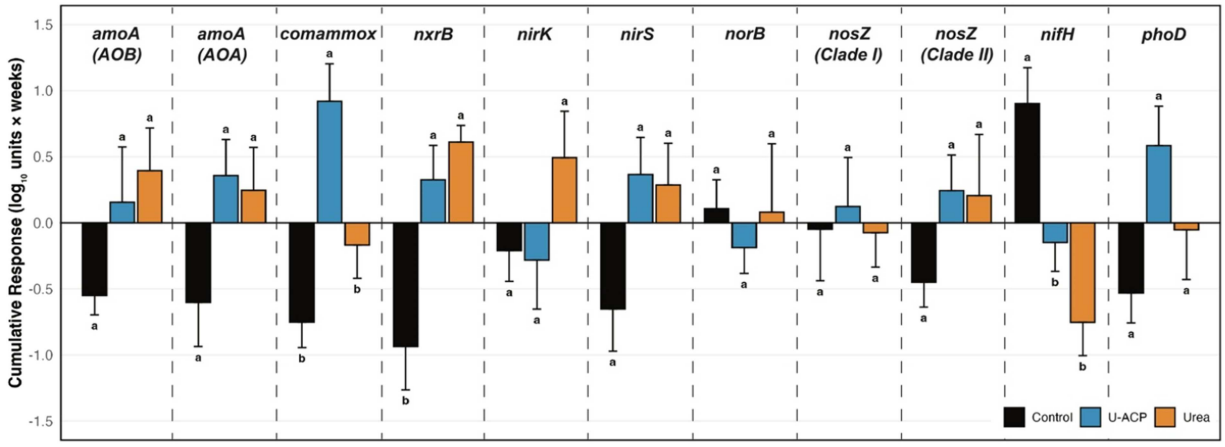

FIGURE 6 | Cumulative gene response across all soil types. AUC analysis showing integrated responses of key nitrogen and phosphorus cycling genes over the eight-week experimental period. Gene abundances were normalised to 16S rRNA gene abundance, and AUC values were calculated using trapezoidal integration between consecutive sampling points (Weeks 0, 1, 2, 4, 6 and 8). To enable cross-gene statistical comparisons, AUC values for each gene were standardised to *z*-scores within each gene target. Responses are shown as standardised AUC values ($\log_{10}$ units × weeks) averaged across Sandy, Sandy Loam and Clay Loam soils. Control treatments (black bars), U-ACP treatments (blue bars) and urea treatments (orange bars) are shown with standard error bars extending in the direction of the bar value. Statistical significance was determined by one-way ANOVA on standardised AUC values for each gene, followed by Tukey's HSD test for pairwise comparisons ($\alpha = 0.05$). Compact letters above bars indicate significant differences between treatments within each gene; treatments sharing the same letter do not differ significantly. Genes shown include bacterial ammonia monooxygenase (*amoA* AOB), archaeal ammonia monooxygenase (*amoA* AOA), complete ammonia oxidiser ammonia monooxygenase (comammox), nitrite oxidoreductase (*nxrB*), copper-containing nitrite reductase (*nirK*), cytochrome cd_1 nitrite reductase (*nirS*), nitric oxide reductase (*norB*), nitrous oxide reductase clade I (*nosZ*-I), nitrous oxide reductase clade II (*nosZ*-II), nitrogenase (*nifH*) and alkaline phosphatase (*phoD*). Error bars represent ± 1 SE ($n = 9$ total replicates across soil types).

conventional urea, which exhibits rapid hydrolysis and subsequent vulnerability to multiple loss pathways including volatilisation, leaching and gaseous emissions (Cantarella et al. 2018).

The reduction in common ion effects observed in $CaCl_2$ solution during dissolution studies indicates that U-ACP release kinetics will be modulated by soil calcium status, potentially providing adaptive release characteristics that respond to local soil conditions. This behaviour contrasts with polymer-coated slow-release fertilisers, which maintain relatively constant release rates regardless of soil chemical conditions (Morales-Cámara et al. 2024). The higher release rates observed in rhizosphere extract suggest that plant-derived organic compounds can facilitate U-ACP dissolution through ligand-enhanced solubility, potentially creating a plant-responsive nutrient delivery system that concentrates availability in the rhizosphere where uptake occurs (Henneron et al. 2020).

4.2 | Gaseous Reactive Nitrogen Emissions Are Reduced in U-ACP Treatments

The reductions in gaseous nitrogen losses achieved by U-ACP represent a generally unexplored area of new generation fertiliser research. Cumulative gaseous reactive nitrogen losses were reduced by 44% in sandy loam, 31% in sandy soil and 4% in clay loam soil compared to conventional urea, with the greatest improvements observed in soils with the highest intrinsic loss potential. These reductions are particularly notable given that they were achieved without compromising plant growth, indicating genuine improvements in efficiency rather than simply reduced nitrogen availability. The lower emission reduction in clay loam (4% vs. 44% in sandy loam) likely reflects the complex interplay of soil physical properties. Clay loam has higher water-holding capacity and finer pore structure, creating microsites favourable for complete denitrification to N_2, while their greater buffering capacity reduces the pH-stabilising advantage of U-ACP's calcium phosphate matrix. Additionally, the sustained substrate availability in finer-textured soils may support higher baseline microbial activity, partially offsetting controlled-release benefits.

Ammonia volatilisation showed the most pronounced treatment differences, with U-ACP reducing losses by up to 60% compared to conventional urea. The reduction in NH_3 volatilisation achieved by U-ACP represents substantial environmental benefit. While the emission factors measured in this pot experiment are lower than the UK Department of Environment, Food & Rural Affairs (DEFRA) field-scale emission factor for urea of approximately 20% (Rathbone and Ullah 2024) due to the controlled environment and 8-week duration, the consistent reduction pattern across soil types demonstrates U-ACP's potential to mitigate ammonia emissions under field conditions. This reduction can be attributed to the controlled urea release preventing the high soil urea concentrations that drive rapid hydrolysis, and subsequent pH increases that favour ammonia volatilisation (Sharma et al. 2022). Controlled-release technologies represent a fundamental approach to mitigating ammonia volatilisation by preventing the formation of high-concentration microsites where rapid hydrolysis occurs (Pan et al. 2016). The calcium phosphate matrix of U-ACP likely provides additional buffering capacity that maintains more stable soil pH conditions, as evidenced by the minimal pH changes observed in U-ACP treatments compared to the significant acidification following urea application. Soil acidification from nitrogen fertilisers is well-documented, with long-term urea application commonly reducing soil pH by 0.5–1.5 units through nitrification processes (Schroder et al. 2011). The buffering capacity of calcium phosphate provides a mechanism to prevent this acidification while simultaneously supporting optimal conditions for microbial nitrogen cycling (Yu et al. 2023). Previous studies have shown that maintaining soil pH within optimal ranges (6.5–7.5) substantially reduces ammonia volatilisation while concurrently supporting beneficial microbial activity (Whetton et al. 2022).

The reduction in nitrous oxide emissions with U-ACP treatment represents an important climate change mitigation benefit given that N_2O has a global warming potential 298 times greater than CO_2 (IPCC 2021). U-ACP reduced cumulative N_2O emissions across all soil types, with 26.5% reduction in sandy loam, 23.2% reduction in sandy soil and 19.1% reduction in clay loam. All treatments maintained N_2O emission factors well below the 1% standard threshold (Cowan et al. 2020), indicating that U-ACP achieves net nitrogen loss reduction without problematic N_2O trade-offs. The controlled nitrogen release from U-ACP appears to reduce the high soil nitrogen concentrations that create anaerobic microsites conducive to incomplete denitrification and N_2O production (Lü et al. 2023). While *nosZ* gene abundances showed no significant treatment differences, the ratio of *nosZ* to *nirK* genes was higher in U-ACP treatments and correlated negatively with cumulative N_2O emissions ($r = -0.47$, $p < 0.01$), suggesting a subtle shift towards more complete denitrification capacity. This improved balance between nitrite reduction and N_2O reduction may contribute to the reduced N_2O emissions observed, even without dramatic changes in absolute *nosZ* abundance (Jones et al. 2014). Other factors including soil texture, moisture regime, native denitrifier community structure and carbon availability, also play important roles in determining N_2O fluxes, all of which need analysis when developing novel fertilisers.

4.3 | Leaching Losses Are Minimised Through Controlled Release and Improved Retention

The substantial reductions in nitrogen leaching achieved by U-ACP, particularly in sandy soils where losses are typically highest, demonstrate a potential pathway to address the groundwater contamination concerns associated with intensive agriculture. The 44% reduction in total nitrogen leaching observed in sandy soil is a significant improvement over conventional urea and exceeds the performance of existing commercial alternatives, such as nitrification-inhibition. Nitrification inhibitors function by temporarily blocking ammonia oxidation, delaying but not necessarily preventing nitrate formation and subsequent leaching (Ruser and Schulz 2015). In contrast, controlled-release approaches address nitrogen availability throughout the N-cycle cascade, providing more comprehensive protection against multiple loss pathways. This is particularly important given that sandy soils represent some of the most challenging environments for nitrogen management due to their low CEC and high hydraulic conductivity (Hina 2024). The greater reduction in ammonium leaching (averaging 78% across soil types) compared to nitrate leaching indicates that U-ACP's primary mechanism of nitrogen retention operates through controlled ammonium release rather than

inhibition of nitrification processes. This contrasts with nitrification inhibitor technologies that specifically target the ammonia oxidation step but may not address other nitrogen loss pathways (Beeckman et al. 2024) and in fact nitrification inhibitors results in high NH_3 volatilisation (Cowan et al. 2020). The controlled release approach provides broader protection against multiple loss mechanisms and seems to maintain a more balanced soil nitrogen cycle, and possibly, long-term soil health. The temporal stability of leachate concentrations observed with U-ACP treatment represents an additional environmental benefit beyond simple reduction in average concentrations. The significantly lower coefficient of variation in nitrogen concentrations indicates more consistent leachate quality, reducing the risk of episodic contamination events that can have disproportionate environmental impacts (Tamagno et al. 2022).

4.4 | Plant Growth and Nitrogen Acquisition Are Enhanced Through Optimised Nutrient Availability

U-ACP achieved comparable or superior plant growth while demonstrating substantially higher NUI (52%–90% improvement across soil types), indicating that the nanocomposite enhances nitrogen acquisition per unit applied without compromising productivity. This improvement represents a departure from common trade-offs observed with reduced fertiliser application rates, where yield maintenance typically requires enhanced nitrogen use efficiency exceeding 50% (Dobermann 2007). The NUI metric used here provides comparative assessment of fertiliser effectiveness, differing from traditional apparent recovery efficiency calculations that account for background soil nitrogen through control subtraction (Congreves et al. 2021). This represents a true improvement in fertiliser effectiveness rather than a trade-off between yield and environmental performance. The improvements in NUI observed across soil types with the U-ACP treatment could enable reduced fertiliser application rates while maintaining yields, further amplifying environmental benefits. This co-delivery approach of nitrogen and phosphorus may provide synergistic benefits for plant nutrition, as phosphorus availability can limit nitrogen metabolism and overall plant growth (Yoon et al. 2020). Soil microorganisms play critical roles in mediating phosphorus availability through mineralisation and solubilisation processes, with phosphatase-producing bacteria responding positively to co-nutrient inputs (Pilotto et al. 2025). The sustained soil phosphatase activity observed in U-ACP treatments suggests enhanced microbial phosphorus cycling capacity, creating a positive feedback loop that amplifies nutrient availability beyond the direct chemical supply from the nanocomposite matrix. The improved phosphorus nutrition likely contributed to the enhanced nitrogen acquisition observed in U-ACP treatments, as phosphorus is essential for energy transfer processes involved in nitrogen assimilation and protein synthesis. The reduced variability in biomass production observed with U-ACP treatment is an important agronomic benefit that translates to more predictable crop performance and reduced production risk. This consistency likely reflects the sustained nutrient availability provided by controlled release, which maintains adequate nutrition throughout critical growth periods and reduces the risk of nutrient deficiency stress that can occur between conventional fertiliser applications (Maaz et al. 2025).

4.5 | Soil Biological Function Is Enhanced Through Stable Chemical Conditions

The enhanced soil enzyme activities observed in U-ACP treatments provide evidence for higher soil biological function that extends beyond simple nutrient supply effects. The sustained elevation of urease, dehydrogenase and phosphatase activities throughout the experimental period indicates that U-ACP supports more active microbial communities compared to conventional fertilisation approaches that can cause periodic disturbance through rapid chemical changes. The maintenance of more stable soil pH conditions with U-ACP treatment likely contributes significantly to enhanced biological function, as soil pH is a master variable controlling microbial community composition and activity (Fierer and Jackson 2006). The buffering capacity provided by the calcium phosphate matrix prevents the rapid acidification associated with urea hydrolysis that can inhibit beneficial microbial groups and reduce overall biological activity.

The cumulative gene response analysis revealed treatment-specific patterns for nitrogen cycling processes that support the enhanced environmental performance observed in U-ACP treatments. Ammonia-oxidising bacteria (*amoA* AOB) and archaeal ammonia oxidisers (*amoA* AOA) showed no significant treatment differences. However, complete ammonia oxidisers (comammox) demonstrated significantly elevated cumulative response in U-ACP treatments compared to both control and urea applications ($p < 0.05$), suggesting that controlled nutrient release may favour organisms capable of performing complete nitrification within a single cell. Comammox bacteria exhibit oligotrophic lifestyles adapted to low, stable ammonia concentrations, with kinetic parameters indicating competitive advantages under substrate-limited conditions compared to canonical two-step nitrifiers (Kits et al. 2017). The controlled nitrogen release from U-ACP may create soil conditions that favour these organisms, potentially contributing to more efficient nitrogen transformation with reduced intermediary accumulation. The detection and quantification of comammox using targeted molecular approaches have revealed their widespread distribution in agricultural soils, though their functional importance relative to canonical nitrifiers remains context-dependent (Pjevac et al. 2017). The significantly enhanced comammox response in U-ACP treatments ($p < 0.05$) represents one of the most pronounced microbial community shifts observed in this study. This finding warrants further investigation, as comammox organisms have been increasingly recognised as important contributors to nitrification in agricultural soils. The ecological significance of comammox in agricultural systems may extend beyond their abundance to their functional role in maintaining efficient nitrogen cycling under variable substrate conditions (Kits et al. 2017). The elevated comammox gene abundance in clay loam soils suggests enhanced nitrification activity, which may contribute to N_2O production via the nitrifier-denitrification pathway. The combination of higher urease activity, better moisture retention and abundant NH_4^+ substrate in clay soils creates conditions favourable for nitrification-derived N_2O, particularly during the transition periods between aerobic and anaerobic conditions characteristic of fine-textured soils. However, their ability to perform complete ammonia oxidation to nitrate within a single cell eliminates the need for nitrite exchange between different microbial populations, potentially reducing opportunities for

nitrite accumulation and associated N_2O production through nitrifier denitrification pathways.

While individual denitrification genes (*nirK*, *nirS*, *norB*, *nosZ* Clade I and II) showed no significant treatment effects, the improved *nosZ*:*nirK* ratio in U-ACP treatments provides mechanistic insight into the reduced N_2O emissions observed in gas flux measurements. This suggests that U-ACP maintains a more balanced denitrification pathway where N_2O reduction capacity better matches N_2O production capacity, rather than dramatically increasing absolute *nosZ* abundance. The temporal analysis revealed relatively stable gene abundances across treatments, with U-ACP primarily influencing the relative proportions of functional guilds rather than causing dramatic shifts in individual gene abundances.

Phosphorus cycling capacity, assessed through alkaline phosphatase (*phoD*) gene abundance, showed significant treatment effects with U-ACP treatments maintaining elevated cumulative responses compared to control treatments. This sustained phosphatase activity reflects the dual-nutrient nature of the U-ACP nanofertiliser, providing both nitrogen and phosphorus components that stimulate microbial phosphorus cycling processes. The temporal analysis revealed gradual increases in normalised *phoD* abundance over time, with U-ACP treatments exhibiting the most pronounced and sustained responses, suggesting progressive stimulation of phosphatase-producing microorganisms throughout the experimental period.

4.6 | Implications for Sustainable Agriculture and Climate Change Mitigation

The results of this study demonstrate that U-ACP, and potentially other nanocomposites, may address multiple sustainability challenges simultaneously, providing an example of a technology that achieves the *win-win* scenario of maintained productivity with reduced environmental impact. The reductions in nitrogen-containing gas emissions, contribute directly to air pollution and climate change mitigation goals, while the reduced leaching addresses water quality concerns that represent a major environmental challenge in intensive agricultural regions. Agricultural nitrogen management represents one of the most cost-effective greenhouse gas mitigation strategies available, with improved nitrogen use efficiency offering substantial climate benefits alongside productivity maintenance (Gu et al. 2023). The nitrogen cascade framework emphasises that interventions reducing nitrogen losses provide multiplicative environmental benefits by preventing sequential impacts across atmospheric, terrestrial and aquatic systems (Galloway et al. 2003). The performance of U-ACP compared to existing commercial alternatives suggests potential for improving upon current best management practices. While technologies like nitrification-inhibition represent improvements over conventional fertilisers, they do not achieve the comprehensive benefits demonstrated by U-ACP across multiple environmental metrics. This performance advantage validates the controlled-release approach and suggests that nanofertiliser technologies may represent the next generation of sustainable fertiliser solutions. The enhanced nitrogen acquisition achieved with U-ACP creates opportunities for reduced fertiliser application rates while maintaining yields, potentially providing economic benefits to farmers while amplifying environmental gains. The soil-specific responses observed throughout this study demonstrate that U-ACP benefits are greatest in soils with the highest intrinsic nutrient loss potential, indicating targeting of environmental benefits where they are most needed.

4.7 | Limitations and Future Research Directions

The pot- and microcosm-based experimental system, while allowing precise control and measurement, may not fully represent field conditions including spatial heterogeneity, weather variability and longer-term soil-crop interactions. Pot experiments commonly demonstrate enhanced treatment effects compared to field trials due to restricted rooting volumes that intensify plant-soil-fertiliser interactions, necessitating cautious extrapolation to field scales (Poorter et al. 2012). The effects observed here, particularly regarding leaching reduction and nitrogen retention, may be amplified relative to field conditions, where lateral water movement and larger soil volumes buffer concentration gradients. Field validation studies will be essential to confirm the benefits observed under controlled conditions and assess performance under commercial agricultural conditions. The 8-week experimental duration, while appropriate for lettuce production, limits conclusions about longer-term effects on soil properties and microbial communities. Extended studies examining multiple growing seasons will be needed to assess the sustainability of observed benefits and potential cumulative effects on soil health. The focus on lettuce as a model crop provides proof-of-concept data but limits generalisability to other crop species with different growth patterns and nutrient requirements. Long-term monitoring of soil health indicators and comprehensive lifecycle assessment of environmental impacts will be essential.

Additionally, the economic viability of U-ACP for commercial agriculture requires evaluation. Current nanoparticle synthesis costs may initially favour application in high-value cropping systems, though economies of scale and simplified production methods could expand applicability. Cost-benefit analyses incorporating the environmental externalities avoided through reduced nitrogen losses would provide a more complete economic assessment. Future research priorities should include field-scale validation studies, detailed economic analysis of adoption potential, optimisation of synthesis methods for commercial production and development of application technologies suitable for existing agricultural equipment.

Finally, the environmental fate and potential risks of engineered nanoparticles in agricultural systems require continued investigation (Servin and White 2016). While calcium phosphate nanoparticles represent biocompatible materials with natural soil analogues, systematic assessment of nanoparticle persistence, transformation and ecological effects remains necessary for regulatory approval and farmer acceptance (Fraceto et al. 2016). The controlled dissolution characteristics observed in this study suggest limited nanoparticle persistence beyond the growing season, though long-term accumulation effects warrant extended monitoring trials.

Author Contributions

Jessica Chadwick: investigation, methodology, formal analysis, visualisation, writing – original draft. **Jingyi Shi:** investigation. **Megan L. Purchase:** investigation, writing – review and editing. **Peng Zhang:**

investigation, writing – review and editing. **Iseult Lynch:** supervision, funding acquisition, writing – review and editing. **Sami Ullah:** supervision, funding acquisition, writing – review and editing. **Deying Wang:** investigation, writing – review and editing. **Ryan M. Mushinski:** supervision, conceptualisation, funding acquisition, methodology, investigation, project administration, writing – review and editing.

Acknowledgements

Jessica Chadwick was supported by the UKRI Biotechnology and Biological Sciences Research Council (BBSRC) and the Midlands Integrative Biosciences Training Partnership (MIBTP) grant number BB/T00746X/1. Megan L. Purchase was supported by the UKRI Natural Environment Research Council (NERC) as part of the Central England NERC Training Alliance (CENTA2), Grant No. NE/S007350/1 and NERC Pushing the Frontiers Grant No. UKRI1284. D.W. was supported by a BBSRC Responsive Mode Grant no. BB/X002187/1. We greatly appreciate the data produced by numerous undergraduate students at Warwick, through both the URSS programme and BS341. We thank Gary Grant and the Warwick phytobiology staff for help with glasshouse experiments. We also thank Dr James Town and the Polymer Research Technology Platform at Warwick for their help with TGA analysis.

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

All raw data is available in the Supporting Data File.

References

Beeckman, F., L. Annetta, M. Corrochano-Monsalve, T. Beeckman, and H. Motte. 2024. "Enhancing Agroecosystem Nitrogen Management: Microbial Insights for Improved Nitrification Inhibition." *Trends in Microbiology* 32, no. 6: 590–601. https://doi.org/10.1016/j.tim.2023.10.009.

Beretta-Blanco, A., O. Pérez, and L. Carrasco-Letelier. 2019. "Soil Quality Decrease Over 13 Years of Agricultural Production." *Nutrient Cycling in Agroecosystems* 114, no. 1: 45–55. https://doi.org/10.1007/s10705-019-09990-3.

Bijay-Singh, B., and E. Craswell. 2021. "Fertilizers and Nitrate Pollution of Surface and Ground Water: An Increasingly Pervasive Global Problem." *SN Applied Sciences* 3: 518. https://doi.org/10.1007/s42452-021-04521-8.

Cantarella, H., R. Otto, J. R. Soares, and A. G. B. Silva. 2018. "Agronomic Efficiency of NBPT as a Urease Inhibitor: A Review." *Journal of Advanced Research* 13: 19–27. https://doi.org/10.1016/j.jare.2018.05.008.

Carmona, F. J., G. Dal Sasso, G. B. Ramírez-Rodríguez, et al. 2021. "Urea-Functionalized Amorphous Calcium Phosphate Nanofertilizers: Optimizing the Synthetic Strategy Towards Environmental Sustainability and Manufacturing Costs." *Scientific Reports* 11, no. 1: 3419. https://doi.org/10.1038/s41598-021-83048-9.

Congreves, K. A., O. Otchere, D. Ferland, S. Farzadfar, S. Williams, and M. M. Arcand. 2021. "Nitrogen Use Efficiency Definitions of Today and Tomorrow." *Frontiers in Plant Science* 12: 637108. https://doi.org/10.3389/fpls.2021.637108.

Cowan, N., E. Carnell, U. Skiba, U. Dragosits, J. Drewer, and P. Levy. 2020. "Nitrous Oxide Emission Factors of Mineral Fertilisers in the UK and Ireland: A Bayesian Analysis of 20 Years of Experimental Data." *Environment International* 135: 105366. https://doi.org/10.1016/j.envint.2019.105366.

Ditta, A., and M. Arshad. 2016. "Applications and Perspectives of Using Nanomaterials for Sustainable Plant Nutrition." *Nanotechnology Reviews* 5, no. 2: 209–229. https://doi.org/10.1515/ntrev-2015-0060.

Dobermann, A. 2007. "Nutrient Use Efficiency: Measurement and Management." In *Fertilizer Best Management Practices: General Principles, Strategy for Their Adoption and Voluntary Initiatives vs Regulations*, 1–28. International Fertilizer Industry Association.

FAO. 2023. The State of Food Security and Nutrition in the World 2023. Food and Agriculture Organization of the United Nations. https://doi.org/10.4060/cc3017en.

Fierer, N., and R. B. Jackson. 2006. "The Diversity and Biogeography of Soil Bacterial Communities." *Proceedings of the National Academy of Sciences* 103, no. 3: 626–631. https://doi.org/10.1073/pnas.0507535103.

Fierer, N., J. A. Jackson, R. Vilgalys, and R. B. Jackson. 2005. "Assessment of Soil Microbial Community Structure by Use of Taxon-Specific Quantitative PCR Assays." *Applied and Environmental Microbiology* 71, no. 7: 4117–4120. https://doi.org/10.1128/AEM.71.7.4117-4120.2005.

Fraceto, L. F., R. Grillo, G. A. de Medeiros, V. Scognamiglio, G. Rea, and C. Bartolucci. 2016. "Nanotechnology in Agriculture: Which Innovation Potential Does It Have?" *Frontiers in Environmental Science* 4: 20. https://doi.org/10.3389/fenvs.2016.00020.

Gaiotti, F., M. Lucchetta, G. Rodegher, et al. 2021. "Urea-Doped Calcium Phosphate Nanoparticles as Sustainable Nitrogen Nanofertilizers for Viticulture: Implications on Yield and Quality of Pinot Gris Grapevines." *Agronomy* 11, no. 6: 1026. https://doi.org/10.3390/agronomy11061026.

Galloway, J. N., J. D. Aber, J. W. Erisman, et al. 2003. "The Nitrogen Cascade." *BioScience* 53, no. 4: 341–356. https://doi.org/10.1641/0006-3568(2003)053[0341:TNC]2.0.CO;2.

Gong, C., H. Tian, H. Liao, et al. 2024. "Global Net Climate Effects of Anthropogenic Reactive Nitrogen." *Nature* 632: 557–563. https://doi.org/10.1038/s41586-024-07714-4.

Gu, B., X. Zhang, S. K. Lam, et al. 2023. "Cost-Effective Mitigation of Nitrogen Pollution From Global Croplands." *Nature* 613: 77–84. https://doi.org/10.1038/s41586-022-05481-8.

Henneron, L., P. Kardol, D. A. Wardle, C. Cros, and S. Fontaine. 2020. "Rhizosphere Control of Soil Nitrogen Cycling: A Key Component of Plant Economic Strategies." *New Phytologist* 228: 1269–1282. https://doi.org/10.1111/nph.16760.

Hina, N. S. 2024. "Global Meta-Analysis of Nitrate Leaching Vulnerability in Synthetic and Organic Fertilizers Over the Past Four Decades." *Water* 16: 457. https://doi.org/10.3390/w16030457.

IPCC. 2021. *Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change*. Cambridge University Press.

Jones, C. M., A. Spor, F. P. Brennan, et al. 2014. "Recently Identified Microbial Guild Mediates Soil N_2O Sink Capacity." *Nature Climate Change* 4, no. 9: 801–805. https://doi.org/10.1038/nclimate2301.

Kits, K. D., C. J. Sedlacek, E. V. Lebedeva, et al. 2017. "Kinetic Analysis of a Complete Nitrifier Reveals an Oligotrophic Lifestyle." *Nature* 549, no. 7671: 269–272. https://doi.org/10.1038/nature23679.

Kottegoda, N., C. Sandaruwan, G. Priyadarshana, et al. 2017. "Urea-Hydroxyapatite Nanohybrids for Slow Release of Nitrogen." *ACS Nano* 11, no. 2: 1214–1221. https://doi.org/10.1021/acsnano.6b07781.

Kuypers, M. M. M., H. K. Marchant, and B. Kartal. 2018. "The Microbial Nitrogen-Cycling Network." *Nature Reviews Microbiology* 16, no. 5: 263–276. https://doi.org/10.1038/nrmicro.2018.9.

Ladha, J. K., A. Tirol-Padre, C. K. Reddy, et al. 2016. "Global Nitrogen Budgets in Cereals: A 50-year Assessment for Maize, Rice and Wheat Production Systems." *Scientific Reports* 6: 19355. https://doi.org/10.1038/srep19355.

Li, X., and Z. Li. 2024. "Global Trends and Current Advances in Slow/Controlled-Release Fertilizers: A Bibliometric Analysis From 1990 to

2023." *Agriculture (London)* 14: 1502. https://doi.org/10.3390/agriculture14091502.

Liu, R., and R. Lal. 2015. "Potentials of Engineered Nanoparticles as Fertilizers for Increasing Agronomic Productions." *Science of the Total Environment* 514: 131–139. https://doi.org/10.1016/j.scitotenv.2015.01.104.

Lü, H., X. Wang, Z. Pan, and S. Zhao. 2023. "Assessment of the Crucial Factors Influencing the Responses of Ammonia and Nitrous Oxide Emissions to Controlled Release Nitrogen Fertilizer: A Meta-Analysis." *Journal of Integrative Agriculture* 22, no. 11: 3549–3559. https://doi.org/10.1016/j.jia.2023.07.008.

Maaz, T. M., A. Dobermann, S. E. Lyons, and A. M. Thomson. 2025. "Review of Research and Innovation on Novel Fertilizers for Crop Nutrition." *npj Sustainable Agriculture* 3: 25. https://doi.org/10.1038/s44264-025-00066-0.

Morales-Cámara, S., B. Parra-Torrejón, A. Rodríguez-Diéguez, J. M. Delgado-López, G. B. Ramírez-Rodríguez, and S. Rojas. 2024. "ZIF-8@Hydroxyapatite Composite as a High Potential Material for Prolonged Delivery of Agrochemicals." *ACS Applied Materials & Interfaces* 16, no. 22: 29305–29313. https://doi.org/10.1021/acsami.4c06016.

Omara, P., L. Aula, F. Oyebiyi, and W. R. Raun. 2019. "World Cereal Nitrogen Use Efficiency Trends: Review and Current Knowledge." *Agrosystems, Geosciences & Environment* 2, no. 1: 1–8. https://doi.org/10.2134/age2018.10.0045.

Pan, B., S. K. Lam, A. Mosier, Y. Luo, and D. Chen. 2016. "Ammonia Volatilization From Synthetic Fertilizers and Its Mitigation Strategies: A Global Synthesis." *Agriculture, Ecosystems & Environment* 232: 283–289. https://doi.org/10.1016/j.agee.2016.08.019.

Pérez-Álvarez, E. P., G. B. Ramírez-Rodríguez, F. J. Carmona, et al. 2021. "Towards a More Sustainable Viticulture: Foliar Application of N-Doped Calcium Phosphate Nanoparticles on Tempranillo Grapes." *Journal of the Science of Food and Agriculture* 101, no. 4: 1307–1313. https://doi.org/10.1002/jsfa.10738.

Pilotto, L., F. Scalera, C. Piccirillo, et al. 2025. "Phosphorus Release From Nano-Hydroxyapatite Derived From Biowastes in the Presence of Phosphate-Solubilizing Bacteria: A Soil Column Experiment." *Journal of Agricultural and Food Chemistry* 73, no. 7: 3918–3929. https://doi.org/10.1021/acs.jafc.4c09325.

Pjevac, P., C. Schauberger, L. Poghosyan, et al. 2017. "AmoA-Targeted Polymerase Chain Reaction Primers for the Specific Detection and Quantification of Comammox Nitrospira in the Environment." *Frontiers in Microbiology* 8: 1508. https://doi.org/10.3389/fmicb.2017.01508.

Poorter, H., J. Bühler, D. van Dusschoten, J. Climent, and J. A. Postma. 2012. "Pot Size Matters: A Meta-Analysis of the Effects of Rooting Volume on Plant Growth." *Functional Plant Biology* 39, no. 11: 839–850. https://doi.org/10.1071/FP12049.

Purchase, M. L., G. D. Bending, and R. M. Mushinski. 2023. "Spatio-temporal Variations of Soil Reactive Nitrogen Oxide Fluxes Across the Anthropogenic Landscape." *Environmental Science & Technology* 57: 16348–16360. https://doi.org/10.1021/acs.est.3c05849.

Ramírez-Rodríguez, G. B., C. Miguel-Rojas, G. S. Montanha, et al. 2020. "Reducing Nitrogen Dosage in Triticum Durum Plants With Urea-Doped Nanofertilizers." *Nanomaterials* 10, no. 6: 1043. https://doi.org/10.3390/nano10061043.

Rathbone, C., and S. Ullah. 2024. "Ammonia Emissions From Nitrogen Fertilised Agricultural Soils: Controlling Factors and Solutions for Emission Reduction." *Environmental Chemistry* 21, no. 1. https://doi.org/10.1071/EN23010.

Raza, S., K. Zamanian, S. Ullah, Y. Kuzyakov, I. Virto, and J. Zhou. 2021. "Inorganic Carbon Losses by Soil Acidification Jeopardize Global Efforts on Carbon Sequestration and Climate Change Mitigation." *Journal of Cleaner Production* 315: 128036. https://doi.org/10.1016/j.jclepro.2021.128036.

Ruser, R., and R. Schulz. 2015. "The Effect of Nitrification Inhibitors on the Nitrous Oxide (N_2O) Release From Agricultural Soils—A Review." *Journal of Plant Nutrition and Soil Science* 178, no. 2: 171–188. https://doi.org/10.1002/jpln.201400251.

Schroder, J. L., H. Zhang, K. Girma, W. R. Raun, C. J. Penn, and M. E. Payton. 2011. "Soil Acidification From Long-Term Use of Nitrogen Fertilizers on Winter Wheat." *Soil Science Society of America Journal* 75, no. 3: 957–964. https://doi.org/10.2136/sssaj2010.0187.

Servin, A. D., and J. C. White. 2016. "Nanotechnology in Agriculture: Next Steps for Understanding Engineered Nanoparticle Exposure and Risk." *NanoImpact* 1: 9–12. https://doi.org/10.1016/j.impact.2015.12.002.

Sharma, B., M. Shrivastava, L. O. B. Afonso, U. Soni, and D. M. Cahill. 2022. "Metal Doped Nitrogenous Hydroxyapatite Nanohybrids Slowly Release Nitrogen to Crops and Mitigate Ammonia Volatilization: An Impact Assessment." *NanoImpact* 28: 100424. https://doi.org/10.1016/j.impact.2022.100424.

Tamagno, S., A. J. Eagle, E. L. McLellan, et al. 2022. "Quantifying N Leaching Losses as a Function of N Balance: A Path to Sustainable Food Supply Chains." *Agriculture, Ecosystems & Environment* 324: 107714. https://doi.org/10.1016/j.agee.2021.107714.

Tang, Y. S., C. F. Braban, U. Dragosits, et al. 2018. "Drivers for Spatial, Temporal and Long-Term Trends in Atmospheric Ammonia and Ammonium in the UK." *Atmospheric Chemistry and Physics* 18, no. 2: 705–733. https://doi.org/10.5194/acp-18-705-2018.

Wang, C., Y. Shen, X. Fang, et al. 2024. "Reducing Soil Nitrogen Losses From Fertilizer Use in Global Maize and Wheat Production." *Nature Geoscience* 17: 1008–1015. https://doi.org/10.1038/s41561-024-01542-x.

Whetton, R. L., M. A. Harty, and N. M. Holden. 2022. "Communicating Nitrogen Loss Mechanisms for Improving Nitrogen Use Efficiency Management, Focused on Global Wheat." *Nitrogen* 3, no. 2: 213–246. https://doi.org/10.3390/nitrogen3020016.

Wu, K., W. Li, F. Ma, et al. 2024. "Urea-Loaded Core–Shell MOF/Silica Nanocarriers for Continuous Nitrogen Release to Crops." *ACS Applied Nano Materials* 7, no. 10: 11645–11654. https://doi.org/10.1021/acsanm.4c01187.

Xun, W., Y. Liu, A. Ma, et al. 2024. "Dissection of Rhizosphere Microbiome and Exploiting Strategies for Sustainable Agriculture." *New Phytologist* 242: 2401–2410. https://doi.org/10.1111/nph.19697.

Yoon, H. Y., J. G. Lee, L. D. Esposti, et al. 2020. "Synergistic Release of Crop Nutrients and Stimulants From Hydroxyapatite Nanoparticles Functionalized With Humic Substances: Toward a Multifunctional Nanofertilizer." *ACS Omega* 5, no. 12: 6598–6610. https://doi.org/10.1021/acsomega.9b04354.

Yu, X., C. Keitel, and F. A. Dijkstra. 2023. "Ameliorating Soil Acidity With Calcium Carbonate and Calcium Hydroxide: Effects on Carbon, Nitrogen, and Phosphorus Dynamics." *Journal of Soil Science and Plant Nutrition* 23: 5270–5278. https://doi.org/10.1007/s42729-023-01400-6.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.
UACP SI. Supplementary raw data complete.