

Review

The Status of Plasma Induced Acidification and Its Valorising Potential on Slurries and Digestate: A Review

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Abstract

This review examines the current status and future potential of plasma-induced acidification (PIA) as a sustainable method for managing nitrogen-rich organic waste streams such as livestock slurry and digestate. Conventional acidification using sulfuric or nitric acid reduces ammonia (NH_3) emissions but raises concerns related to safety, cost, and environmental impacts. Plasma-assisted systems offer an alternative by generating reactive nitrogen and oxygen species (RNS/ROS) in situ, lowering pH and stabilizing ammonia (NH_3), as ammonium (NH_4^+), thereby enhancing fertiliser value and reducing emissions of NH_3 , methane (CH_4), and odours. Key technologies such as dielectric barrier discharge (DBD), corona discharge, and gliding arc reactors show promise in laboratory-scale studies, but barriers like energy consumption, scalability, and N_2O trade-offs limit commercial adoption. The paper reviews the mechanisms behind PIA, compares it to conventional approaches, and assesses its agronomic and environmental benefits. Valorisation opportunities, including the recovery of nitrate-rich fractions and integration with biogas systems, align plasma treatment with circular economy goals. However, challenges remain, including reactor design, energy efficiency, and lack of recognition as a Best Available Technique (BAT). A roadmap is proposed for transitioning from lab to farm-scale application, involving cross-sector collaboration, lifecycle assessments, and policy support to accelerate adoption and realise environmental and economic gains.

Keywords: plasma; acidification; valorisation effect; organic fertilisers; ammonia mitigation; sustainable agriculture; nitrogen fixation; reactive nitrogen species



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1. Introduction

The global push for more sustainable food production systems has intensified the spotlight on the environmental impacts of livestock farming, particularly the management of slurry and digestates. Collectively, these organic fertilisers are increasingly produced and applied across agriculture, horticulture, forestry, and land restoration, valued for their capacity to complement mineral fertilisers and improve soil fertility [1]. For instance, in the UK alone, it is estimated that close to 2 million tonnes of digestate are produced each year, equivalent to approximately 92,000 tonnes of nitrogen entering agricultural soils [2]. Studies show that these renewable fertilisers can raise the mineral fertiliser equivalent (MFE) by about 26 kg fertiliser N, equating to an average increase in nitrogen supply of

around 43% [3–5]. The MFE metric allows comparison of the nutrient performance of bio-based fertilisers relative to standard mineral fertilisers [6].

Despite these clear benefits, the management of ammonia (NH_3) emissions from animal slurry and digestates remain a significant challenge. Uncontrolled volatilisation not only reduces fertiliser value but also contributes to air pollution, ecosystem acidification, and indirect greenhouse gas formation [7]. Conventional acidification using strong acids, such as sulphuric acid, has been widely applied to lower slurry pH and stabilize ammonia [8]. While proven effective, these approaches raise concerns about operational safety, potential risks of foaming, slurry quality degradation, and downstream soil or water acidification [8].

An alternative mitigation system involves introducing reactive nitrogen species (RNS) such as nitric oxide (NO) and nitrogen dioxide (NO_2) directly into the slurry. Research by Ingels [8] and Nyvold and Dorsch [9] shows that RNS can lower slurry pH and promote the formation of ammonium nitrate (NH_4NO_3), thereby enhancing the proportion of stable ammonium ions relative to volatile ammonia. Chen et al. [10] report that this equilibrium shift can result in NH_3 emission reductions ranging from 15% to 98%, depending on factors like additive pH, slurry type, and treatment timing. Moreover, RNS pathways may enhance the fertiliser value of slurry by boosting nutrient accessibility, including nitrogen and phosphorus, while potentially influencing microbial communities involved in nutrient cycling [11,12].

Building on this concept, plasma-assisted nitrogen fixation and acidification have emerged as promising innovations in sustainable nitrogen management. Non-thermal plasma systems—including Radio Frequency (RF) discharge, Dielectric Barrier Discharge (DBD), Corona Discharge, and DC Glow Discharge—generate reactive nitrogen species (RNS) and reactive oxygen species (ROS) in situ. Originally explored as decentralised alternatives to the Haber–Bosch process [13,14], these plasma technologies are now being adapted for direct environmental applications, particularly for the treatment of ammonia-rich agricultural effluents [15].

Consequently, Plasma-Induced Acidification (PIA) has emerged as a key derivative application of these plasma systems, utilising plasma-generated RNS and ROS to achieve controlled acidification of livestock slurry and digestate. In PIA, nitrogen oxides formed in the plasma phase dissolve into the liquid matrix to produce nitric (HNO_3) and nitrous (HNO_2) acids, leading to a reduction in pH, stabilisation of nitrogen, and suppression of gaseous ammonia (NH_3) and methane (CH_4) emissions during storage. By leveraging the acid-forming potential of plasma-activated species, PIA enables on-site acidification without reliance on externally produced mineral acids, offering a decentralised, low-carbon approach to nutrient preservation and emission control. Accordingly, recent studies have demonstrated that introducing plasma-derived RNS into slurry through PIA can substantially reduce volatile losses while improving the mineral fertiliser efficiency of organic fertilisers [9].

However, these benefits are tempered by well-known challenges, chiefly the energy demands associated with plasma processes [9,15]. As Tripathi et al. [16] point out, the growing availability of renewable energy sources may help mitigate these costs, but it remains critical to understand the reaction kinetics, energy requirements, and system-level life cycle impacts. Practical upscaling pathways must consider reactor design, maintenance needs, integration with biogas plants, and the environmental trade-offs of shifting from chemical reagents to electrical power [17,18].

Detailed research is therefore needed to establish robust techno-economic and environmental benchmarks for PIA. This includes a clearer understanding of how RNS interact with the heterogeneous chemical and microbial composition of slurry and digestate, the

impact on heavy metals, and pathogen loads, when these treated materials are applied as bio-fertilisers [19,20].

Against this backdrop, this review aims to critically evaluate the status of PIA, its mechanistic underpinnings, environmental performance, potential for enhancing the value of organic fertilisers, and its integration into circular nutrient management frameworks. It highlights the opportunities and the unresolved questions that must be addressed to advance this innovation from laboratory studies to farm-scale application supporting a more productive, and climate-smart agricultural future.

2. Problem Definition and Current Mitigation Landscape

2.1. Ammonia Emission Sources and Current Mitigation Techniques

One of the proposed benefits of PIA is its potential to mitigate ammonia emissions. To appreciate this benefit, it is worthwhile evaluating the scale of the problem and the current practices and techniques employed to mitigate the ammonia emissions. Table 1 below provides a general overview of the various sources of ammonia emissions particularly within the agriculture sector, probable mitigation techniques and their respective challenges and contribution. Ammonia (NH_3) emissions from agricultural practices remain a significant environmental challenge, contributing to air pollution, eutrophication, and biodiversity loss while also resulting in substantial nitrogen losses that reduce fertiliser efficiency and farm profitability. As summarized in Table 1, multiple mitigation techniques have been trialled to reduce NH_3 emissions across various stages of livestock and crop production each with distinct effectiveness, operational barriers, and practical opportunities for adoption.

For example, dietary manipulation can cut emissions by up to 74% [21] but demands precise feed management and higher input costs. Physical covers for slurry storage and closed-slot injection into soils have shown reductions ranging from 70% to over 90% [22,23], yet these approaches are often limited by high capital or maintenance costs and site-specific feasibility. Slurry acidification, a well-established technique, consistently achieves up to 95% NH_3 emission reduction [23,24] but introduces risks related to acid handling, potential corrosion, and soil acidification when not properly managed.

In parallel, technologies like urease inhibitors and coating-based fertilisers offer moderate emission reductions (50–70%) but can vary widely in performance depending on local conditions [25,26]. More advanced options, like air scrubbers and biofilters, deliver high removal efficiencies for ventilation air but come with substantial installation, maintenance, and energy demands [27].

PIA may offer a multi-functional pathway with the potential to complement or even outperform conventional acidification methods. However, the feasibility of any mitigation option depends on cost-effectiveness, practical constraints, and farmer acceptance. Plasma systems currently face challenges of high energy demand like the persistent hurdles in plasma-based nitrogen fixation pathways and require further innovation to match the simplicity and affordability of traditional acidification, storage covers, or mechanical injections.

Table 1. Overview of ammonia emissions sources in agriculture, mitigation techniques and their respective challenges and opportunities.

Emission Source/Stage	Current Mitigation Technique(s)	Typical Challenges	Opportunities/Effectiveness	References
Feed and Animal Housing (Cattle, Pigs, Poultry)	- Dietary manipulation (lower crude protein, amino acid supplementation)—Urine–faeces segregation—Improved floor design and frequent slurry removal—Ventilation and humidity control	High feed cost; infrastructure modification; increased labour and equipment needs; limited retrofitting feasibility	Reduces NH ₃ emissions by 10–74%; improves feed efficiency, animal welfare, and indoor air quality	[20,26–28]
Slurry Storage and Handling	- Physical covers (solid, flexible, or oil layers)—Slurry acidification (e.g., sulphuric acid)—Solid–liquid separation—Anaerobic digestion for biogas recovery—Air scrubbers and biofilters	High capital and maintenance cost; acid safety and corrosion issues; potential foaming; energy demand	Achieves 40–95% NH ₃ reduction; reduces odours and conserves N; potential for renewable energy recovery	[21,23,26,29,30]
Field Application of Slurry/Digestate	- Closed-slot or deep injection—Band spreading and soil incorporation	Requires specialized machinery; limited feasibility on some soils; higher operational cost	Reduces NH ₃ volatilisation by 22–99%; improves N retention and crop uptake	[21,22,29]
Synthetic Fertiliser Use	- Urease inhibitors—Controlled-release or coated fertilisers—Deep placement of urea or ammonium fertilisers	High cost; variable effectiveness under different soils and climates; user training required	50–90% NH ₃ reduction; improved nitrogen use efficiency and reduced losses	[24,27]
Poultry Litter and Solid Manure	- Litter amendments (alum, zeolites)—Composting under controlled conditions	Cost of additives; risk of soil acidification if misapplied; potential N loss during composting	Reduces NH ₃ emissions by 40–73%; odour control and pathogen reduction	[31–33]

The question remains whether to address the challenges associated with the already implemented techniques or to introduce newer techniques such as PIA, which is at its infancy and likely to present its own challenges. In light of the persistent challenge of ammonia emissions and the varied effectiveness of existing mitigation strategies, it is increasingly evident that aligning both current and emerging technologies will be essential to achieving sustained, system-wide reductions in nitrogen losses. While established methods have delivered measurable benefits, their limitations, whether technical, economic, or environmental—highlight the need for continued innovation. PIA, though still in early development, offers a mechanistically distinct and potentially transformative pathway. By enabling in situ generation of reactive species without reliance on corrosive acids, it introduces new possibilities for safer, more controllable, and environmentally compatible nitrogen stabilization. Realizing its full potential will require sustained research and development, pilot deployment, and techno-economic validation. However, its forward-looking capabilities suggest that it could become a cornerstone technology in next-generation nitrogen management systems.

2.2. Fundamentals of Slurry and Digestate Management

The composition and characteristics of slurry and digestate may vary widely depending on animal type, feed regime, slurry handling practices, and subsequent treatment steps. Livestock slurry typically contains a large fraction of nitrogen in the ammonium form, which is highly susceptible to volatilisation if not properly stabilised [34]. Digestate, the residue left after anaerobic digestion generally has a higher concentration of mineralised ammonium nitrogen due to the breakdown of organic nitrogen, alongside residual organic matter and trace contaminants [3].

These properties affect storage, transport, and land application strategies. As Zielinska and Bulkowska [33] noted, the physical state (solid and liquid fractions), pH, dry matter content, and macro- and micronutrient profiles all influence how effectively nutrients can be recycled and what environmental risks must be mitigated. For example, elevated ammonia concentrations mean that significant nitrogen can be lost to the atmosphere if emission control measures are not employed, undermining the fertiliser value and contributing to regional air quality problems.

To address these challenges, a combination of current treatment and valorisation methods is widely used. Anaerobic Digestion (AD) remains the principal approach for organic waste stabilisation and renewable energy recovery through biogas production [35,36]. However, the process also increases the proportion of nitrogen in ammonium form, exacerbating the risk of NH_3 emissions during post-digestion handling and storage if not properly treated.

Beyond AD, composting is often used to further stabilise the digestate, reduce moisture content, and suppress pathogens and odours [33]. Nevertheless, if not tightly controlled, composting can inadvertently result in additional nitrogen losses, offsetting the intended environmental benefits. Similarly, chemical amendments, including acidification and nutrient recovery technologies such as struvite precipitation, have gained traction for capturing valuable nutrients and minimising emissions [37,38].

Regulatory and policy drivers add further complexity to slurry and digestate management decisions. EU frameworks like the Nitrates Directive and the National Emission Ceilings (NEC) Directive as well as the UK's Environment Land Management Scheme strongly encourage technologies that mitigate ammonia losses and nitrate pollution [39]. At the same time, policy inconsistencies and gaps in standardisation for digestate quality particularly in relation to heavy metals and pathogen thresholds create uncertainties that can deter investment in advanced treatment solutions [33,40].

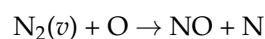
Despite technical advances, critical gaps remain. Nutrient recovery technologies have yet to achieve significant commercial scale, hindered by high energy requirements, complex integration needs, and limited market support for recovered nutrient products. Many farms lack the infrastructure to combine AD, composting, and chemical recovery processes efficiently, leading to fragmented systems that fall short of realising a closed nutrient loop. Recent work emphasises the importance of robust Life Cycle Analysis (LCA) to quantify the net environmental benefits and trade-offs of these technologies, as energy demands and operational complexity can offset gains in emissions reductions if not properly managed [41].

While slurry acidification with conventional acids primarily sulphuric acid—remains an effective mitigation practice, it is not without drawbacks. Issues such as foaming, equipment corrosion, soil acidification, and worker safety underline the need for innovative pathways that can retain nitrogen, reduce greenhouse gases, and improve overall system sustainability. It is therefore not surprising that PIA is being explored as an alternative.

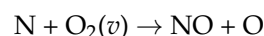
3. Fundamentals and Mechanistic Insights into Plasma Systems for Plasma-Induced Acidification

PIA leverages the unique reactivity of non-thermal plasma technologies to generate reactive nitrogen and oxygen species (RNS, ROS) that interact with volatile ammonia and carbonate species in livestock slurry and digestate, driving pH reduction and enhancing nutrient retention.

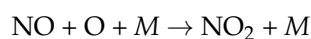
In non-thermal plasma environments, energetic electrons collide with N_2 and O_2 molecules, promoting them to vibrationally excited states (denoted $N_2(v)$, $O_2(v)$) or dissociating them into atomic radicals (N and O). These vibrationally excited species act as pre-activated intermediates, lowering the effective activation barrier for nitrogen bond cleavage and subsequent NO formation. The dominant reaction route follows a vibrationally enhanced Zeldovich mechanism, wherein excited N_2 reacts with atomic oxygen to form nitric oxide:



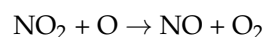
The nascent nitrogen atom then participates in secondary oxidation Via:



These reactions are strongly promoted by the vibrational excitation of N_2 , which reduces the activation barrier for dissociation by up to an order of magnitude relative to ground-state reactions [12,42]. Once formed, NO is further oxidized to NO_2 Via a termolecular recombination reaction:



while partial reduction to NO may occur through:



These interconversions establish a dynamic equilibrium between NO and NO_2 depending on plasma energy density and residence time. The resulting NO_x species dissolve into the liquid phase, producing nitrous (HNO_2) and nitric (HNO_3) acids, which acidify the slurry and shift the equilibrium toward ammonium (NH_4^+) rather than volatile ammonia (NH_3), thereby enhancing nitrogen retention and minimizing gaseous losses [43].

Non-thermal plasma systems including microwave discharges, gliding-arc plasmas, dielectric-barrier discharge (DBD) reactors, corona discharges, and radiofrequency (RF) discharges have shown significant promise for decentralized NO_x synthesis and ammonia emis-

sion control [9,44]. Unlike historical thermal plasma approaches such as the Birkeland–Eyde (B–E) arc process—which suffered from high energy penalties of $2.4\text{--}3.1\text{ MJ mol}^{-1}\text{ N}$ [11]—modern non-thermal plasmas sustain high-energy electrons at near-ambient bulk gas temperatures. This enables the selective excitation and oxidation of N_2 without degrading the sensitive biological and chemical integrity of slurry or digestate. DBD and corona-discharge reactors are among the most scalable and practical configurations for pilot- or farm-scale use, offering operational simplicity, modularity, and proven capacity for treating gaseous exhausts or open slurry storage systems [45,46].

3.1. Mechanisms and Kinetic Constraints of Plasma-Induced Acidification

In non-thermal plasma, energetic electrons initiate a coupled network of RNS and ROS reactions. Vibrationally and electronically excited N_2 and O_2 species form NO and NO_2 through the reactions outlined above, after which these gas-phase products dissolve into the aqueous phase. Their uptake and hydrolysis yield HNO_2 and HNO_3 ($2\text{ NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3$; $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{ HNO}_2$), which dissociate to $\text{NO}_2^-/\text{NO}_3^-$ and H^+ ($\text{HNO}_2 \rightleftharpoons \text{NO}_2^- + \text{H}^+$; $\text{HNO}_3 \rightleftharpoons \text{NO}_3^- + \text{H}^+$), driving acidification.

Concurrently, electronic and photolytic processes activate water and oxygen to form oxidizing species including ozone (O_3), hydroxyl radicals ($\bullet\text{OH}$), superoxide ($\text{O}_2\bullet^-$), hydroperoxyl ($\text{HO}_2\bullet$), and hydrogen peroxide (H_2O_2). Radical recombination ($2\bullet\text{OH} \rightarrow \text{H}_2\text{O}_2$) and peroxide reactions ($\text{H}_2\text{O}_2 + \text{O}_3 \rightarrow \bullet\text{OH} + \text{HO}_2\bullet + \text{O}_2$) regenerate $\bullet\text{OH}$, sustaining oxidation potential. The coupled NO_x/O_x chemistry further produces peroxyxynitrite ($\text{NO}\bullet + \text{O}_2\bullet^- \rightarrow \text{ONOO}^-$) and its conjugate acid (ONOOH), which decomposes to $\bullet\text{OH}$ and $\bullet\text{NO}_2$. In acidic media, ONOOH can also form via $\text{NO}_2^- + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{ONOOH} + \text{H}_2\text{O}$. Over seconds to minutes, short-lived radicals decay while H_2O_2 , NO_3^- , O_3 , and excess H^+ accumulate, establishing the sustained acidification and oxidizing character of plasma-activated liquids.

3.2. Physico-Chemical Processes and Reactor Configurations

The physico-chemical processes underlying PIA are strongly influenced by plasma type, discharge geometry, and operational parameters. PIA involves the generation of NO_x and oxidizing agents like ozone (O_3) and hydroxyl radicals ($\bullet\text{OH}$). These species, produced through electron-impact reactions, interact with ammonia either in the gaseous phase or at the liquid–gas interface [46]. In humid conditions, O_3 and $\bullet\text{OH}$ enhance the breakdown of carbonates and organic buffering agents, further contributing to the observed pH reduction.

Different non-thermal plasma configurations—including DBD, corona discharge, gliding arc, and RF reactors—offer distinct advantages for decentralized treatment. Their modularity and scalability make them well suited for farm-level integration, allowing effective treatment of gaseous emissions or open slurry systems without external acid dosing. The cascade of radical-driven reactions differentiates plasma treatment from direct acid addition, yielding self-sustaining acidification governed by plasma chemistry and gas–liquid transfer dynamics.

3.3. Plasma-Activated Liquids (PAL): Composition and Function

The nitrogen oxides (NO_x) generated by air plasma undergo a series of aqueous-phase reactions upon entering plasma-activated water (PAW), forming a mixture rich in reactive oxygen and nitrogen species (RONS) such as nitrate (NO_3^-), nitrite (NO_2^-), hydrogen peroxide (H_2O_2), and peroxyxynitrite (ONOO^-). When this plasma treatment is extended beyond pure water to more complex matrices—such as slurries, digestates, or wastewater—the resulting medium is referred to as plasma-activated liquid (PAL). PAL therefore represents a broader category of plasma-treated liquids that include organic and nutrient-rich substrates, where plasma-generated oxidants and nitrogen species interact with ammonia, carbon compounds, and buffering agents to yield nitrate-enriched, acidified products [10,47].

While PAW and PAL differ mainly in chemical complexity and matrix composition, both provide the reactive nitrogen and acid-forming basis that underpins PIA. In agricultural contexts, PAL produced through air plasma exposure drives the same acidification mechanisms that are intentionally exploited in PIA—namely, the conversion of plasma-derived nitrogen oxides into nitric acid species that stabilise nitrogen, suppress ammonia volatilisation, and mitigate methane emissions. The reaction pathways linking these processes particularly the transformation of NO and NO₂ into HNO₂ and HNO₃ and their equilibrium with transient radicals are summarised in Figure 1, illustrating how PAW and PAL chemistry collectively form the mechanistic foundation of PIA [48,49].

PAL provides a platform for nitrogen fixation from waste streams such as soil residues and livestock effluent. As demonstrated by Graves et al. [50], NO_x species in PAL can react with ammonia (NH₃) to form ammonium nitrate (NH₄ NO₃), a valuable nitrogen fertiliser, thereby reducing dependency on industrial nitrogen production.

The behaviour of reactive nitrogen and oxygen species in environmental systems is profoundly influenced by the physical context in which they occur, with significant differences emerging between clean aqueous systems and heterogeneous slurry conditions. In the context of selective non-catalytic reduction (SNCR) of NO_x, computational and experimental studies have shown that while reactions such as the conversion of NH₂ with NO proceed efficiently in controlled, well-mixed environments, the use of aqueous urea or cyanuric acid under slurry-based or non-uniform injection conditions introduces rate limitations driven by poor mixing, delayed vaporization, and localized temperature gradients. These physical constraints shift the rate-limiting steps from intrinsic chemical kinetics to transport phenomena, resulting in elevated ammonia slip and incomplete NO reduction [51].

Similarly, phosphorus adsorption onto waste alum sludge has been demonstrated to depend on a concentration-driven interplay between film diffusion and intraparticle pore diffusion, where surface exchange reactions occur rapidly but deeper diffusion becomes limiting at higher phosphate levels [52]. These findings parallel the observations that nitrification intermediates such as NH₂OH and NO₂[−] in soil slurries undergo redox transformations governed primarily by microscale oxygen availability, pH heterogeneity, and surface-catalysed reactions involving iron and manganese oxides, rather than by their intrinsic aqueous reactivity [53].

Extending this understanding to reactive oxygen species (ROS), it has been shown that interfacial domains—such as soil–water or air–water boundaries—act as hotspots for ROS generation and transformation due to light exposure, catalytic surface effects, and diffusion barriers, which represent rate-limiting processes absent in clean homogeneous systems [54]. Complementing this view, molecular-level analyses reveal that even in pure water, the presence of under-coordinated hydroxyl groups and unpaired lone-pair sites controls reactivity, and that in slurry systems such structured microenvironments are amplified by mineral surfaces and hydration shells that stabilize or sequester these reactive species [55].

Collectively, these studies indicate that while clean aqueous systems are dominated by intrinsic chemical kinetics, heterogeneous slurry systems are constrained by physical transport, interfacial effects, and spatial heterogeneity, requiring kinetic models and engineering strategies that explicitly account for these complex, rate-limiting dynamics [51–55].

The efficiency of these plasma-activated transformations is governed by physical and operational factors. Due to the higher density of liquids, mass-transport limitations often necessitate gas injection (e.g., air or N₂) between electrodes to sustain discharge [56]. Parameters such as electrode configuration, voltage, pulse width, plasma energy, temperature, pH, and initial composition must be precisely controlled to optimise reactive-species generation and stability [57,58].

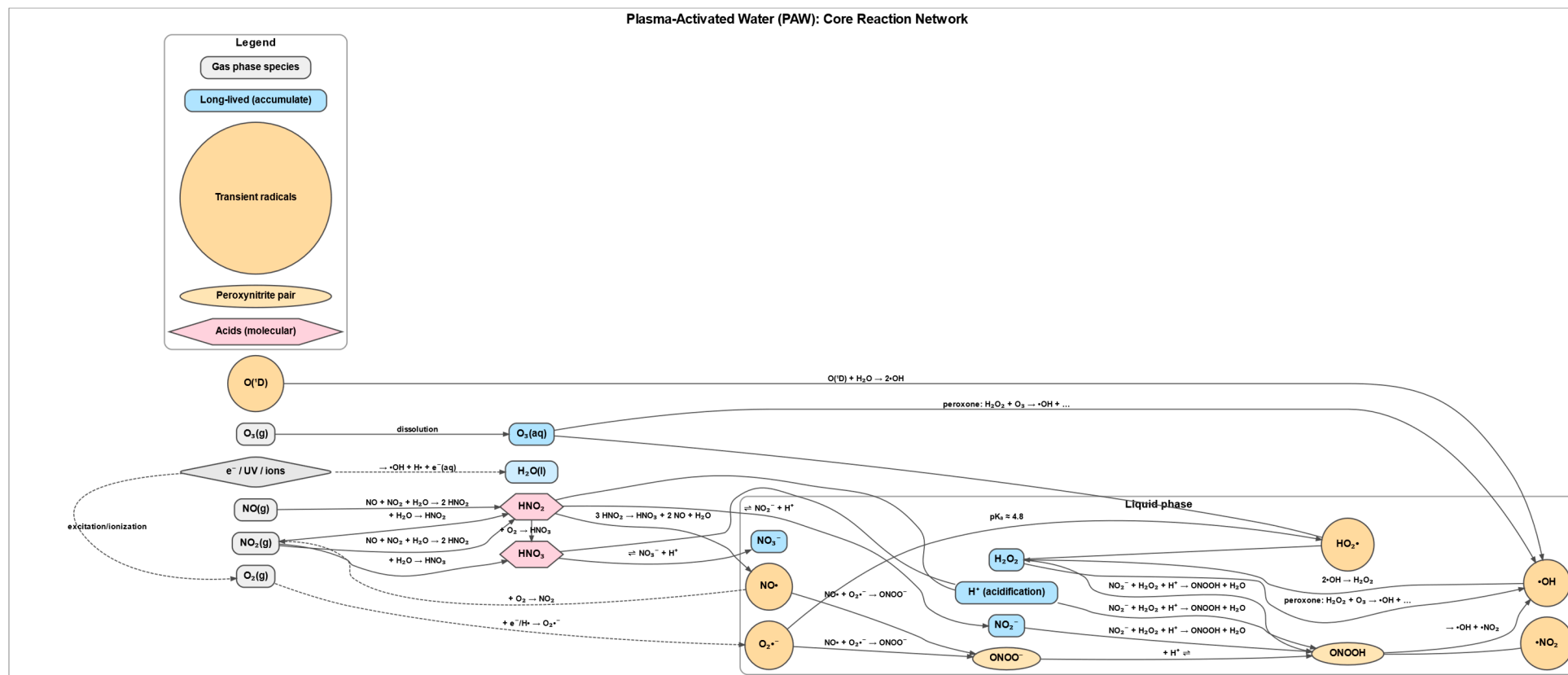


Figure 1. Diagram of the major reactive species and reactions in Plasma Activated Water (and by extension in Plasma Activated Liquids) Inspired by Graves et al. [50].

3.4. Plasma-Induced Acidification as an Intervention in the Nitrogen Cycle

According to Galloway et al. [59], four key interventions can mitigate nitrogen losses and restore balance to the global nitrogen cycle: reducing NO_x emissions from fossil fuel combustion, improving nitrogen use efficiency (NUE) in crop production, optimizing animal systems through better feed and manure management, and expanding advanced wastewater treatment to convert reactive nitrogen to N_2 .

PIA aligns with these goals as a sustainable technology capable of both reducing emissions and improving nutrient recycling. It can operate as a decentralized, on-farm alternative to conventional Haber–Bosch fertiliser inputs, contributing directly to improved NUE. The oxidizing plasma environment also offers co-benefits including pathogen suppression, odour control, and partial methane (CH_4) mitigation through inhibition of methanogenic pathways [60].

Current research remains at the proof-of-concept stage, with small-scale NTP systems demonstrating reliable generation of reactive species for ammonia protonation [61]. Comparative studies indicate that such systems can match or exceed the ammonia-reduction efficiency of conventional sulphuric-acid acidification under controlled conditions [14]. Scaling up to treat continuous slurry flows under farm conditions requires improvements in energy efficiency, system integration, and reaction control. Pilot-scale concepts coupling plasma reactors with barn ventilation or recirculation loops have been proposed, though field-validated data remain limited [62].

Computational models and early life-cycle assessments suggest that plasma pathways could outperform chemical acidification in nitrogen retention and sustainability metrics. While presently largely pre-commercial, PIA holds strong potential to transform manure management and reduce reactive nitrogen emissions. With further optimization, integration into circular agricultural systems, and supportive policy frameworks, it may evolve into a scalable tool for sustainable nitrogen stewardship.

3.5. Environmental & Agronomic Impacts of Plasma-Based Treatments in Agriculture

Plasma-based treatments in agriculture are increasingly recognized for their capacity to improve nutrient retention and mitigate greenhouse gas emissions. These treatments not only suppress ammonia (NH_3) and methane (CH_4) losses [9,63,64] but also enrich slurry and digestate with nitrate (NO_3^-) and nitrite (NO_2^-), enhancing their fertiliser value [65]. Table 2 summarises representative plasma-based treatments and their reported agronomic and environmental outcomes, alongside operational considerations such as scalability and energy demand. This integrative view highlights how plasma processes influence nutrient retention, emission control, and plant growth performance across different configurations.

However, these agronomic benefits are accompanied by important environmental trade-offs. Elevated nitrous oxide (N_2O) emissions have been observed in some plasma-treated systems, particularly when excess NO_3^- or NO_2^- accumulates in acidic or oxygen-limited soils [66,67]. The enhanced availability of oxidised nitrogen species can stimulate both nitrification and denitrification pathways, potentially leading to higher N_2O fluxes under suboptimal soil aeration. These emissions are highly sensitive to soil moisture, pH, and microbial community structure, highlighting the need to balance nitrogen enrichment with controlled application timing and dose.

Soil acidification and nutrient leaching are additional concerns, particularly under repeated or high-frequency plasma treatments [68]. The acidifying action of PAL can increase the solubility of base cations such as Ca^{2+} , Mg^{2+} , and K^+ , enhancing nutrient mobility but also raising the risk of leaching losses in permeable soils. Over time, excessive acid input may lower soil buffering capacity, alter cation exchange equilibria, and impact long-term fertility if not counterbalanced by liming or organic amendments.

Table 2. Agronomic, Environmental, and Operational Characteristics of Plasma-Based Treatments in Agriculture.

Treatment	Agronomic/Environmental Outcome	Operational Notes (Energy & Scalability)	Undesirable/Observed Effects	Ref.
Plasma-activated liquid (PAL) for seed treatment	↑ Germination (15–20%), ↑ root growth (23%), ↓ NH ₃ volatilisation potential	Operates at 50 W–1.5 kW ($\approx 2\text{--}3 \text{ kWh m}^{-3}$ PAL); scalable with DBD reactors and irrigation systems	Over-exposure causes oxidative stress; PAL acidity may injure seedlings	[68]
Plasma catalytic systems for N fixation	On-site NH ₃ /NO _x production enhancing fertiliser availability	Moderate energy input ($\sim 0.2 \text{ MJ mol}^{-1} \text{ N}$); modular, decentralised design for farm use	O ₃ interference; catalyst degradation over time	[10]
PAL for crop growth	↑ Foliar weight ($\sim 25\%$), ↑ chlorophyll ($\sim 11\%$); improved N uptake efficiency	Low-input process noted for energy efficiency; scalable on large farms via irrigation	High reactive species levels may inhibit growth; nitrate accumulation	[69]
Plasma catalysis with heated catalyst	Enhanced N conversion yield; improved fertiliser value	200–250 GJ tN ^{−1} energy use; heated catalyst raises efficiency $\sim 20\%$; scalable with increased gas flow	Catalyst performance declines at high flow rates	[11]
DBD plasma reactor for NO _x generation	Produces NO ₃ [−] -rich solutions for liquid fertilisers	Operates $\sim 300 \text{ W}$ ($\approx 1.1 \text{ g-NO}_x \text{ kWh}^{-1}$); continuous mode supports scale-up	pH fluctuation in treated water; diminishing returns at long residence times	[70]
Nitrogen fixation plasma system	Generates $\sim 15,500 \text{ ppm NO}_x$; precursor for nitrate fertilisers	$\sim 4.2 \text{ MJ mol}^{-1} \text{ NO}_x$; energy drops 35% at high flow; suited to moderate throughputs	Discharge instability at high O ₂ levels	[10]
PAL for horticulture	↑ Leaf area ($\sim 75\%$); lower plant NO ₃ [−] accumulation	Operates at 125 W; low running cost; adaptable to greenhouses	Reduced phenolic content; species-dependent response	[71]
Gliding arc discharge (GAD) system	↑ Seed germination (12–13%) and FGP ($\sim 17\%$)	$\approx 415 \text{ W}$ low-input system; highly scalable	Water acidification possible; crop-specific variation	[72]
Cold plasma	Improved germination and crop vigour via ROS/RNS stimulation	Low-energy room-temperature discharge; field applicable	Repeated use may acidify soils	[68]
Plasma treatment of digestates	↓ NH ₃ and CH ₄ emissions; enhanced N retention	$\approx 60 \text{ kWh kg}^{-1} \text{ NO}_x$; scales with slurry buffer capacity; renewable-compatible	Nitrite toxicity; possible NO ₃ [−] leaching or nitrification inhibition	[14]
Plasma-treated pig slurry	↓ CH ₄ ($>90\%$) but ↑ N ₂ O after application	Moderate electric load for air ionisation; farm-scale integration feasible	Higher GHG intensity than mineral fertilisers if N ₂ O uncontrolled	[65]
Plasma elimination of CH ₄ in slurry	100% CH ₄ removal; microbial suppression of CH ₄ & N ₂ O	High-load operation; suited to renewables; avoids S-acid issues	Requires NO ₃ [−] /NO ₂ [−] control to limit denitrification	[9]
Plasma-treated cattle slurry	9% ↑ dry matter yield vs. untreated; ↓ CH ₄ emission	Electrical discharge ionises air; renewable integration possible	Lower N uptake than mineral fertiliser; clover content sensitivity	[73]

Table 2. Cont.

Treatment	Agronomic/Environmental Outcome	Operational Notes (Energy & Scalability)	Undesirable/Observed Effects	Ref.
Decarbonising N fertiliser with NTP	Efficient $\text{NO}_3^- + \text{NH}_4^+$ generation; $\uparrow$ NUE potential	$\approx 5.3 \text{ kWh mol}^{-1}\text{-N}$; modular, renewable-driven design	Risk of N_2O emissions; nitrite toxicity; monitor water quality	[66]
Plasma-fixated N for turf grass	Biomass $\uparrow \sim 60\%$; enhanced yield at optimal concentration	450 W reactor; decentralised irrigation integration	Acidification risk; potential run-off toxicity	[74]
Plasma for gerbera plants	Biomass gain in peat substrates	5–25 kV DBD; scalable for controlled environments	Substrate sensitivity; microbial reduction	[67]
Plasma agriculture (lab $\rightarrow$ farm)	$\uparrow$ Germination and biochemical health indices	50–400 W systems; APP adaptable to field irrigation	Over-exposure reduces germination; crop specificity	[62]
Plasma agriculture for sustainability	$\uparrow$ Seed germination; $\uparrow$ root/shoot growth (~ 2 min exposure)	High-voltage DBD; renewable operation recommended	Over-exposure reduces growth; nutrient (P, K, S) deficiency possible	[75]
Plasma-assisted N fixation	Produces 1–5% NH_3 , 6% NO ; $\downarrow$ GWP ($\sim 19\%$) for HNO_3 synthesis	$\sim 17 \text{ g NH}_3 \text{ kWh}^{-1}$; modular plant design	Low product yield; energy still limiting factor	[76]
Plasma-activated water (PAW) in agriculture	$\uparrow$ Germination (50%), $\uparrow$ dry weight ($6.6\times$), 61% disease control	6–30 kW power range; easy integration with irrigation	ROS toxicity if overdosed; reactive species short-lived ($<48 \text{ h}$)	[28]
Plasma-fixed N for lettuce	250% $\uparrow$ marketable yield; high NUE at low rate (8 lb acre^{-1})	1.8 kW DBD reactor; farm scale adaptable	Product pH $\sim 1.5 \rightarrow$ soil acidification risk; low P content	[64]
Plasma dinitrogen pentoxide for plants	Complete $\text{N}_2\text{O}_5 \rightarrow \text{NO}_3^-$ conversion; efficient fertilisation	$\sim 70 \text{ MJ mol}^{-1}\text{-N}$; portable renewable devices emerging	High dose phytotoxicity; nodulation reduction in legumes	[77]
Plasma agriculture (advancements)	$\uparrow$ Yield and growth (spinach, sunflower); pathogen control	Up to 30 kV DBD systems; modular and portable	Over-exposure inhibits seedlings; potential soil acidification	[78]
Plasma-activated organic fertiliser (PAOF)	$\downarrow$ VOC, CH_4 , NH_3 emissions; $\uparrow$ N retention in organic waste	Moderate–high energy use ($\sim \text{€}2\text{--}3 \text{ kg}^{-1} \text{ N}$ converted); distributed renewables scalable	$\uparrow \text{N}_2\text{O}$ after application; soil acidification risk	[50]
Plasma agriculture and ecosystem studies	$\uparrow$ Germination and growth at optimal (4–20 min) exposure	Generally, energy-efficient vs. traditional processes; irrigation integration possible	Over-exposure damages seeds; microbiome impacts at high RNS	[79]

Note: While several studies report lower short-term nitrogen use efficiency (NUE) for plasma-treated fertilizers compared to conventional mineral fertilizers, this difference primarily reflects variations in nitrogen form and release dynamics. PIA produces more stabilized nitrogen compounds (e.g., NH_4NO_3) with lower volatilization and leaching potential, enhancing long-term nitrogen retention and environmental performance. When broader sustainability and life-cycle factors—such as reduced chemical acid use, improved safety, and nutrient recovery from waste streams—are considered, plasma-derived fertilizers demonstrate a higher overall fertilizer value (Nyvold & Dörsch [9]; Ingels & Graves [8]; Attri et al. [62]). $\uparrow$ -Increase, $\downarrow$ -decrease

Plasma-derived oxidants also influence the soil microbiome and organic matter dynamics. Moderate concentrations of reactive oxygen and nitrogen species (RONS)—including ozone, hydroxyl radicals, and peroxyxynitrite can suppress pathogenic microorganisms and contribute to odour mitigation. Yet, at higher exposure levels, these same oxidants may disrupt beneficial microbial populations involved in nutrient cycling or organic matter decomposition. Shifts in microbial community composition could affect soil respiration rates, carbon sequestration, and the turnover of humic substances, with downstream impacts on soil health and greenhouse gas fluxes [9,14].

Managing this oxidation balance is therefore critical: an optimal plasma dose should provide sufficient oxidative capacity for sanitization and ammonia stabilization without impairing microbial function or accelerating organic matter mineralization.

Given these complexities, the environmental and agronomic outcomes of plasma-based interventions must be assessed through long-term field trials and comprehensive LCA that capture both direct and indirect effects on nitrogen retention, emission control, and soil ecosystem function [28,69]. Overall, plasma-based systems present a promising pathway for sustainable nutrient management, but their implementation should be guided by robust agronomic evidence, site-specific calibration, and integration into precision nutrient management frameworks.

Operational aspects, including energy use and scalability, are further examined in Sections 5–7.

4. Evidence of Efficacy of Plasma-Induced Acidification

Efficient management of ammonia (NH₃) emissions constitutes a central component of sustainable agricultural practice and enhanced nitrogen use efficiency. Numerous mitigation strategies have been developed to address NH₃ volatilisation, including dietary manipulation, urease inhibitors, slurry storage covers, and conventional acidification. While these approaches demonstrate verifiable emission reductions, they vary considerably in their economic feasibility, scalability, and environmental trade-offs. As shown in Table 3, PIA has recently emerged as a promising alternative, offering the potential to overcome many of the limitations inherent in existing methods, particularly when the associated valorisation pathways are considered [14].

Table 3. Efficiency indicators of Plasma-Induced Acidification and other Mitigation Techniques.

Technique	Efficiency (NH ₃ Reduction)	Challenges	Opportunities	References
Dietary Manipulation	Up to 74%	High precision in feed formulation; increased costs	No infrastructure changes; improves feed efficiency	[21]
Slurry Storage Covers	Up to 95%	Labor-intensive; maintenance of covers	Reduces other pollutants; suitable for large-scale operations	[21,24]
Urease Inhibitors	53.7%	Variable effectiveness depending on conditions	Enhances nitrogen retention	[25]
Slurry Acidification	Up to 95%	Safety risks; potential soil acidification	Highly effective; improves nitrogen use efficiency	[23,24]
Plasma-Induced Acidification	Over 99% for CH ₄ ;	High energy use; increases N ₂ O emissions post-application	Increases nitrogen content; reduces need for synthetic fertilisers; stabilises pH	[9]

From an economic perspective, PIA exhibits competitive potential owing to its capacity for long-term nutrient preservation and decreased dependence on synthetic fertiliser inputs.

In contrast to dietary manipulation—whose efficacy is contingent upon consistent feed composition and stringent management practices—or urease inhibitors, which often display variable performance under heterogeneous environmental conditions, plasma systems provide direct electrochemical control over NH_3 conversion pathways. Although initial capital and energy requirements are relatively high, these expenditures may be offset by the dual environmental benefits of stabilised nitrogen retention and methane (CH_4) emission reductions exceeding 99% [9,65,66]. As indicated in Table 3, the variability in NH_3 reduction observed for PIA reflects differences in slurry composition, pH buffering capacity, and plasma reactor configuration rather than a fundamental limitation of the process. While NH_3 abatement efficiency remains under optimisation, the near-complete suppression of CH_4 and enhanced nitrogen stabilisation demonstrate PIA's broader potential for integrated emission control and nutrient retention, warranting further refinement and scale-up studies. Conventional slurry acidification remains both cost-effective and operationally mature, achieving NH_3 emission reductions of up to 95%. However, its reliance on chemical acids introduces occupational and environmental hazards, including risks of soil acidification and corrosion, which plasma systems inherently circumvent.

In terms of scalability, PIA is most suitable for medium- to large-scale agricultural enterprises capable of exploiting economies of scale and integrating with renewable energy or biogas infrastructure. Such integration enables synergistic use of existing digestate streams, biogas-derived electricity, and exhaust gas treatment systems, thereby facilitating cost distribution across farm operations. Conversely, smaller-scale farms may find dietary modification or conventional acidification approaches more practical due to their lower capital intensity and reduced technical complexity.

From an environmental standpoint, plasma-based systems confer multiple co-benefits that extend beyond NH_3 and CH_4 mitigation. The treatment process enhances fertiliser quality by facilitating the conversion of ammonia into stable ammonium nitrate and producing nitrate-enriched fractions that elevate the mineral fertiliser equivalent (MFE) of organic fertilisers [9,65,66]. These improvements contribute to nutrient circularity within agricultural systems by promoting the retention and recirculation of nitrogen, reducing reliance on fossil-fuel-based fertiliser production, and eliminating hazards associated with the storage and transport of corrosive acids.

Furthermore, PIA unlocks distinct valorisation opportunities. The generation and recovery of nitrate-rich by-products can yield marketable fertiliser formulations, particularly when integrated with membrane separation or crystallisation processes [20,33]. Coupling plasma reactors with anaerobic digestion (AD) systems further enhances process efficiency by enabling the concurrent treatment of ammonia-rich exhaust gases and digestate effluents [14,80]. This integrated framework aligns with European Union nutrient recycling directives [81], and contributes to broader net-zero agricultural strategies by combining emission abatement, nutrient valorisation, and renewable energy utilisation within a single technological platform.

Key Parameters Affecting Process Efficiency

The optimisation of PIA for practical implementation necessitates meticulous control of operational parameters governing plasma chemistry and reactor dynamics. As highlighted by Zhou et al. [82], factors such as input gas composition, humidity, discharge voltage, electrode configuration, and reactor geometry exert significant influence over the yield and selectivity of nitrogen oxides (NO_x) and reactive oxygen species (ROS). Among these, the presence of water vapour is particularly critical, as it promotes the formation of hydroxyl (OH) radicals that facilitate enhanced ammonia oxidation pathways [83].

As highlighted previously, energy efficiency remains the principal constraint to large-scale deployment. Recent advancements in plasma reactor design, including high-

frequency spark discharge (HFSD), surface dielectric barrier discharges (DBDs), and gliding arc configurations, have markedly improved energy performance. Laboratory studies have reported energy costs as low as $0.28 \text{ MJ mol}^{-1} \text{ N}$ [45,80,83], representing a substantial enhancement in conversion efficiency. Nevertheless, translating these laboratory-scale efficiencies to continuous, high-throughput slurry treatment systems remains challenging. Achieving this transition requires precise flow regulation, real-time diagnostic monitoring, and robust system integration to mitigate performance degradation under variable operating conditions.

Catalytic enhancement offers an additional pathway for improving process efficiency. The incorporation of catalysts such as tungsten trioxide (WO_3) and molybdenum trioxide (MoO_3) has been shown to increase NO_x yields while simultaneously reducing energy consumption [84]. Despite these promising results, the long-term economic viability and structural stability of such catalysts under the harsh physicochemical conditions characteristic of slurry treatment warrant further investigation.

Despite notable advancements in plasma reactor design and NO_x synthesis efficiency, the scaling of plasma acidification systems from laboratory to industrial settings presents persistent technical and economic challenges. Key barriers include maintaining uniform discharge characteristics across larger reactor volumes, mitigating by-product accumulation (e.g., excess ozone or undesired nitrogen oxides), and ensuring consistent performance under fluctuating feed compositions and environmental conditions [11,12,80].

Dynamic control strategies that employ feedback-based adjustments to input power, flow rates, and reaction conditions in real time may provide a viable route toward improved stability and energy efficiency [85]. Such adaptive systems could help sustain optimal plasma states, ensuring high selectivity and reproducibility across operational cycles. Moreover, comprehensive life cycle assessments (LCAs) are required to evaluate whether gains in nitrogen retention and emission mitigation sufficiently offset the additional electricity demand of plasma systems. This consideration is particularly pertinent when assessing system performance under renewable energy supply scenarios [17].

5. Economic and Environmental Assessment of Plasma—Induced Acidification

PIA represents a promising low-carbon approach for decentralised acid generation and nutrient management, offering a sustainable alternative to conventional fossil-based acidification methods. Unlike the Haber–Bosch–Ostwald route which relies on natural gas and sulphur feedstocks, PIA operates without fossil hydrogen or sulphur inputs and can be powered entirely by renewable electricity. Conventional acidification processes emit between 1.9 and 3.6 t CO_2 per $\text{t NH}_3\text{-N}$ and generate additional nitrous oxide (N_2O) during nitric acid oxidation, contributing significantly to the greenhouse gas footprint of industrial nitrogen production [66,86]. By contrast, PIA eliminates direct CO_2 emissions and, when supplied with renewable power, achieves near-zero life-cycle emissions [17,85,87].

From an economic perspective, however, the current performance of PIA remains constrained by high specific energy demand. Modern plasma-based nitrogen fixation systems consume approximately $2.0\text{--}2.4 \text{ MJ mol}^{-1} \text{ N}$ ($\sim 100\text{--}200 \text{ GJ tN}^{-1}$), compared to $0.50\text{--}0.64 \text{ MJ mol}^{-1} \text{ N}$ ($\sim 25\text{--}35 \text{ GJ tN}^{-1}$) for conventional ammonia and acid production [12,66]. This efficiency gap directly translates into higher operating costs, with present-day plasma-based nitrate or acid production costing between USD 800 and 1200 per tonne of nitrogen equivalent—two to four times the cost of conventional sulphuric or nitric acid routes [85,88]. Although significant advances have been made in plasma–catalytic integration and energy recovery, PIA’s economic competitiveness still depends on further reductions in power consumption and capital costs [76].

Despite these limitations, PIA provides several advantages that improve its overall economic and environmental feasibility, particularly in decentralised or renewable-intensive contexts. PIA eliminates the need to transport, handle, or store hazardous mineral acids—reducing safety risks, regulatory burdens, and logistical costs [50]. More importantly, it enables on-site acidification of manure and digestate, directly preventing gaseous nitrogen losses. Empirical studies show that PIA can suppress methane (CH_4) emissions completely and reduce ammonia (NH_3) volatilisation by up to 100% during storage, while enhancing nitrogen retention in the effluent [14,89]. These environmental gains, when internalised under carbon pricing or emissions-trading schemes, substantially narrow the economic gap between PIA and conventional systems. Assuming a carbon price of USD $50\text{--}100\text{ t}^{-1}\text{ CO}_2$, the avoidance of $2\text{--}3\text{ t CO}_2$ per tonne N corresponds to a potential credit of USD $100\text{--}300\text{ t}^{-1}\text{ N}$, offsetting a significant portion of the cost difference [88].

PIA's flexibility also enhances its competitiveness in renewable-rich grids. Unlike the rigid, continuous operation of conventional chemical plants, plasma reactors can be switched on and off to follow electricity price fluctuations, operating preferentially during low or negative price periods—a growing feature in renewable-dominated markets such as those in Northern Europe [12,85,88]. As renewable electricity costs continue to fall below USD 0.03 kWh^{-1} , energy-related expenses become less prohibitive, enabling intermittent or demand-responsive operation to significantly improve cost efficiency. In such energy environments, decentralised plasma systems could offer a viable complement to centralised acid production, particularly where grid flexibility and on-site energy use are valued [66,87].

Nevertheless, several technical and operational barriers continue to constrain PIA deployment. The energy intensity of plasma-based nitric oxide (NO) formation remains high, and system performance can be affected by electrode degradation, dielectric aging, and plasma–liquid transfer inefficiencies [90]. In practical applications, the heterogeneous composition and high buffering capacity of livestock slurries reduce plasma discharge stability and nitrate yield [14,91]. Furthermore, the need for corrosion-resistant materials adds to capital costs, while limited long-term field data make it difficult to predict maintenance and lifespan economics [85]. These issues highlight that while PIA is environmentally superior, its short-term economic feasibility remains context-dependent, improving substantially only in renewable-rich, carbon-priced, or cooperative deployment models [88].

From a policy standpoint, PIA aligns with European Union directives on ammonia abatement and circular nutrient management but is not yet recognised as a Best Available Technique (BAT), limiting its access to subsidies or compliance incentives [21,39,92]. However, as carbon pricing expands and fossil-based acid producers face increasing exposure to emissions trading systems, PIA's relative competitiveness is expected to improve [88]. When considered within a decarbonised energy framework, PIA can thus be viewed as a transitional yet strategically important technology that integrates nutrient management, renewable utilisation, and emission reduction [85].

Overall, PIA exemplifies the trade-off between higher immediate energy costs and long-term environmental and operational benefits. It provides complete elimination of direct CO_2 emissions, suppresses CH_4 and NH_3 losses, and enhances nitrogen recycling while improving safety and regulatory compliance through on-site acid production. Under conditions of falling renewable electricity prices, rising carbon costs, and improved plasma energy efficiency, PIA is expected to transition from a research-stage technology to a commercially viable component of sustainable, decentralised nitrogen management [9].

6. Integration of Full Lifecycle Costing in Techno-Economic Analyses of Plasma Acidification Systems

Recent advances in techno-economic analyses (TEA) of plasma-assisted nitrogen fixation and related plasma processes have increasingly aimed to incorporate full lifecycle cost (LCC) parameters, reflecting a shift from narrowly focused energy-efficiency assessments to more comprehensive evaluations of sustainability and economic viability. As summarised in Table 4, several studies—including Anastasopoulou [93], Anastasopoulou et al. [93], and Osorio-Tejada et al. [88]—have progressively expanded TEA frameworks to capture the interrelated cost dimensions of equipment depreciation, maintenance scheduling, electricity consumption, and process monitoring. Through factorial cost-estimation methods and advanced process simulations (e.g., ASPEN Plus), these works consistently demonstrated that electricity demand is the dominant cost contributor, accounting for approximately 60–75% of total lifecycle costs, while maintenance and diagnostic monitoring constitute a further 10–25% of operating expenditures [92,94].

Subsequent developments, such as geometry- and scale-dependent degradation models introduced by Anastasopoulou et al. [92], have enhanced understanding of reactor-component wear and its influence on total system costs—particularly in decentralised or modular plasma reactor configurations. Expanding on this, Osorio-Tejada et al. [88] incorporated environmental externality internalisation, monetising the impacts of acidification, eutrophication, and photochemical oxidant formation within a cradle-to-gate techno-economic framework. That study explicitly included annualised equipment costs, maintenance and replacement intervals, renewable electricity variability, and automation systems, concluding that non-thermal plasma fertiliser systems could achieve cost competitiveness under low-carbon electricity scenarios if reactor lifetimes exceeded ten years [85].

Despite these advancements, persistent methodological limitations continue to constrain the robustness and transferability of existing full-lifecycle techno-economic assessments. Most TEAs rely on static cost assumptions—such as linear depreciation and fixed maintenance intervals—that fail to reflect the nonlinear degradation behaviour of key plasma components (electrodes, catalysts, and dielectrics) under cyclic, high-voltage conditions [88,93]. Likewise, monitoring and control subsystems, vital for process safety and plasma stability, are frequently modelled as proportional overheads rather than dynamic, performance-linked costs. Electricity-pricing models also remain temporally static, overlooking variability in renewable energy supply and storage, which critically affects decentralised and intermittently operated systems [85,94]. Furthermore, the geographical scope of most analyses is limited, relying predominantly on European industrial cost data, reducing relevance to developing or off-grid regions where decentralised plasma fertiliser production could be most impactful [85]. The omission of end-of-life and recycling phases, particularly for high-value reactor materials such as tungsten and advanced ceramics, further restricts the completeness of lifecycle-cost representations [95]. These limitations collectively highlight the need for dynamic, empirically grounded TEA–LCA–LCC models that integrate real-time degradation, variable energy pricing, and regionalised cost datasets, ideally underpinned by digital-twin technologies and predictive-maintenance frameworks [93,94]. Such innovations would provide a more accurate reflection of operational realities and enable the commercial scaling of plasma-assisted nitrogen-fixation systems as sustainable, renewable-integrated fertiliser technologies.

Table 4. Recent Techno-Economic Analysis (TEA) and Life Cycle Cost (LCC) of Plasma Induced Acidification Studies.

System Studied	Lifecycle Cost Parameters Considered	Key Findings/Contributions	Identified Shortfalls/Gaps	Reference
Plasma-assisted NH ₃ and HNO ₃ synthesis	Equipment: Factorial estimation of CAPEX (reactor, gas feed, power supply) Maintenance: Preventive and corrective scheduling costs Electricity: Modelled for grid and renewable supply Monitoring: Included as control and diagnostic subsystem	Integrated TEA–LCA–LCC assessment for plasma nitrogen fixation; electricity consumption dominated ($\approx 70\%$ of total LCC); maintenance and monitoring 10–15%.	Static depreciation and linear maintenance assumptions; no end-of-life or recycling costs; limited regional cost calibration.	[93]
High-power plasma reactors for nitrogen fixation	Equipment: CAPEX scaling by geometry and reactor size Maintenance: Reactor degradation model based on electrode wear Electricity: Detailed energy consumption model per reactor design Monitoring: Partial inclusion (diagnostic costs estimated as % of CAPEX)	Developed geometry-dependent cost model showing monitoring and degradation can increase OPEX by 25%; underscored need for durability data.	Empirical maintenance data limited; simplified treatment of monitoring; constant energy cost assumptions.	[76]
Decentralised NH ₃ /nitrate plasma fertiliser systems	Equipment: Annualised CAPEX for reactors and storage Maintenance: Included scheduled replacement intervals Electricity: Dynamic renewable vs. grid cost integration Monitoring: Included Via automation and control system costs	Conducted cradle-to-gate TEA–LCA integrating environmental externalities; predicted cost competitiveness for NTP systems under renewable electricity.	Monitoring and degradation data remain low-resolution; regional monetisation uncertainty; end-of-life impacts omitted.	[88]
Plasma-catalytic CO ₂ conversion	Equipment: CAPEX and depreciation Maintenance: Operating and downtime maintenance Electricity: Regional grid-mix based consumption Monitoring: Not explicitly modelled	Combined TEA–LCA for plasma catalysis; identified electricity intensity and maintenance as main economic burdens.	No explicit monitoring inclusion; lacks time-resolved degradation data.	[95]
Plasma-assisted syngas production	Equipment: Industrial-scale CAPEX functions Maintenance: Annual repair and replacement costs Electricity: Dynamic time-varying pricing Monitoring: Included as continuous control and diagnostic module	Integrated dynamic TEA–LCA model; found maintenance + monitoring contribute 18% of total OPEX; electricity variability strongly influences LCC.	End-of-life excluded; model limited to energy systems (not fertiliser context).	[94]
Electrolyser-Haber–Bosch systems	Equipment: CAPEX Maintenance: Generic fixed O&M factor Electricity: Renewable vs. grid scenario analysis Monitoring: Not included	Showed future cost parity of renewable ammonia under CO ₂ taxation; benchmark for plasma comparisons.	Oversimplified O&M costs; monitoring and replacement phases not modelled.	[87]

A similar methodological gap is evident in the techno-economic literature on slurry acidification as an ammonia-mitigation and nutrient-retention strategy. As outlined in Table 4, studies such as Tan et al. [96], Chadwick et al. [97], and Aghdam et al. [98] provide valuable cost estimates for reagents, labour, and basic equipment, and demonstrate that conventional acidification methods (e.g., using H_2SO_4 or HNO_3) are both environmentally effective and economically feasible, especially under large-scale operations or favourable policy incentives. These analyses also highlight co-benefits such as enhanced nitrogen-use efficiency, reduced $\text{PM}_{2.5}$ formation, and improved fertiliser–nutrient balance [29,99]. However, none of these studies offer a complete cradle-to-grave lifecycle-cost model that accounts for capital depreciation, scheduled and unscheduled maintenance, electricity consumption, pH-monitoring systems, or regulatory-compliance and safety costs. Moreover, health and occupational risks associated with acid handling and emissions monitoring remain largely unquantified, despite their potential influence on long-term economic and environmental performance [21].

Emerging concepts such as PIA show promise for reducing chemical reagent use and leveraging renewable electricity for on-site fertiliser acidification. Nevertheless, no existing techno-economic study comprehensively evaluates system integration, infrastructure-retrofitting requirements, or indirect environmental impacts—including greenhouse-gas mitigation, soil-acidification feedback, and water-quality outcomes—associated with such systems. The absence of standardised, engineering-grade lifecycle-economic models for both plasma-based and chemical acidification technologies thus represent a major gap in current research. To facilitate accurate cross-comparison and policy evaluation, future research should prioritise the development of integrated, dynamic lifecycle frameworks capable of capturing true operational complexity, accounting for regional and scale-dependent variables, and evaluating long-term sustainability trade-offs across technology pathways and farm typologies.

7. Path to Deployment of Plasma Induce Acidification Technology

The deployment of PIA technologies will depend on coordinated advances in energy efficiency, reactor engineering, systems integration, and enabling policy frameworks. Achieving economic and environmental viability requires not only technical optimisation but also social acceptance and regulatory alignment to ensure scalability beyond pilot settings.

A key technical priority is enhancing reactor energy efficiency. Future research should focus on hybrid catalytic plasma systems capable of exploiting vibrational excitation and warm plasma regimes to reduce the specific energy consumption of nitrogen fixation reactions [12]. Advances in electrode materials, dielectric configurations, and reactor geometry are essential for improving discharge stability, reducing fouling, and extending reactor lifetime under humid, high-load agricultural conditions [85]. Integration of real-time sensors and adaptive control algorithms will further enable dynamic optimisation of plasma power input and nitrogen conversion rates [94,100].

In parallel, integration with renewable energy systems represents a critical pathway for cost reduction and decarbonisation. Modular, decentralised plasma units powered by on-farm photovoltaics or wind energy can operate flexibly with intermittent electricity supply, converting surplus renewable energy into storable nitrogen compounds such as ammonium nitrate [86,101]. These distributed systems offer an opportunity to close nutrient loops locally, reduce reliance on fossil-based fertilisers, and strengthen energy self-sufficiency in rural regions. Co-integration with anaerobic digestion (AD) or waste-to-energy (WtE) plants can further improve process synergies by linking plasma nitrogen fixation with existing carbon recovery, gas upgrading, and bioenergy infrastructures [18,102].

Complementary approaches such as membrane separations, biochar-assisted adsorption, and controlled nitrification inhibition could enhance nutrient recovery and overall process efficiency. These hybrid configurations should be validated under realistic operating conditions, including diverse slurry compositions and variable feed rates, to develop reliable techno-economic models.

From a sustainability perspective, comprehensive life-cycle assessments (LCAs) and techno-economic analyses (TEAs) are essential to quantify net greenhouse gas mitigation, resource use, and economic competitiveness relative to conventional acidification systems. Standardising LCA methodologies across research groups and publishing open-access datasets will promote transparency, comparability, and faster progress toward industrial benchmarking [18].

Equally crucial is the institutional and policy framework underpinning deployment. Establishing regional demonstration hubs where farmers, engineers, and policymakers collaborate on pilot projects will facilitate real-world validation, operational learning, and trust-building among end-users [20]. Policymakers should prioritise inclusion of plasma acidification within BAT reference frameworks [92] and develop financial mechanisms—such as innovation grants, tax incentives, and carbon credits—to reduce the investment risk that often stalls promising agri-environmental technologies at the pre-commercial stage.

Ultimately, the path to deployment requires a systems-level approach that aligns plasma reactor innovation with renewable energy integration, circular nutrient management, and supportive regulation. Through sustained interdisciplinary research, collaborative pilot programs, and targeted policy incentives, PIA can evolve from a promising research concept into a practical, scalable solution for carbon-neutral nutrient recovery and sustainable agricultural transformation.

7.1. Market Outlook and Enabling Conditions for Plasma Acidification

Assuming steady progress in research, development, and pilot-scale validation over the next three to five years, PIA could plausibly attain limited adoption—on the order of 1% market share—by 2030, consistent with general trajectories for emerging clean technologies [101]. This projection is supported by techno-environmental assessments of plasma treatment of digestates showing modest scaleup potential under favourable conditions [14,73]. Plasma acidification remains highly energy-intensive, with reported energy consumptions in plasma treatment of digestates on the order of 110–150 kWh per tonne of liquid material ($\approx 0.40\text{--}0.54\text{ GJ t}^{-1}$), which scales to roughly 110–150 GJ per tonne of nitrogen when applied to N-rich slurries [14,85]. Thus, the commercial viability of plasma acidification is strongly tied to availability and cost of renewable electricity. The 2030 horizon also coincides with anticipated increases in renewable generation capacity across the EU, particularly wind and solar, which are expected to drive down electricity costs and associated carbon intensity [86,103]. These shifts would directly enhance the techno-economic and environmental credentials of plasma-based mitigation technologies.

Initial deployment is most plausible in regions with high livestock densities, stringent air quality regulation, and elevated marginal abatement costs for conventional acidification—such as the Netherlands, Germany, and Denmark (as seen in EU ammonia hotspot analyses) [104]. However, achieving even minimal market penetration requires coordinated advances across multiple fronts: (1) development of robust, field-proven high technology readiness level (TRL) systems [14,73]; (2) independent validation via integrated LCA and marginal abatement cost curve (MACC) analyses to confirm cost competitiveness and greenhouse gas co-benefits [85,88]; (3) regulatory recognition through inclusion in national ammonia mitigation plans or EU compliance frameworks; (4) policy instruments to de-risk capital-intensive innovation (e.g., Horizon Europe, CAP eco-schemes, LIFE

Programme) [18,20]; and (5) sustained growth in renewable electricity deployment to ensure alignment with agricultural decarbonization goals [86,103].

Absent these enabling conditions especially inexpensive, low-carbon electricity—plasma acidification is unlikely to scale commercially before 2030. In the near term, it should thus be treated as a complementary, long-horizon innovation supporting, rather than supplanting, conventional slurry acidification strategies in the EU’s ammonia mitigation portfolio [39].

7.2. Existing Pilot and Demonstration Projects for Plasma-Induced Acidification and Nitrate Enrichment

The deployment of PIA technologies has decisively shifted from controlled laboratory experiments toward real-world field demonstrations. As summarised in Table 5, a diverse portfolio of pilot and demonstration projects is currently underway across Europe, North America, and Asia. These initiatives range from containerised, on-farm nitrate production systems to integrated plasma–aeration hybrids for raw slurry treatment.

A key observation from these projects is the strong emphasis on decentralisation and renewable integration. Companies such as N2 Applied and Nitricity have focused on compact, containerised units that operate directly on farms or within greenhouse systems, often powered by local solar or wind energy—reducing transport and storage costs while enabling nitrate-based fertiliser production on demand, in step with seasonal crop needs [105,106]. For instance, N2 Applied’s Nitrogen Enriched Organic Fertiliser (NEO) system has demonstrated ammonia emission reductions of 70–90% in storage tests with biogas digestate, and field trials indicate very low field ammonia losses upon application [105,107]. Performance metrics from pilot reactors (e.g., plasma reactors developed by Nitricity) report energy input efficiencies in the 3–10 kWh per kg N range while maintaining competitive cost projections relative to conventional fertiliser routes—though published peer-reviewed data remain limited [89,106].

Other innovative projects, such as the MAPS effort in Denmark, combine plasma treatment with ventilation and acidification to achieve ammonia emission reductions of 65–85% in slurry handling, illustrating the co-benefits of integrating PIA into established manure management systems [108] while more experimental systems like electrodialysis–plasma hybrids or microwave plasma nitric acid units illustrate the adaptability of plasma acidification across agricultural and wastewater contexts [94,102]. Several systems have now reached Technology Readiness Levels (TRL) of 7–8, indicating a high degree of maturity and readiness for integration into existing farm infrastructure [88,108]. Nonetheless, persistent engineering challenges remain—particularly in achieving long-term electrode stability, robust performance across variable humidity and temperature, and efficient coupling with raw slurry matrices [85,93].

Overall, the diversity of applications—from fertigation in protected cultivation to on-site raw manure treatment—underscores the flexibility and scalability of plasma-based systems. These field pilots provide strong empirical support that PIA may serve as a foundational element of more sustainable, decentralised nitrogen management in agriculture [106,108].

Table 5. Plasma Induced Acidification Pilot Projects.

Project/Partner	Location	Technology Type	Key Findings/Outcomes	Application	Ref.
NEO—Danish Studies (N ₂ Applied)	Denmark	Plasma-treated organic fertiliser (N ₂ Applied NEO system)	Demonstrated substantial reduction in ammonia (NH ₃) emissions from field application and verified long-term chemical stability of the NEO-treated slurry.	Sustainable agriculture, emissions reduction	[105]

Table 5. Cont.

Project/Partner	Location	Technology Type	Key Findings/Outcomes	Application	Ref.
Snarum Gartneri Pilot (N ₂ Applied)	Norway	On-farm plasma manure acidification system	Reduced ammonia losses during storage and application of manure; improved nitrogen utilisation in greenhouse fertigation.	Horticulture, fertigation	[109]
Galåvolden Gård (N ₂ Applied)	Norway	Plasma reactor for manure treatment	Increased nitrogen retention and reduced greenhouse gas emissions in dairy farm trials; improved nutrient recovery.	Dairy farming, circular agriculture	[110]
Møre Biogas Collaboration (N ₂ Applied)	Norway	Biogas-integrated plasma acidification system	Combined plasma technology with anaerobic digestion to enhance nutrient value and reduce odour emissions.	Biogas, renewable energy integration	[111]
Van den Borne Aardappelen Pilot (N ₂ Applied)	The Netherlands	Plasma-treated slurry demonstration	Field trials indicated nitrate-enriched slurry improved potato crop yields and reduced nitrogen losses.	Arable farming, precision agriculture	[112]
Nitricity	United States	Non-thermal plasma nitrogen fixation system	Renewable electricity-driven plasma process that converts air and water into nitrate fertilizer, enabling on-site, carbon-free production and reducing dependence on industrial ammonia supply chains.	Sustainable fertilizer production, decentralized agriculture	[106]
VitalFluid Plasma System	The Netherlands	Atmospheric plasma reactor	Converts air and water into plasma-activated water for on-site fertiliser generation using renewable electricity.	Horticulture, fertigation, greenhouse systems	[113]
Plasma2X	United Kingdom	Plasma and electrocatalytic ammonia synthesis system	Demonstrated renewable, CO ₂ -free ammonia and fertilizer production directly from air and water using low-energy plasma technology.	Sustainable fertilizer production, green chemicals	[114]

8. Research Gaps

PIA represents a transformative advancement in sustainable nutrient management and agricultural waste valorisation. Unlike conventional acidification methods reliant on chemical acids such as sulphuric acid, plasma technologies utilise electrical energy to produce reactive nitrogen species (RNS) and reactive oxygen species (ROS) directly from air and water. This enables the stabilisation of nitrogen by converting volatile ammonia (NH₃) into stable ammonium nitrate (NH₄NO₃), effectively doubling nitrogen retention, reducing NH₃ emissions, and enriching slurry with nitrate-based nutrients [12].

Despite recent progress, several realistic barriers continue to prevent plasma-based nitrogen systems from reaching the <30 GJ tN^{−1} energy threshold required for economic

competitiveness with the Haber–Bosch process. The most significant limitation remains the intrinsic energy inefficiency of plasma-driven NO_x synthesis, which typically operates between 100 and 200 GJ tN^{-1} [12,101]. Although emerging innovations—such as hybrid plasma–catalyst systems, vibrational excitation, and warm plasma configurations—have shown potential to improve energy utilisation, these approaches have yet to achieve stable performance outside controlled laboratory environments [11,85]. Under realistic agricultural conditions, complex process variables introduce further inefficiencies: the heterogeneous composition of livestock slurry, its high solids and moisture content, and strong buffering capacity all disrupt plasma discharge stability, lower ion transfer efficiency, and reduce overall nitrogen conversion yield [20]. Additional engineering constraints, including electrode degradation, dielectric ageing, and limited energy recovery from exhaust gases, further erode efficiency gains [93]. Collectively, these technical and operational challenges explain why current systems remain well above the desired energy benchmark, underscoring the need for integrated reactor optimisation, materials innovation, and process adaptation to field conditions before PIA can become economically competitive.

Upscaling and system integration present further challenges. Pilot and demonstration facilities must overcome engineering issues including electrode degradation, dielectric fouling, discharge instability, and process control under field conditions [19]. The integration of plasma reactors with existing anaerobic digestion (AD) or manure management systems also raises operational and safety concerns, particularly regarding heat management and high-voltage operation in moist environments.

Environmental assessment frameworks are also underdeveloped. To date, few life-cycle assessments (LCAs) comprehensively evaluate PIA across emissions categories such as avoided NH_3 , CH_4 , and indirect N_2O , alongside embodied energy and equipment impacts [18,19]. Without these evaluations, the net environmental benefit of PIA relative to conventional acidification remains uncertain.

Current research rarely investigates how conventional and plasma-based acidification systems could be integrated—either sequentially or through hybrid configurations—to optimise both operational performance and environmental outcomes. Furthermore, comparative techno-economic and context-specific evaluations remain limited, constraining understanding of their practical feasibility across diverse agricultural settings. Advancing these studies is essential to guide the development of scalable, adaptable nitrogen mitigation strategies that align environmental gains with agronomic effectiveness [88].

Finally, socioeconomic and policy barriers persist. The lack of standardised performance metrics, limited farmer awareness, and absence of regulatory recognition as a Best Available Technique (BAT) impede early adoption. Evidence from related ammonia mitigation technologies shows that perceived operational complexity and maintenance burdens can deter farmers even when environmental benefits are clear [115].

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