Review

An Overview of N₂O Emissions from Cropping Systems and Current Strategies to Improve Nitrogen Use Efficiency

Antonio Manco [1], Matteo Giaccone [1], Terenzio Zenone [2], Andrea Onofri [3], Francesco Tei [3], Michela Farneselli [3], Mara Gabbrielli [4], Marina Allegrezza [4], Alessia Perego [4], Vincenzo Magliulo [1] and Luca Vitale [1,*]

[1] Institute for Agriculture and Forestry Systems in the Mediterranean (ISAFoM), National Research Council of Italy, P.le E. Fermi 1-Loc, Porto del Granatello 1, 80055 Portici, Italy

[2] Institute on Terrestrial Ecosystems (IRET), National Research Council of Italy, Via P. Castellino 111, 80131 Naples, Italy

[3] Department of Agricultural, Food and Environmental Sciences, Borgo XX Giugno, 74, University of Perugia, 06121 Perugia, Italy

[4] Department of Agricultural and Environmental Sciences, University of Milan, Via Celoria 2, 20133 Milan, Italy; marina.allegrezza@unimi.it (M.A.)

* Correspondence: luca.vitale@cnr.it; Tel.: +39-06499327526

Abstract: Arable soils significantly contribute to atmosphere pollution through N₂O emissions due to the massive use of N-based fertilizers and soil managements. N₂O formation in the soil occurs mainly through nitrification and denitrification processes, which are influenced by soil moisture, temperature, oxygen concentration, pH, and the amount of available organic carbon and nitrogen. This review synthetically presents the mechanisms of N₂O formation and emission in arable land and some of the current strategies to improve crop nutrient use efficiency. Biological nitrification inhibitor-based agronomic strategies are also presented as future prospects for the sustainable management of crops, which is missing in most of the reviews.

Keywords: nitrification; denitrification; N₂O fluxes; nutrient use efficiency; mitigation strategies; fertigation

1. Introduction

Agricultural activities are currently heavily affected by climate change but are also a driver of climate change itself. Agronomic practices significantly contribute to emissions of a key greenhouse gases (GHGs), mainly in the form of nitrous oxide (N₂O) emitted directly from managed soils through microbial activities and due to the use of synthetic/organic nitrogen fertilizers. Strategies to mitigate soil N₂O emissions are critical, as they are long-living GHGs with a radiative force that is ~300 times higher than CO₂ [1]. Over the last decades, N₂O emissions from the agricultural sector showed a worldwide increase, and the largest contributions were from Asia (63%), followed by the Americas (20%), Europe (13%), and Africa (3%) [2]; moreover, N₂O represents the main stratospheric ozone-depleting substance and is predicted to remain so in this century [3].

There are different agricultural practices responsible for GHG emissions, in particular for N₂O emissions into the atmosphere. Among these, we can include the following:

- Nitrogenous mineral fertilization [4,5] in its scheduling [6], methods, and fertilizer form [7];
- Organic fertilization [8,9];
- Irrigation in its methods [10] and scheduling [11,12];
- Pastures [6,13];
- Tillage systems [10];
- Cultivated plant species [14].

Current agricultural practices, such as soil management and fertilization, are often responsible for low nitrogen use efficiency. Approximately only half of the N fertilizer inputs are recovered in the harvested yield [15]. Consequently, N application is likely to cause losses in the agroecosystem. Nitrate can be leached to the soil and surface waters [16,17], ammonia emissions can easily volatilize from topsoil soon after N fertilizer application [18], and gaseous N_2O is emitted because of nitrification and denitrification processes [19]. Accordingly, increasing NUE is regarded as an effective measure to protect the environment and enhance crop production [20].

To enrich our understanding of the concurrent effect of crop type (being characterized by physiological and genetic traits) and agronomic management on NUE, it is crucial to analyze the whole cropping system following the sequence of crops and fallow over time [21] and to study the N processes driven by microbiota, which is responsible for the immobilization of N and the availability of N mineral forms and tightly interacts with C dynamics [22]. Although the extent that agricultural soils are the dominating source of N_2O is well established, the complex relationship underlying microbial production/consumption processes and its links to biotic (e.g., inter- and intraspecies competition, plant–microbe interaction) and abiotic (e.g., soil, climate, and agronomic practices) factors requires an interdisciplinary cooperation and knowledge transfer between the scientific communities working on agronomic practices, soil microbial processes, microbial diversity, biosphere–atmosphere exchange, and modeling.

The aim of this review is to provide a brief overview of the biological processes involved in soil N_2O emissions and the key factors controlling its production, as well as the mitigation strategies. Prospectives to mitigate GHG emissions from cropping systems are also provided through new strategies that allow for ammonium to be retained longer in the soil. This issue is not addressed much in most of the reviews, and this paper aims also to fill this gap.

2. Soil Nitrous Oxide Emissions from Arable Soils: Microbial Processes and Key Controlling Factors

2.1. Nitrous Oxide Production Pathways

N_2O is produced through pathways interrelated and interacting to share intermediates or products. These pathways include the following:

(a) Nitrification-related pathways, including ammonia (hydroxylamine) oxidation and nitrite oxidation—respectively operated by chemoautotrophic ammonia-oxidizing bacteria (AOB) and archaea (AOA), and nitrite-oxidizing bacteria (NOB)—and the nitrifier denitrification consisting in the reduction in nitrite by ammonia-oxidizing bacteria (Figure 1).

(b) Heterotrophic nitrification, operated by heterotrophic bacteria and fungi, consists of ammonia or organic compound oxidation (Figure 2).

(c) Heterotrophic denitrification, operated by bacteria and fungi, consists of a microbial respiratory process that reduces oxidized mineral forms of N to gases, including N_2O (Figure 3).

Nitrification:

$$\text{Organic N} \longrightarrow NH_4^+ \longrightarrow NH_2OH \longrightarrow NO_2^- \longrightarrow NO_3^-$$
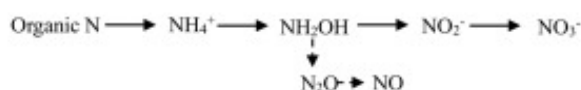$$N_2O \rightarrow NO$$

Figure 1. N_2O production through the nitrification pathway operated by nitrifiers.

Nitrifier denitrification:

$$NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

Figure 2. N_2O production through the autotrophic denitrification pathway operated by nitrifiers.

Denitrification:

$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

Figure 3. N_2O production through the denitrification pathway operated by heterotrophic microbes.

Nitrification is the biological conversion of ammonium in nitrite or nitrate (nitrifier nitrification, NN) and is performed by different groups of microorganisms, including ammonia-oxidizing bacteria (AOB), ammonia-oxidizing archaea (AOA), and nitrite-oxidizing bacteria (NOB) [23]. Ammonium oxidation, the first step of the NN pathway and catalyzed by the *amoA* gene encoding ammonia monooxygenase (AMO), is performed by AOA and AOB [24]. Nitrite oxidation, the second step of NN, is catalyzed by the *nxrA* or *nxrB* genes encoding nitrite oxidoreductase and is performed by NOB [25,26]. N_2O is produced during ammonium oxidation as a byproduct of the conversion of NH_2OH, an intermediate product of NN.

Heterotrophic nitrification is a further pathway producing N_2O. This pathway, operated by bacteria and fungi, consists of transformations of ammonium ions or labels of organic molecules to produce NO_2^- or NO_3^-, but the heterotrophic bacteria perform ammonia transformation by genes coding for AMO-type enzymes [27]. However, information regarding this pathway is scarce compared to that on autotrophic nitrification. It is known that this pathway prevails in acidic soils, such as forest soils, but recent studies also found it in arable soils [27].

Ammonia-oxidizing bacteria can also perform NO_2^- reduction through the nitrifier denitrification (ND) pathway [28]. In this pathway, ammonium is oxidized to NO_2^-, followed by NO production that is further reduced to N_2O. Ammonia oxidation is the rate-limiting step for the whole nitrification process [29], so it represents a critical step for the production of the nitrification-originated N_2O.

Denitrification is performed by heterotrophic microbes and involves the reduction in nitrate and nitrite in the presence of carbon availability and leads to N_2 synthesis. During these transformations, N_2O is generated as a byproduct. Different reductases are involved in the bacteria denitrification pathway [30]. The nitrate reductase, encoded by *narG* or *napA* genes, catalyzes the NO_3^- reduction to NO_2^-; the nitrite reductase, encoded by *nirK* or *nirS* genes, catalyzes the NO_2^- reduction to NO; the nitric oxide reductase, leading to N_2O formation, is mediated by the *cnorB* or *qnorB* genes; and the nitrous oxide reductase, encoded by the *nosZ* gene, which catalyzes the reduction in N_2O to N_2. Fungi produce N_2O through a nitrite-reducing system consisting of a copper–nitrite-containing reductase encoded by *nirK* homologs and a cytochrome P45 nitric oxide reductase encoded by the *P450nor* gene [31].

Extensive field measurements of N_2O exchange between soils and the atmosphere and laboratory incubation studies under controlled conditions provide a good understanding of the emission. Nevertheless, the dynamic and temporal trend of N_2O soil emissions are characterized by 'hot spots' with an enormous spatio-temporal variability [32,33] caused by a multitude of interacting control factors [34]. Among them, the availability of reactive nitrogen, coming from the use of fertilizer, represents the major driver of soil N_2O emissions. To better understand how soil microorganisms contribute to N_2O emissions, studies that applied next-generation sequencing (NGS) and bioinformatics technologies for the metagenomic analysis of soil microbiota appear to be of pivotal importance, as well as a quantitative real-time polymerase chain reaction (qPCR) for the quantification of the abundance of key genes [35,36]. The extraction of total genomic DNA from soils is conventionally used as a template to perform metagenomic studies by High-Throughput Sequencing (HTS) or qPCR [37].

2.2. Drivers of Nitrous Oxide Production and Soil Emissions

Microbial N_2O production is affected by several key factors such as soil oxygen levels, water content, pH, temperature, and the availability of nitrogen and carbon. Those factors

are, in turn, influenced by climate conditions, soil texture, soil and crop management, and fertilizer type. Soil microbial biomass, responsible for nitrification and denitrification and of N_2O production emissions, requires adequate environmental conditions that control the N_2/N_2O ratio [38].

2.2.1. O_2 Levels

Soil oxygen level (O_2) is the key factor simultaneously controlling nitrification and denitrification by influencing both processes and determining the partitioning of the end products between N_2 and N_2O [39]. Enzymes involved in N_2O production are sensitive to O_2. soil O_2 concentration is probably the most critical variable that directly regulates N_2O production and consumption at the cellular level. It is well known that high O_2 levels in the soil promote N_2O production by nitrifier nitrification and reduce N_2O production by heterotrophic denitrification and nitrifier denitrification. Moreover, high O_2 levels inhibit N_2O reductase, the only enzyme catalyzing a reduction in N_2O to N_2, resulting in a net emission of nitrous oxide gas. On the other side, at moderately low O_2 levels, N_2O production is mainly promoted by nitrifier denitrification due to an increasing expression of denitrification enzymes in AOB, whereas at very low O_2 levels, heterotrophic denitrification dominates on the other N_2O producing processes. Song et al. [40] found that the soil N_2O concentrations increased quadratically as soil O_2 decreased during hot moments in dryland agricultural soil in Northern China, with the highest N_2O production occurring when O_2 levels dropped below 0.2%.

O_2 levels in the soil are affected by soil texture. It is generally considered that fine-textured soils provide more favorable conditions for N_2O emissions by denitrification than coarser-textured soils that favor nitrification [39,41]. This occurs because fine-textured soils have small pores that become more easily anaerobic after rainfall or irrigation and remain that way for longer durations than coarser-textured soils.

2.2.2. Water Content

Soil humidity affects N_2O emissions by influencing O_2 availability for biological transformations. Irrigation and precipitation increase soil water content, thus reducing the pore space that can be occupied by oxygen and influencing the soil O_2 diffusion in the water phase, which is much lower than in air. From this consideration, it follows that the diffusion rate of O_2 in the soil following heavy rain or irrigation declines below the soil O_2 consumption rate by microbes. The water-filled pore space (WFPS), a parameter that combines the soil water content with the soil's physical properties, such as soil porosity and apparent density, is inversely correlated with O_2 availability. The highest N_2O emissions occur for a WFPS of 60–65% and are mainly attributed to denitrification, whereas nitrification is responsible for N_2O emissions for a WFPS below 60% [11]. For higher WFPS levels (70–90%), N_2O emissions are mainly due to denitrification, but in soils saturated by water, N_2O emissions are minimal due to N_2O consumption during heterotrophic denitrification (Figure 4).

The irrigation dose, by influencing the soil moisture, affects N_2O emissions. Carbonell-Bojollo et al. [42] report that a full irrigation dose on crop demand produces more N_2O than a reduced dose, whereas Guo and colleagues [43] report that an excessive water in a vineyard increased N_2O loss. These findings highlight the role of irrigation management in nitrous oxide production.
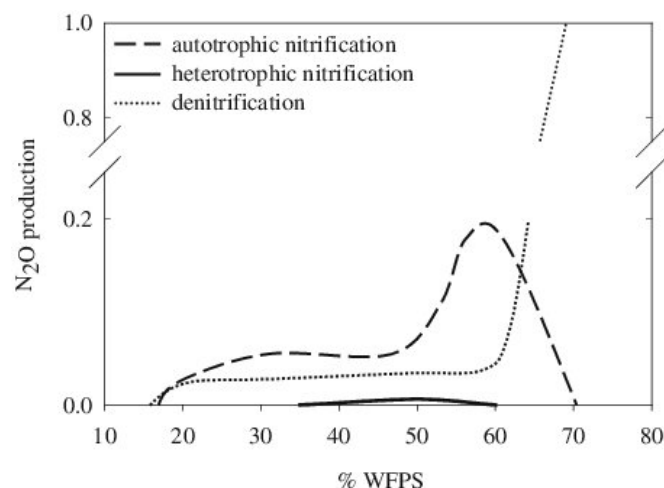
Figure 4. Contribution of nitrification and denitrification to N_2O soil emissions; from Bateman and Baggs (2005).

2.2.3. pH

pH affects N_2O emissions by affecting the growth of microbes. Acid pH is more beneficial to nitrifiers than denitrifiers. More specifically, the growth of ammonia-oxidizing bacteria (AOB) is limited in acid soils—in which optimal growth is restricted to neutral and subalkaline soils—but not ammonia-oxidizing archaea (AOA), which have been detected in a wide range of soil pH from acid (pH < 5) to alkaline values (pH > 7) [44,45]. The causes of limited growth of AOB in acid soil might be attributed to the limited diffusivity of NH_4^+ across the AOB membrane upon acid pH, which instigates the strong ionization of NH_3 to NH_4^+, limiting AOB's ability to oxidize. Acid pH also favors heterotrophic nitrification, promoting fungi growth using organic over inorganic N [46]. On the contrary, the alkaline environment strongly affects microbial denitrification [47]. Alkaline soils promote denitrification because reductase activities are more instigated at alkaline pH [48].

Long-term or excessive application of N fertilizers can lead to soil acidification [49], which promotes N_2O emissions. Different approaches have been tested to counteract soil acidification. Among these, pH change through soil liming is one of the most efficient strategies to mitigate soil N_2O emissions from acid soils [50].

2.2.4. Temperature

Temperature is another key factor controlling N_2O production. N_2O emissions increase with increasing temperature up to 35 °C [51]. Nitrification and denitrification seem to respond similarly to temperature. Temperatures above 35 °C reduce N_2O production, likely due to enhanced O_2 consumption through an increased microbial respiration, creating anaerobic conditions, a circumstance that increases the reduction in N_2O to N_2 [51]. Soil texture is a factor affecting the temperature sensitivity of N_2O emissions. Cui et al. [52] showed that the temperature sensitivity of N_2O emissions was lower as soil texture became more clayey. This might occur because in a warming environment, clay soil has a greater possibility to create an anaerobic microenvironment as a result of the greater oxygen consumption resulting from C mineralization in small unconnected pores, which would accelerate N_2O production by denitrifiers.

2.2.5. Nitrogen and Carbon Availability

Soil nitrogen (N) availability is the main driver of N_2O production [53]. Different N forms are used by soil microbes for their growth, contributing to nitrous oxide emissions from arable soils. Therefore, N fertilization is the main cause for environmental pollution by nitrogen. The ammonium in urea and ammonium nitrate fertilizers is rapidly transformed after their application in the field into nitrate through nitrification, thus producing a substrate (NO_3^-) utilizable by autotrophic and heterotrophic microbes through denitrification.

Under soil conditions promoting nitrification, a decrease in the amount of NH_4^+ and an increase in NO_3^- in the soil occurs during the N_2O emission peak, as NO_3^- is being produced while NH_4^+ is being consumed by nitrifiers [54].

Heterotrophic denitrifiers use a carbon (C) source as an electron donor to produce nitrous oxide under anaerobic conditions [53]. However, the quantity and quality of soil carbon affect denitrification [55]. As the quantity of C available to denitrifiers increases, the rate of denitrification increases if a sufficient NO_3^- substrate is present and anaerobic conditions occur. C in soil derives from organic fertilization through the deposition of manures and slurries and from the mineralization of organic matter or root exudation. Increasing availability of labile C in the soil can enhance O_2 consumption due to an enhanced microbial respiration, thus increasing anaerobic conditions that favor denitrification and, in turn, N_2O production. However, excessive oxygen consumption due to enhanced respiration because of higher labile carbon content can limit oxygen availability to microbes and favors complete denitrification to N_2.

The C/N ratio might affect soil N_2O emissions, even if contrasting results have been found. For instance, negative [56], positive [57], or no relationships [58] between the soil C/N ratio and N_2O emissions were observed in field studies, evidencing that the soil C/N ratio alone may be insufficient to predict N_2O emissions, unlike labile forms, such as soluble organic carbon and particulate and light fraction organic carbon, which are more palatable to N_2O producers.

3. Strategies for Improving Nitrogen Use Efficiency by Crops and Mitigating N_2O Emissions in Agro-Ecosystems

In the last 50 years, the EU has become increasingly concerned with the efficiency of the use of fertilizers. Indeed, these substances may exert strong beneficial effects in agriculture, but they also hold the potential to negatively impact human health and environmental safety.

This is particularly true for nitrogen due to the peculiar characteristics of such a nutrient. Indeed, on one side, N has a huge effect on crop productivity and, therefore, its fertilization rate is often pushed far beyond the actual crop demand, as cheap insurance against yield losses. On the other side, however, this element is known to be rather mobile in soil and prone to high losses through leaching, especially with high rainfall levels and irrigation volumes [59]. Furthermore, several crops, especially leafy vegetables, can accumulate luxury nitrogen in their leaves, leading to health problems for humans and animals. These possible side effects of N fertilization have promoted great concern regarding the efficiency with which the crops use the N fertilizer that we provide. Obviously, the efficiency of the use of fertilizers is a general problem that concerns all nutrients, but the way we have to tackle it for N is rather peculiar due to the aforementioned mobility of this element in soil.

3.1. Nitrogen Use Efficiency (NUE)

Nitrogen use efficiency (NUE) has been the object of a remarkable research effort. In general, it has been shown that NUE is rather small for most crops; for example, years ago, it was estimated that worldwide NUE for cereals used to be as low as 33% [60]. Ref. [61] highlighted that NUE comprises three main components: (i) nitrogen uptake efficiency (NUpE), (ii) nitrogen utilization efficiency (NUtE) in producing biomass, and (iii) the nitrogen harvest index (NHI). NUtE and the NHI can be merged into one component: the utilization efficiency for harvestable products.

Of those three components, NUpE is rather important since, despite the high demands, the great majority of crops can only absorb a small fraction of mineral N in the soil. In this respect, [62] studied the amount of N absorbed by the crop (excluding fibrous roots) with and without the application of N fertilization and defined the concept of the Apparent Recovery (REC) of the N fertilizer; these authors proved that the REC declined when the fertilization rate was increased. Later studies showed that the REC is strongly variable

depending on the crop species, according to their root physiology and architecture [61,63]. Furthermore, the REC was also shown to be influenced by soil conditions (e.g., it is reduced by water shortage, which decreases crop growth and N uptake), weather conditions (e.g., high rainfall levels), agronomic practices (e.g., high irrigation volumes), and fertilization methods (e.g., broadcast application over localized application) [64,65].

In order to improve NUpE, we can use different tools and strategies as follows [66]:

- Breeding N-efficient genotypes. In the past, several research has been carried out in order to select physiological, biochemical, and molecular traits affecting nitrogen uptake by plants through roots. In particular, studies have addressed the spatial root arrangement in the soil evaluating the root depth, lateral root expansion, and root length densities, together with a variety of components, such as roots and root segments [63]. Studies have also been carried out in order to understand the molecular basis of the transport systems involved in the absorption of NO_3^- from the soil and its systemic fluxes within plants, as well as studies that have been addressed to identify the Ammonium Transporters (AMTs) and the gene family of the Amino acid Transport Family (ATF) [63]. All that knowledge has made it possible to start crop breeding programs with high nitrogen absorption through the introgression of the improved trait into the gene pool of the new genotype [63].

- Adopting appropriate agronomic practices, with particular reference to, e.g., tillage, crop rotation, green manuring, intercropping, grafting, the use of biostimulants, and, obviously, organic/mineral fertilization. This latter aspect (mineral fertilization) is understandably receiving a lot of attention, for example, through the 4R Nutrient Stewardship [67,68], which provides a framework for applying the right nutrient source at the right rate, at the right time, and at the right place. Recently, the use of biostimulants to improve NUE by crops has received more and more attention, with encouraging results. Navarro-León et al. [69] demonstrated that L-α-amino-acid-based biostimulants enhance plant productivity through improved photosynthesis and increased the assimilation of essential nutrients, such as nitrogen (N). Cozzolino et al. [70] found that legume-derived protein hydrolysates and the extract of brown seaweed *Ecklonia maxima* applied on the leaves improved the yield and quality of tomato grown in the field. The use of lignite-derived humic substances applied to the soil has also proven effective in improving NUE through an improvement in nitrogen uptake efficiency (NUpE) and nitrogen utilization efficiency (NUtE) by tomato crops [71]. Among biostimulants, microbial biostimulants also are currently used in agriculture to improve the efficiency of the use of fertilizers and, in particular, N fertilizers. Bacteria and other microorganisms, through their metabolic processes, exude or secrete a wide range of biochemical compounds into the soil that allow plants to efficiently use nutrients [72].

With particular reference to nitrogen, increasing NUpE should be based on the following [66]:

a. Determination of the N demand from the crop.
b. Determination of the right N fertilizer rates to meet crop demand, considering the interactions between crop uptake, soil supply, environmental risks, and field operation logistics.
c. Correct application techniques, favoring localized over broadcast applications.
d. Selection of the proper nutrient source to ensure the best match between nutrient availability and crop requirements.

The problem of selecting the right nutrient source brings in the so-called Enhanced Efficiency N Fertilizers (EEFs), which may play a key role in ensuring a better synchronization between N root uptake and N release kinetics, which is one of the fundamental aspects used to reduce the spread of N into the environment. Currently, EEFs can be classified into five categories: (i) slow-release N fertilizers, (ii) controlled-release N fertilizers, (iii) nitrification inhibitor-treated N fertilizers, (iv) urease inhibitor-treated N fertilizers, and (v) fertilizers treated with both nitrification and urease inhibitors [73–75].

3.2. Slow- and Controlled-Release Fertilizers (SRFs and CRFs)

Slow-release fertilizers (SRFs) are characterized by low solubility in water, and they include urea-formaldehyde (UF) and isobutylenediurea (IBDU); the first compound releases N through microbial decomposing activities, which are strongly affected by several environmental factors, such as temperature and soil characteristics. In contrast, IBDU releases N through hydrolysis at low temperatures and is, therefore, preferred for winter applications [76]. Field studies demonstrated the effectiveness of slow-release fertilizers. For example, SRFs improved the yield of sugarcane [77] and winter Chinese chives [78] and, at the same time, mitigated the adverse effects of excessive fertilizer use in agricultural practices.

In controlled-release fertilizers (CRFs), N release is regulated by the presence of a water-insoluble coating, which is made of, e.g., sulfur, organic polymers, inorganic polymers, or several types of combinations. This coating material slows down the release of fertilizers, depending on the type of coating, soil temperature, and soil humidity [76,79,80]. Regarding the type of coating, organic and inorganic materials have been used. Organic polymer materials are mostly made of thermoplastic resins, such as polyolefin, polyvinylidene chloride, and copolymers, which cannot degrade easily in soil. Sometimes, natural organic polymers have been used, such as starch, chitosan, and cellulose. In general, [81] lists more than 10 types of organic coating materials, with very different characteristics and release times. Inorganic coating materials are usually made from sulfur and minerals, such as hydroxyapatite, bentonite, zeolite, and attapulgite. Among these inorganic coating materials, calcium phosphates (CaPs) have been gaining attention as CRFs due to their relatively high phosphorus content, pH-dependent solubility in water, and ability to act as carriers of micro- and macro-nutrients, including nitrogen. The beneficial effects of CRFs on grain yield and NUE largely depend on the synchronization of the N release rate with the N needs of crops. By slowing down the release of available N, the CRF reduces N availability for microbial transformation, limiting soil N_2O emissions [82].

In general, SRFs and CRFs have been successfully used in field and vegetable crops, wherein they have demonstrated an ability to improve NUE, reduce nutrient losses due to leaching and the volatilization of fertilizers, and provide economic advantages due to decreased fertilization rates [83] and increased agronomic efficiency. Furthermore, SRFs and CRFs have been proven to reduce possible toxicity phenomena to plants and seedlings by reducing the local concentration of ions, which can induce osmotic stress and damage in the case of traditional fertilizers [84]. On the other hand, SRFs and CRFs have also shown some disadvantages, mainly related to the lack of reliable methods to forecast the release of nutrients to the plant; indeed, it has been shown that especially with short-cycled crops, nutrients may continue to be released after crop harvest in a prolonged manner [85]. In addition, the use of sulfur-coated urea (SCU) can increase soil acidity, while polymer-coated CRFs with synthetic materials can be difficult to degrade, producing a different form of pollution. Last, but not least, SRFs and CRFs can be more costly than conventional N fertilizers [59].

3.3. Nitrification Inhibitors (NIs)

Another way to obtain EEFs is based on the use of the so-called nitrification inhibitors (NIs); these compounds decrease the speed of conversion of ammonium to nitrate, thereby reducing the risk of nitrate leaching and N_2O emissions. The most used NIs are 3,4-dimethylpyrazole phosphate (DMPP) and dicyandiamide (DCD) [86–88]. Several studies show the potential usefulness of such compounds in terms of NUE and environmental side effects, such as nitrate leaching and N_2O emissions [89]. According to a comprehensive meta-analytic work [89], the reduction in N leaching following the application of NIs was, on average, 48%. Other authors showed that the use of NIs permitted a decrease in the number of N applications [86] and a reduction in nitrate concentration in leafy vegetables [90]. Analogously to CRFs and SRFs, the activity of NIs may depend on soil properties, such as temperature and pH. In particular, the activity of DMPP is more dependent on soil type than that of DCD, although the efficacy of both inhibitors was lower in more

alkaline, low-organic matter soil [91]. The inhibitory activity of DCD and DMPP was shown to last for, respectively, 50 and 95 days, as measured in incubation experiments with cauliflower residues [92].

Apart from NIs, urease inhibitors (UIs) can also be used in EEFs. These compounds block the activity of the urease enzyme, resulting in the inhibition of the hydrolysis of urea into ammonium. Such activity is beneficial because it reduces the volatilization of ammonia—which may occur in soils with high pH or poorly buffered against pH changes where the rapid hydrolysis of the urea may result in the accumulation of ammonia rather than ammonium—and limits N_2O production and, in turn, emissions from the soil to the atmosphere. Products with known UI activity are N-(n-butyl) thiophosphoric triamide (NBPT) and N-(n-propyl) thiophosphoric triamide (NPPT). These active ingredients are found in products with tradenames of Agrotain™ (NBPT) and Limus™ (NBPT and NPPT), but, to date, it is also possible to find NBPT in other commercial products since this compound is no longer patent protected. UIs have proven effective in increasing yields and NUE and protecting against ammonia losses.

Of course, NIs and NUs can also be used in combination with each other in order to 'close' all possible N escape routes, which is not achieved when these inhibitors are applied individually [73]. It has been shown that the use of UIs reduced the volatilization of ammonia but increased the volatilization of nitrogen oxides, which was avoided by combining the two inhibitors [93]. Ref. [94] found that the application of a double inhibitor combining NBPT and 2-(3,4-dimethylpyrazole-1-YL)-succinic acid (DMPSA) produced a 50% reduction in N volatilization.

Although both NIs and NUs have been proven useful [95], in some circumstances, their activity may not be sufficient, especially when weather and soil conditions are favorable to N losses or when excess N doses are used [96]. For these conditions, research is needed to obtain improved formulations and elucidate possible ways for improved distribution and better integration with correct agronomic practices to reduce N losses and increase NUE. Moreover, [59] observed that given the concern of consumers and retailers regarding healthy food, attention will need to be paid to ensure that there are no or minimal residues of NUs and NIs and their degradation products in edible vegetable organs.

A survey of the literature shows that all the above types of EEFs have been around for several years, and a lot of information is available in relation to their behavior in the environment. However, far less is known about their optimal usage in agriculture (e.g., timings, dosages, and methods of application), which is strongly affected by the complex interactions between the environment (soil and weather conditions), crop development, and the dynamics of the release of nutrients. Furthermore, it is not yet totally clear to what extent these EEFs can increase NUE, depending on the crop and on main environmental and agronomic factors. Last, but not least, not much information is available to predict the environmental impact of these compounds using reliable life cycle assessment methods.

3.4. Fertigation

Fertigation is a valid strategy to increase NUE [96] by crops while decreasing leached N [97] and fertilizer-induced N_2O emissions from soil. Fertigation consists in the application of nutrients through irrigation systems; it presents advantages over dry fertilization, such as a more precise N management in coordination with crop demand [98]. By splitting the nitrogen fertilizer application, so-called 'high frequency' fertigation, the risk of nitrate leaching is minimized [99] and the N uptake by roots is improved [100]. High frequencies with a low quantity of N fertigation also have a third priority, i.e., to reduce N_2O emissions. By allowing the reduction in fertilizer quantity to be applied each time, high-frequency N fertigation limits N availability for microorganisms under environmental conditions that promote N_2O production during nitrification and denitrification processes. However, the benefits of fertigation in improving crop NUE and mitigating N_2O production depend on the N source. It should be expected that there will be greater N_2O emissions in crops

fertigated with urea or ammonium fertilizer than with nitrate-based fertigation [101], resulting in greater NUE by crops for NO_3^--based fertilizers under high frequencies [102].

4. Future Prospective

To limit soil N_2O emissions and improve fertilizer use efficiency by crops, it is necessary to create a low-cost and convenient agronomic strategy that keeps (or improves) crops' quantity and quality. Regulating nitrification is central to any strategy for improving nitrogen use efficiency; one of these strategies could be represented by the biological nitrification inhibition (BNI) where nitrification inhibitors exuded from plant roots suppress soil nitrifying activity, thus favoring N uptake by plant roots [103]. Different botanical species produce NIs; among these are pasture grasses, such as *Panicum maximum* Jacq. and *Lolium perenne* L., cereal crops, such as *Sorghum bicolor* L. and *Pennisetum glaucum* L., and legume crops, such as *Arachis hypogaea* L. To some extent, the release of NIs from roots is related to the plant N status [104] and by the N form applied. So, plants grown with NO_3 as a nitrogen source do not release NIs from roots, whereas plants grown with NH_4 as their nitrogen source release them.

Different molecules have been identified as nitrification inhibitors. For example, methyl 3-(4-hydroxyphenyl) propionate and sorgoleone are exuded from sorghum roots, 1,9-decanediol from rise roots, and brachialactone linolenic acid and linoleic acid from *Brachiaria humidicola* roots. Karanjin, a furanoflavonoid (3-methoxy furano-2′,3′,7,8-flavone), is obtained from *Pongamia glabra* seeds. All these BNIs block both AMO and HAO enzymatic pathways [105]. However, new molecules potentially having inhibitory properties have to be discovered or tested. For example, cannabinoids have a molecular structure, like synthetic inhibitors, and, for this reason, they have the potential ability to inhibit the enzymatic pathways involved in nitrification. By exploiting the ability of plants to produce nitrification-inhibiting substances, it could be interesting to develop new cultivation strategies involving target species in association with BNI species or introduce the BNI-controlling chromosome region in target plants, which is unable to produce inhibiting substance constitutively [106]. These new strategies will allow ammonium to be retained longer in the soil, which will be absorbed and assimilated easily by the target crops. In this way, the effectiveness of fertilizer uses increases, and fewer nitrogen fertilizers will be required by crops, thus preventing the salinization and eutrophication of water bodies.

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