Multiple Facets of Nitrogen

Subjects: Agronomy

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Nitrogen is a gas present in the air with an atomic mass of 14.007, a boiling and melting points of 77.36 K and 63.15 K, respectively, and a density of 0.0012506 g·cm^{-3}. N was first discovered in 1772 by the Scottish physician and chemist Daniel Rutherford. The multiple facets of N are described. A paradigm shift is important to shape to the future use of N-rich fertilizers in crop production and their contribution to the current global greenhouse gases (GHGs) budget would help tackle current global environmental challenges toward a sustainable agriculture.

Keywords: nitrogen ; agriculture ; environment

1. Basic Properties of Nitrogen and N-Containing Compounds

Nitrogen is the fifth most abundant element in the universe after hydrogen (H, first), helium (He, second), oxygen (O, third), and neon (Ne, fourth), and it makes up approximately 78.1% of the earth's atmosphere. Reports indicate that an estimate of 4000 trillion tons of N can be found in the atmosphere in the form of N_2 (https://pubchem.ncbi.gov/element/Nitrogen, accessed on 31 May 2022). The most popular use of N is for the production of ammonia (NH_3) when combined with hydrogen (H), in a process called the "Haber process" [1]. Then, large amounts of NH_3 are used to produce mineral fertilizers in a process known as the "Ostwald process", among other uses [2]. N is found in all living systems as part of the makeup of biological compounds. During the decomposition of organic matter (OM), sodium nitrate ($NaNO_3$) and potassium nitrate (KNO_3) are formed. Other inorganic N compounds include HNO_3, NH_3, the oxides (nitric oxide (NO), nitrogen dioxide (NO_2), N_2O_4, and nitrous oxide (N_2O)), and cyanides (CN). NO_2, NO, nitrous acid (HONO), and nitric acid (HNO_3) belong to a group of highly reactive gases known as oxides of nitrogen or nitrogen oxides (NOx) [3].

NO_2 is formed during nitrification and denitrification processes, in which N_2O and NO are released, with N_2O reported to be formed from NO_3-dependent NO formation [4]. N_2O is a potent greenhouse gas (GHG), with a global warming potential (GWP) 300 times greater than the mass of carbon dioxide (CO_2) in the atmosphere, right before methane (CH_4) and CO_2 [5][6]. As for NO, reports indicate that this molecule is versatile and bioactive, with the potential to diffuse through biological membranes owing to its physiological properties. NO can act as a signaling molecule, which may involve a very wide web with reactive oxygen species (ROS). However, excessive accumulation of NO induces stressful conditions in plants [7][8]. NO and its derived molecules are reported to be involved in abiotic and biotic stress response mechanisms.

2. Historical Use of Nitrogen and N-Rich Fertilizers in Agriculture

The history of agriculture revealed that a number of plant species were domesticated from wild ancestors [9][10][11][12][13][14] during the Early Pre-Pottery Neolithic period, at various locations and different times between 10,500 and 10,100 years before common era, BCE [15][16][17]. During this period, crops exhibited a low productivity, poor yields, and poor quality, mainly attributed to their genetic makeup [16][18][19][20][21][22][23]. Since then, significant progress has been made using plant breeding and the establishment of plant nutrition schemes. According to Pennazio [24], the development of mineral nutrition of plants began between the 17th and 18th centuries. The patterns of mineral fertilizer applications in different cropping systems, as well as their impact on the environment, continue to nourish the debate globally [25][26][27][28][29][30][31][32][33][34][35][36][37][38]. However, the increase in food demands due to the rapid increase in the global population has shown the necessity to enhance the productivity of food crops. To achieve that, the common strategies used are crop improvement and the use of mineral fertilizers during crop cultivation, which have increased over the years [39][40]. Despite the recorded progress in plant breeding, N remains an indispensable macronutrient, among the 14 mineral elements (macro- and micronutrients) required by plants for optimum growth and development, high productivity, quality, fitness, and resistance toward environmental and biotic stresses [41][42].

Data indicate that the application of N-rich fertilizers increased over the years concomitant with the expansion of crop cultivation areas and the use of improved or high-yielding crop varieties that are demanding of nutrients, particularly observed in large-scale farming systems. This trend could be partially attributed to the increase in food demands subsequent to the increase in the world's population. An estimate of the global population growth shows that the number of people on Earth increased by 219.1% in 72 years, from about 2,499,322,157 in 1950 to nearly 7,975,105,156 in 2022 (https://www.macrotrends.net/countries/WLD/world/population, accessed on 15 July 2022), in contrast to the decreasing pattern of the annual population growth rate during the same period (nearly 1.75% in 1951 down to 0.83% in 2022, a decrease by 47.4%). Available data on land coverage, as reported by the Food and Agriculture Organization of the United Nations (FAO) statistics (https://www.fao.org/faostat/en/#data/LC/visualize, accessed on 15 July 2022), suggest that herbaceous crops occupied about 1,877,418.8 ha of cultivated lands in 1992 compared to 1,904,136.4 ha in 2020 globally. In addition, the report on the use of nutrients for agricultural production during the last six decades indicates that nearly 4,155,951,874 metric tons of N was used between 1961 and 2020 (11,455,804.3 mt in 1961 and 113,291,696.7 mt in 2020) (https://www.fao.org/faostat/en/#compare, accessed on 15 July 2022). When compared with other macronutrients (phosphorus (P) and potassium (K)), N is by far the most abundantly used plant nutrient element in agriculture (nearly 4.15 billion tons (BT) within 59 years). For instance, a report by FAO showed that during 1961–2020, more than 1.9 BT of phosphate (P_2O_5) and 1.4 BT of potash (K_2O) were used for agricultural production globally (**Figure 1**).

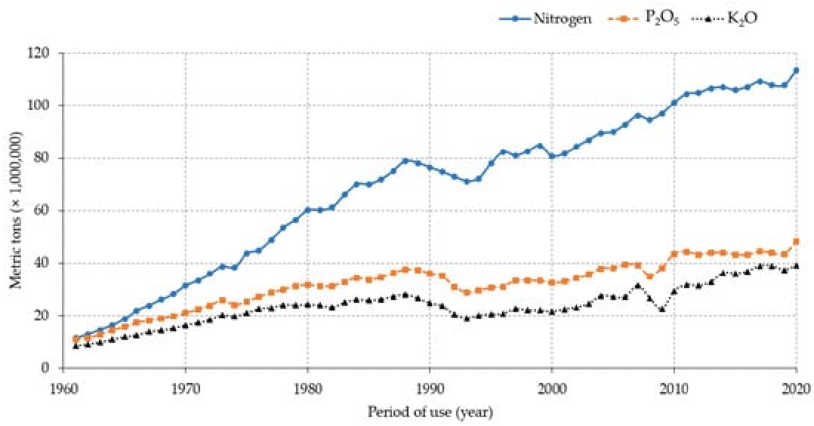

Figure 1. Pattern of global macronutrients use in agriculture from 1961 to 2020.

3. Essentiality of Nitrogen, Sources, and Availability

Arnon and Stout [43] proposed three criteria for the essentiality of a plant nutrient as follows: (1) a deficiency of the element makes it impossible for a plant to complete its lifecycle; (2) the deficiency is specific to the element in question; (3) the element is directly involved in the nutrition of the plant, such as a constituent of an essential metabolite or required for the action of an enzyme system. Other reports suggested that a more inclusive definition of the essentiality of a plant nutrient should be considered, which is not limited to those elements when they are deficient in the soil or unavailable, when they may cause symptoms of deficiency, and when their correction may involve an external supply through fertilization [44][45][46]. Therefore, on the basis of the abovementioned criteria, N and 15 other elements, namely, carbon (C), hydrogen (H), oxygen (O), phosphorus (P), potassium (K), calcium (Ca), magnesium (Mg), sulfur (S), iron (Fe), manganese (Mn), copper (Cu), zinc (Zn), molybdenum (Mo), boron (B), and chlorine (Cl), are considered essential for the growth of higher plants. Of this list, C, H, and O are acquired by the plant directly from the air and soil water, while the remaining 13 are supplied by the soil [47][48]. On the basis of the amounts in which the essential nutrients are acquired by the plant (except C, H, and O), they are categorized as primary (N, P, and K) and secondary macronutrients (Ca, Mg, and S), and micronutrients (Fe, Mn, Zn, Cu, B, Mo, and Cl).

Plants are sessile living organisms, which do not have the ability to move from one environment to another looking for food in the case of nutrient deficiency in their immediate environment [49][50]. Soil is the principal source of nutrients (including N) necessary for plants to complete their life cycle [51][52]. The availability of N is affected by various factors that may be extrinsic or intrinsic to the plant [53][54][55][56][57][58]. Crop productivity relies heavily on N fertilization [59][60][61]. N is found abundantly in the air but in a form that plants cannot absorb. The major sources of N are atmospheric nitrogen gas N_2, exogenous N supply, and OM through fertilization. Atmospheric N_2 gas (plentiful in the air but cannot be absorbed by plants in this form) is acquired through the nitrogen fixation cycle mediated by plant species belonging to Fabaceae (leguminous, along with a few non-leguminous plants containing nodules in their roots) in a symbiotic association with soil microorganisms known as nitrogen-fixing bacteria belonging to the genus *Rhizobium*. The latter mediate the conversion of atmospheric N_2 to ammonium (NH_4) in the soil, which in turn is converted to nitrate (NO_3) during the nitrification process.

According to Maier [62], the growth of many bacteria, either free-living in the environment or in symbiosis with plants, is promoted during N fixation in areas where fixed N is deficient in the soil. The root nodule bacteria have many O_2-binding terminal oxidases, with a high O_2 affinity, which are associated with N_2 fixation and help maintain a steady O_2 supply, coupled with ATP supply for high energy-demanding N_2 fixation. The fertility of soil depends on several factors, including the quantity and quality of nutrients present in the soil, soil physical, biological, and chemical properties [63].

NO_3 and NH_4 are the major forms of N taken up by the plant, with NO_3 being the most abundant [61]. However, roughly half of N (all N sources and forms considered) is used by the plant, while the remainder is either lost to groundwater (percolation or leaching), consumed by soil microorganisms (bacteria) involved in the decomposition of OM to humus, or converted back to atmospheric N_2 via the denitrification process.

4. Nitrogen-Based Fertilizers

Nitrogen is commonly applied using commercial N-containing fertilizers or OM (composts, liquid organic fertilizers, and animal feces) [64][65][66][67][68]. One of the most abundant forms of N commercially available is urea 46% N ($(CO(NH_2)_2)$ or CH_4N_2O) also known as carbamide, or it can be found together with P in the form of diammonium phosphate (DAP, $(NH_4)_2HPO_4$). The latter is also referred to as ammonium monohydrogen phosphate, ammonium hydrogen phosphate, or ammonium phosphate dibasic, with the typical formulation of 18% N, 46% P_2O_5, 0% K_2O) or triple superphosphate (TSP) referred to as calcium dihydrogen phosphate or monocalcium phosphate ($(Ca(H_2PO_4)_2{\cdot}H_2O)$, containing 45% phosphate (P_2O_5) (0–45–0), 15% Ca), whereas, K is supplied as potash (K_2O) [58]. Together, they make up the trio widely known as NPK. In the soil, N is available to the plant and transported in the form of NO_3 and NH_4, with NO_3 transport being predominant over NH_4 and the major source N [69][70]. DAP is known as the world's most widely used phosphorus fertilizer and one of the known water-soluble ammonium phosphate salts that can be produced when ammonia (NH_3) reacts with phosphoric acid (H_3PO_4) ($(NH_4)_2HPO_4$ (s) $\rightleftharpoons$ NH_3 (g) + $(NH_4)H_2PO_4$ (s)) [71]. Reports indicate that, when applied as a source of N and P, DAP temporarily increases the soil pH but becomes more acidic over the long term upon nitrification of the NH_4, and it is said to be incompatible with alkaline chemicals due to the high potential for the NH_4 ion to convert to NH_3 in a high-pH environment (pH 7.5–8.0).

5. Tracking Nitrogen Uptake and Assimilation in Plants

Fertilizers labeled with radioactive isotopes, such as phosphorus and nitrogen-15 have been used to investigate fertilizer uptake, retention, and utilization [72][73][74]. The N-15 (^{15}N) isotopic technique, which may help identify the source of N_2O generation and reduce the emission of this potent GHG during nitrification and denitrification processes, offers comparative advantages over conventional techniques for measuring the impact of climate change [74]. Stable isotope enrichment approaches have long been established to trace the source of N_2O following the application of ^{15}N-labeled fertilizers, such as ^{15}N-labeled NH_4 and NO_3 [75]. This technique enables the determination of the source of fertilizer-derived ^{15}N-N_2O.

In general, nitrification derived N_2O is quantified upon the supply of $^{15}NH_4$, while that mediated by denitrification is measured following the supply of $^{15}NO_3$. In the same way, considering that multiple pathways mediating N_2O formation and consumption occur simultaneously in various microenvironments in soils, nitrification inhibitors and isotope signature techniques are commonly utilized to separate N_2O-producing and -reducing pathways [76]. Stevens and Laughlin [77] suggested that the reduction of N_2O to N_2 could be quantified by determining ^{15}N in N_2 following the supply of $^{15}NO_3$. Similarly, Baggs et al. [78] demonstrated that application of $^{14}NH_4/^{15}NO_3$ and $^{15}NH_4/^{14}NO_3$ helped determine the relative contributions of nitrification and denitrification to N_2O production. Furthermore, He et al. [79] proposed the use of the stable ^{15}N isotope as a means for quantifying N transfer between mycorrhizal plants, considering that plants acquire nutrients from soil, and mycorrhizae play vital roles in plant nutrient acquisition, performance, and productivity. In the same way, the use of the carbon-13 (^{13}C) stable isotopic technique helps evaluate the source of carbon sequestered in the soil.

Isotopic fractionation [80][81][82][83] can cause the isotope amount ratio $n(^{15}N)/n(^{14}N)$ to increase systematically through food chains via assimilation of N compounds in biomolecules such as proteins. Isotopic fractionation occurs because of assimilation, storage, and excretion of proteins and other N compounds. Isotope amount ratio $n(^{15}N)/n(^{14}N)$ measurements have been widely used to test hypotheses about predator–prey relations and detect disruptions to the trophic structure of ecosystems that might be caused by toxic contaminants, invasive species, harvesting, or organisms. Similar principles are used to detect differences in diets among animals, including humans [84][85][86].

Artificially enriched ^{15}N tracers are used to study movement and transformation of N in biological and environmental systems, such as the uptake and loss of N fertilizers by crops. A common experiment involves introducing an isotopically labeled compound into the environment and then analyzing various samples taken from the environment for the presence of the enriched isotope to determine where the labeled compound moved and whether it transformed into another compound. Artificially enriched ^{15}N has also been employed to study uptake and dispersal of N in feed supplies used in food production industries such as aquaculture [87].

The stable isotopes of N are subject to isotopic fractionation via physical, chemical, and biological processes. Variations in the isotope amount ratio $n(^{15}N)/n(^{14}N)$ are commonly used to study Earth system processes, especially those related to biology, because N is a major nutrient for growth [88]. To illustrate this, isotope fractionation occurs when dissolved solutes, such as nitrate (NO_3), are transformed to more reduced compounds (i.e., N_2) because NO_3 with higher ^{14}N abundance tends to be more readily broken down. This leaves the residual unreacted NO_3 with a higher $n(^{15}N)/n(^{14}N)$ ratio than the initial ratio prior to reaction. Changes in the isotopic composition of biologically reactive compounds can be used to detect such reactions in aquatic environments, which are important mechanisms for removing reactive contaminants such as NO_3 [89].

Variation in N stable isotopes has been used to track fertilizer N accumulation into plants, soils, and infiltrating groundwater to improve efficiency and reduce impact on the environment, such as experimental agricultural fields where various amounts of excess N from fertilizers and plant residues can be found in groundwater.

6. Paradigm Shift to a Sustainable Agricultural Production System

Agriculture is a major source of food. Food production is required to double within the next 8–10 decades or so from the perspective of the rapid population growth. Agriculture has been identified as a sink and source of GHGs, as well as the economic sector that suffers the most from climate change. As a source, reports support that the application of N-rich fertilizers is regarded as one of the factors contributing significantly to enhancing GHGs formation during crops cultivation. Rodale [90] proposed paths to transition to a sustainable agricultural production system on the basis of the following observations: (i) because renewable resources are the basis of operation and productivity of modern agriculture, in the event of depletion of nonrenewable resources, either food will become extremely expensive or productivity will decline; (ii) the current food production system contributes to the environmental degradation (soil erosion, soil degradation, and deforestation); (iii) lines of evidence indicate that a number of agricultural practices, including the pattern of N-rich fertilizer application, contribute to the escalation of pollution problems; (iv) there is a strong agreement that the natural resources are limited and should be used in a sustainable manner; (v) conventional technologies and secular agricultural production systems are likely to be unsustainable in the future in the event that agricultural production becomes the major source of energy and feed stocks; (vi) a major concern exists over whether the good life in rural areas can be maintained if family farms are replaced by large-scale industrialized farms, which produce all the food.

Owing to the above, sustainable agriculture, as proposed by diverse sources and condensed by the International Food and Agriculture Development (IFAD) task force report [91], could be portrayed as follows: (i) the successful management of resources to satisfy changing human needs, while maintaining or enhancing the natural resources base and avoiding environmental degradation; (ii) the ability of an agricultural system to maintain production over time in the face of social and economic pressures; (iii) one that should conserve and protect natural resources and allow for long-term economic growth by managing all exploited resources for sustainable yields. Other sources argue that stainability can only be achieved when resources, inputs, and technologies are within the capabilities of the farmers to own, hire, and manage with increasing efficiency to achieve desirable levels of productivity with minimal effects on the resources base, human life, and environmental quality. In this regard, sustainable agricultural production system is referred to as "one that maintains an acceptable and increasing level of productivity that satisfies prevailing needs and is continuously adapted to meet the future needs for increasing the carrying of the resource base and other worthwhile human needs" [92][93][94][95].

Nevertheless, the major challenge remains the reduction in GHG emissions from agriculture during crop cultivation. The last two decades have been marked by a hunt for sustainable and effective strategies toward achieving a sustainable agriculture, here referring to agricultural practices that help reduce, in a sustainable manner, the emission of GHGs. Among them, improving N use efficiency (NUE, from uptake to assimilation and remobilization) is considered the most promising and effective approach, because it allows significantly reducing the application of N-rich fertilizers, which helps cut down the production cost, with a low impact on the environment. Reports have demonstrated that NUE is controlled genetically, and this complex trait allows optimizing the use of N available to the plant. NUE is equally important when plants experience nutrients shortage or unavailability caused by environmental stresses, such as drought [96][97][98], salinity [99], heat stress [100], or heavy-metal toxicity, whereby the acquisition of N is either restricted or impaired. In addition to the well-characterized NO_3 or NH_4 transport- and assimilation-related genes [101], N remobilization (one of the components of NUE) from NO_3 stored in the vacuole regulated through a process known as autophagy carries the potential to salvage poor N supply or transport within the plant, and it offers an alternative for balanced plant productivity and reduced GHG emissions [100][102][103][104]. Likewise, NO, an ancient molecule with multiple roles in the plant, previously suggested to play an important role in N acquisition and assimilation events through NR activity [105][106], could serve as a potential target for improving NUE in plants.

Other alternative approaches may include intermittent drainage, especially in flooded or irrigated cultivation systems, the use of nitrification inhibitors, and the application of biochar. Unlike in the industrial sector, it is important to indicate that net zero GHG emission may not be a realistic target from agriculture with regard to the biological nature of CH_4 and N_2O production, involving soil microorganisms such as methanotrophs and methanogens, and the requirement of CO_2 in plant metabolic processes.

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