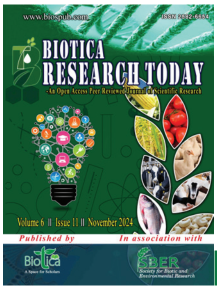
Bio. Res. Today 2024, 6(11):465-467



Biotica Research Today

e-ISSN: 2582-6654

November, 2024

Article ID: RT1736 **Popular Article**

Importance of Nickel in Plant Nitrogen Metabolism

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Conflict of interests: The author has declared that no conflict of interest exists.

How to cite this article?

Patra, A., Singh, R.P., Singh, B.K., *et al*., 2024. Importance of Nickel in Plant Nitrogen Metabolism. *Biotica Research Today* 6(11), 465-467.

Abstract

Nickel (Ni) is a very critical micronutrient for plants and more importantly linked with nitrogen (N) metabolism, involved indirectly as a trace element. An essential and direct function of Ni is as a co-factor for enzymes; such as, urease, which facilitates the conversion of urea into usable forms of nitrogen helping assimilation and recycling of N within the plant. It has been associated with some other enzymatic activities that are necessary for amino acid synthesis, protein metabolism and secondary metabolite production. Besides, Ni also involves abiotic stress tolerance due to enhanced catalysis of antioxidant enzymes against oxidative stress to maintain stability in the metabolism under stressed conditions. More recently found is the role of Ni in increasing N use efficiency which has made it significant in sustainable agriculture aimed at reducing dependence on fertilizers.

Keywords: Nickel, Nitrogen, Urea, Ureide

Introduction

Nickel (Ni) is a trace element that is necessary in the field of plant physiology, and its main function is in the nitrogen metabolism. The fact that plants require Ni in such trace amounts does not diminish its significance for numerous biochemical and physiological activities. The importance of Ni in plant biology was historically underestimated, partly because plants only require trace amounts for optimal growth and development. However, recent research has highlighted the critical functions of Ni, especially in N metabolism, which is fundamental to plant nutrition, growth and productivity (Patra *et al.*, 2019). Understanding the role of Ni in plant N metabolism is particularly valuable in agricultural science, as it influences plant health, N use efficiency and tolerance to environmental stressors. Nickel is one of the micronutrients but has a special feature in nitrogen metabolism. The realization in the 1970s that Ni was a cofactor for the enzyme urease meant that Ni is deemed as an essential micronutrient. Nickel's role is said to be central in plants as it serves as a cofactor for urease which catalyzes the hydrolysis of urea into ammonia and carbon dioxide. Urea is a widely used N source in soil. Always urea would be the source of N for plants must first be hydrolysed by urease. Nickel is critical for urease activation, as the enzyme active site contains a nickel species. In addition to urease, Ni is necessary for the activity of hydrogenase and carbon monoxide dehydrogenase both important enzymes in N fixation by symbiotic as well as free living N-fixing organisms -. Plants do not fix N by themselves, but acquire it *via* symbiosis with N-fixing bacteria, notably in root nodules of legumes. Nickel indirectly plays an important role in N availability by maintaining the functional status of these bacterial enzymes which are involved in fixation of N. The requirement of Ni for plant N metabolism is critical for our understanding of plant health and has noticeable consequences for sustainable agriculture. Nickel is essential because it provides support to the enzymes involved in N recycling, amino acid synthesis and stress tolerance that contribute to effective nitrogen use efficiency and increased resilience against environmental stresses. To fulfil the micronutrient nutrition with special emphasis on Ni, it is necessary to understand and manage their nutrifying behaviour due to shifting of global agriculture towards sustainability.

Role of Nickel in Ureide Metabolism

Ureide metabolism is a biochemical pathway that consists mainly of purines degradation, giving origin to different nitrogenous compounds for plants or animals use and excretion (de Queiroz Barcelos *et al.*, 2017). Specifically, Ni is involved in catalytic reactions that transform ureides into more simple molecules which can then be redirected into cellular metabolism or excreted as waste (Figure 1). This pathway is essential in N management, especially in legumes

Article History

RECEIVED on 01st November 2024 RECEIVED in revised form 09th November 2024 ACCEPTED in final form 10th November 2024

and other plants that rely on N-fixing symbiosis with bacteria (Izaguirre-Mayoral *et al.*, 2018).

Overview of the Pathway

• The ureide process starts with purine breaking down. Purines are bases with nitrogen that are part of nucleic acids like DNA and RNA. When they break down, first they turn into xanthine. Then xanthine gets oxidized more by an enzyme called xanthine oxidase, which makes uric acid.

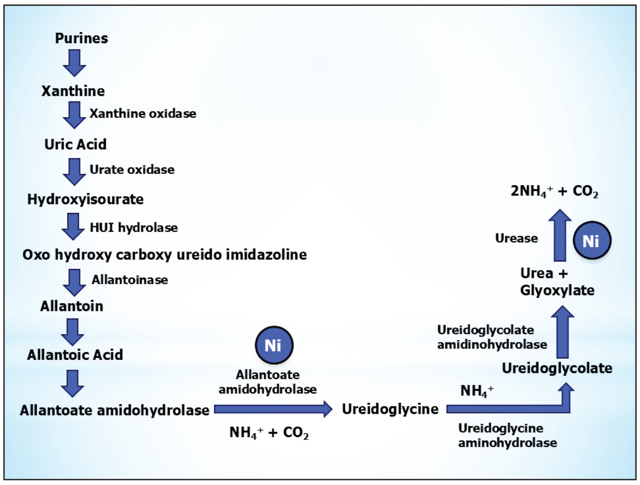

Figure 1: Ureide cycle in plant

• In the presence of the enzyme urate oxidase, uric acid is converted into hydroxyisourate. Hydroxyisourate is an intermediate compound that is then transformed into oxo-hydroxy carboxy ureido imidazoline through the action of HUI hydrolase.

• Following this, the enzyme allantoinase catalyzes the conversion of oxo-hydroxy carboxy ureido imidazoline to allantoin.

• Allantoate amidohydrolase, needing Ni as part, changes allantoate to allantoic acid, which then turns into ureidoglycine. This enzyme's work makes ammonium ions (NH_4^+) and carbon dioxide (CO_2) that are used in the N processes of the organism.

• Without adequate Ni, allantoate amidohydrolase cannot function optimally, leading to a build-up of intermediate compounds, which can disrupt N recycling within the organism.

• The breakdown of ureidoglycolate has two main reactions done by ureido glycolate amidinohydrolase and ureido glycine aminohydrolase.

• Nickel is again very important as a helper for these enzymes, especially urease, which helps change urea and glyoxylate into NH_4^+ and CO_2. Urease, one of the enzymes in this process needing Ni, has a key part in making sure N from ureides gets out well as NH_4^+, which plants can easily take in and use.

• Nickel deficiency can impair urease function, potentially leading to inefficient N recycling, accumulation of ureides and adverse effects on plant health.

Role of Nickel in Urea Metabolism

Urea use is very important for breaking down and getting rid of N waste. This is especially true for creatures that eat lots of protein (Li *et al.*, 2022). Urea is the main way to get rid of N and making it is the key to keeping nitrogen levels in check. Nickel plays an essential role in specific enzymatic reactions within this pathway, ensuring efficient N recycling and urea formation (Figure 2). The uploaded figure illustrates how Ni dependent enzymes contribute to urea metabolism, particularly through reactions involving amino acids, ammonia and urea (Miśkowiec and Olech, 2020).

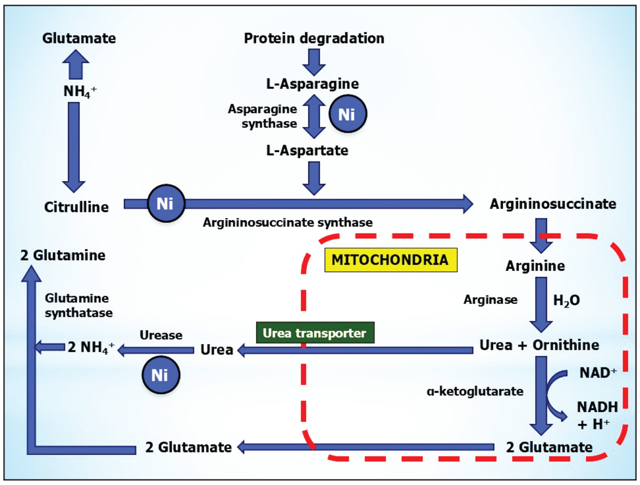

Figure 2: Urea cycle in plant

Overview of the Pathway

• Nitrogen metabolism and urea synthesis amino acids (L-asparagine and L-aspartate). Nickel is depicted as the cofactor for the enzyme using L-asparagine and converting this into L-aspartate (the asparginine synthease). In this reaction asp is provided, entering the urea cycle as a N-donor for argininosuccinate synthesis.

• The Ni dependent reaction catalyzed by asparagine synthase is essential for maintaining adequate levels of aspartate, which is a critical amino acid for N transport and urea formation. The presence of Ni in this process ensures that asparagine synthase functions efficiently, helping to maintain a steady supply of aspartate for the urea cycle. When Ni is not present, the enzyme would be less active owing to the concentration of aspartate being unfavourable, which in turn might impair the urea cycle leading to potentially toxic levels of N.

• In addition, citrulline then combines with aspartate to form argininosuccinate.

• Another important step of the urea cycle is the conversion of argininosuccinate to arginine. On the other hand, arginine formation is important as it will convert to urea.

• After arginine has been generated, further hydrolysis of arginine by arginase releases urea and ornithine and permits the continuation of the urea cycle. At this step, urea is released as a final product and exported out of the mitochondria to be excreted.

• Here, Ni is again crucial for the production of aspartate (*via* the asparagine synthase reaction) and regulating ammonia levels (*via* urease activity), both of which are necessary for promoting an effective urea cycle and N excretion.

• In fact the formation of glutamate from α-ketoglutarate and NH_4^+ also yields a crucial N donor which can be fed into the urea cycle, allowing for efficient excretion of N in excess.

• The urease is a Ni dependent enzyme and one of the keys in urea metabolism, catalysing the conversion of urea to NH_4^+ and CO_2. Although urease is not a classical urea cycle enzyme, it does perform an essential function in N metabolism and helps the recycling of N efficiently particularly in some bacteria and plants that require the direct recycling of ammonium.

• Urease activity ensures that N can be reclaimed from urea, when necessary, particularly under conditions where N is limited. Nickel is a critical cofactor for urease; without it, urease cannot catalyze urea breakdown efficiently, leading to accumulation and potential N wastage.

• Nickel is not directly involved in the reactions that produce glutamine and glutamate two important amino acids involved in N transport and ammonia detoxification but it is needed during the process of synthesizing them. Ammonia is extremely harmful to cells, hence the conversion of NH_4^+ to glutamate and glutamine; this process entraps free ammonia in a nontoxic form.

Agricultural Importance of Nitrogen Metabolism

• Apart from that, in legumes the ureide cycle plays a role in symbiotic nitrogen fixation (for example with *Rhizobium* species).

• Bacteria assimilate nitrogen and convert it to ammonia, which is then recast into ureides *via* the ureide cycle for more efficient transport.

• Efficient nitrogen assimilation and recycling through the ureide cycle and urea metabolism improve NUE, reducing nutrient wastage.

• High nitrogen use efficiency (NUE) is a requirement for sustainable agriculture because it means that more nitrogen is retained in plant biomass and will eventually be removed from the system than lost to leaching or emissions.

• The system helps legumes go well in nitrogen-deficient soils and decreasing the dependency on industries to produce synthetic nitrogen fertilizers a breakthrough for agricultural practices.

• Applying fewer synthetic fertilizers also lowers greenhouse gas emissions from fertilizer production and use.

Conclusion

In summary, Ni is an essential but commonly overlooked component for plant N metabolism primarily through incorporation into many enzymes such as urease which catalyses urea hydrolysis to utilisable forms of N. Nickel also indirectly increases soil N availability by aiding N-fixing bacterial symbionts of legumes. This underscores the importance of Ni in promoting not only plant health but also sustainable agricultural practices. Understanding and managing Ni levels in crops can thus be a vital step toward sustainable and efficient agricultural systems.

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