

The Fallacy of Organic Fertilizers and Synergistic Interactions Between Zn²⁺ and Inorganic Phosphate Groups

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Abstract

 Zn^{2+} and phosphate groups are crucial plant nutrients for several plant species. However, uptake and availability of these ions in most plants face negative synergy from themselves and other factors. While use of organic fertilizers has numerous advantages over inorganic ones, it has been criticized to support antagonism of Zn^{2+} uptake in plants. This mini review sought to address some of the factors leading to antagonism of Zn^{2+} uptake in plants in the presence of inorganic phosphate groups (Pi) and other organic moieties. Herein, we address these factors from a molecular and psychological perspective. We also describe some of the structural and bonding factors leading to formation of insoluble and immobile Zn^{2+} complexes in plants in organic moieties. The authors conclude that organic fertilizers meant for application needing high Zn^{2+} such as in seedbeds and during drought seasons should include chelating agents or rice straws that ameliorate soil pH.

Keywords: Zn²⁺; Inorganic phosphate groups; Organic fertilizers

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Introduction

Organic fertilizers are very key in the 'going green movement' especially as The World seeks to fulfill its sustainable development goals, SDG numbers 2 (zero hunger) and 13 (Climate Action) [1]. In-arability of farming land has necessitated artificial input of plant nutrients to the soil or directly to plants to increase agricultural production. While the shift towards green farming has more pros than cons, it is prudent to address some of the cons to better the move. One of the cons identified in application of green fertilizers is their inability to address the negative synergy resulting from interactions between Zn²+ and inorganic phosphate groups (Pi) in the fertilizer.

Both phosphorus and Zn^{2+} are fundamental nutrients for plant growth. Pi is used in development of plants structure compounds and as catalysts in several biochemical processes [2]. The Adenosine Di and Triphosphates (ADP and ATP) are essential compounds used in conversion of light energy to chemical energy (food) by plants during photosynthesis [3]. Phosphorus also forms a key part of deoxyribonucleic acid, DNA and ribonucleic acid, RNA genetic codes essential for plant structure, seed yield and genetic transfer [4]. On the other hand, Zn^{2+} are essential micronutrients that play a key role in regulating drought stress, improving seed germination, water-use efficiency and photosynthesis [5]. Zn^{2+} requirements in plants vary due to varying efficiencies in uptake from the soil, transport and sequestration in plant organs. Like other trace metal ions, the availability of free Zn^{2+} is more important than its concentration in a certain soil sample. In a typical soil sample consisting of these two plant nutrients, there exists negative interactions that inhibit uptake of either of these species in plants.

Pi and Zn^{2+} are both relatively inaccessible to plants due to their low solubility and immobilization in soil [6]. While Pi availability is likely to be high in plant biomass fertilizers, Zn^{2+} availability is dependent on the type of soil present. Most organic fertilizers lack or have inadequate Zn^{2+} due to scarce sources of these ions. Even then, uptake in plant is hindered by many factors, key amongst them Pi in the root periphery. Anergy, or negative synergy, is the term used to describe the interactions of Zn^{2+} and Pi. The two are inversely proportional at both molecular and psychological levels. There exists cross-talks between the homeostasis of

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these two nutrients amongst themselves and with other essential plant nutrients such as nitrogen and ferric ions [7]. These crosstalks have been reported in many different plant species. Organic moieties in green fertilizers come along with other factors that antagonize $\rm Zn^{2+}$ uptake, especially in presence of Pi. It is therefore pertinent to study the pathways for $\rm Zn^{2+}$ uptake in soil samples with organic fertilizers, to identify and counter the possible challenges encountered.

For successful Zn^{2+} acquisition, there need to be sufficient transmembrane transporters and zinc-inducing proteins (ZIP) [8]. Zn^{2+} can act as receptors for various Pi groups using several types of interactions such as by electrostatic or H-bonding interactions with NH_4^+ moieties present. Some of the common Pi groups involved in these interactions include ADP, ATP, pyrophosphate (PP) and monophosphate (MP). Pj groups act as substrates or inhibitors to Zn^{2+} by reversibly coordinating to one or more Zn^{2+} in their enzymatic pockets [9]. In mineral (inorganic) fertilizers, Pi anionic receptors interact with Zn^{2+} in a relatively ideal environment. There are limited factors to antagonize their interactions and successive uptake by roots. A basic pH (>8.3) is favorable for aqueous interactions [10]. In organic fertilizers, many factors influence Zn^{2+} -Pi synergistic interactions thus limiting the already strained interactions.

Unlike in mineral fertilizers where the ratios and concentrations of plant nutrients are definite, in organic fertilizers these ratios are irregular and the concentrations undefined. Many biotic factors are involved in the sorption processes of water and plant nutrients. One of the key players in absorption of Zn^{2+} and Pi in organic fertilizers is the arbuscular mycorrhizal fungi (AMF) [11]. These fungi are fundamental in uptake of the two nutrients, especially due to their ability to penetrate in soil structures compared to plant roots i.e mycorrhizal colonization. According to Zhang et al. [12], abundance of biomass from organic fertilizers reduces the survival of mycorrhizal fungi, necessary for Zn²⁺ uptake in plants. Organic matter in organic fertilizers is known to inhibit Pi from soil fixation. Organic moieties also inhibit mobilization of Zn²⁺. In organic moieties, Zn²⁺ receptors bind to anions such as Pi differently depending on the aqueous media [13]. Anionic binding is not very efficient in regimes involving many players like those in organic fertilizers.

Anionic binding is affected by several factors that reduce uptake of both Zn^{2+} and Pi in plants. Some of these factors include inorganic nucleotide phosphates, large sizes of anions, variation in anion shapes, high hydration enthalpies, wide range of hydrophobicities and limited pH range of existence due to their propensity to undergo protonation in water [14]. These factors combine to reduce uptake of Zn^{2+} in plants. The binding sites also exhibit selective attachments for Pi groups. There are two main approaches used in attaching Pi groups to Zn^{2+} i.e via coordination covalent bonds in Zn^{2+} metal complexes and using poly ammonium cation interactions [15] as expected in organic moieties. In the latter, which is more common, NH_4^+ in organic fertilizers interact with Pi groups via multiple charge-charge and H-bonding interactions. Here, binding rely upon

weak intermolecular forces like H-bonding, π -stacking, electrostatic and hydrophobic interactions. These interactions cooperatively compete with water ligands via topological complementarity thus lead to insoluble complexes. These bonds are relatively numerous and overlap each other thus lead to irreversible complexes. They are insoluble and irreversible contrary to the corresponding Zn^{2+} -Pi coordination covalent bonds formed when mineral fertilizers are in question, where Pi groups perfectly fit in coordination pockets of Zn^{2+} . From these explanations, it is clear that Zn^{2+} uptake in organic fertilizers is really challenged.

 Zn^{2+} uptake in plants can be increased by increasing their availability as well as regulating factors that counter their existence. Luckily enough, there exists organic fertilizers abundant in zinc ions. Phosphate rocks used as organic fertilizers are a rich source of zinc sulfate, a common salt used to replenish soil Zn^{2+} . Some composts and green manure also have significant Zn^{2+} . Several remedies have been proposed to improve Zn^{2+} uptake in plants utilizing organic fertilizers. They include application of Zn^{2+} chelating agents such as ZnEDTA [16]. These chelating agents increase the diffusability of Zn^{2+} . Application of compost from rice straw is also known to improve Zn^{2+} uptake due to amelioration of soil pH and exchangeable sodium ions with synergistic interactions with Zn^{2+} .

Conclusion

Uptake of Zn^{2+} and Pi by plants face a lot of antagonisms from these respective species and other factors. When organic fertilizers are used, the organic moieties involved further complicate uptake of Zn^{2+} by sequestering in immobile and insoluble complexes. This coupled with the antagonistic effects from Pi and other nutrients serve to minimize Zn^{2+} levels in plants. There is need to involve organic chelating agents and other composts with zinc ions when applying organic fertilizers, especially for germination purposes and drought resistance where Zn^{2+} play a key role.

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