Exploring the Potential of Organophosphorus Compounds as Chelators for Enhancing Zinc Bioavailability in Agriculture

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Abstract. This study explores the complexation of zinc ions by organophosphorus compounds as potential agricultural chelators. Compared to APCA chelators, the results show similar complexation properties, with organophosphorus chelators potentially offering superior biodegradability, highlighting their promise for more sustainable agricultural practices.

Keywords: chelates, agriculture, organophosphorus compounds, micronutrients, zinc, differential pulse voltammetry

Introduction

According to the UN report „World Population Prospects 2024", the global population is projected to increase significantly in the upcoming decades. At the same time, climate change is impacting agriculture by reducing yields, altering growing seasons, and increasing extreme weather events. In the face of these changes, one of the key global challenges is ensuring an adequate food supply for the growing population while simultaneously reducing the negative impact of agriculture on the environment. Intensifying agricultural production, although necessary, carries the risk of soil degradation, water pollution, and reduced biodiversity [1, 2].

Plants require many nutrients for growth and proper functioning, which they mainly absorb from the soil in the form of assimilable chemical compounds. Liebig's Law of the Minimum states that plant growth is limited by the nutrient in the least supply relative to demand, regardless of the abundance of other nutrients. Therefore, a key goal of agriculture is to provide plants with all the essential nutrients through proper fertilization, ensuring their healthy growth and functioning. Both mineral and organic fertilizers are commonly used for this purpose; however, their excessive application can lead to environmental pollution. To reduce the use of agrochemical products, a comprehensive fertilization approach is necessary - one that not only supplies essential nutrients but also enhances their bioavailability under challenging soil conditions [3, 4].

. Compounds with cheating properties enable effective delivery of micronutrient ions to limestone and alkaline soils. Chelators contain at least two donor groups in their structure, which can form stable, claw-like" structures - known as chelates - by binding metal ions through coordination bonds. This prevents metal ions from precipitating or becoming immobilized in the soil, ensuring they remain soluble and accessible to plants. As a result, chelators improve the efficiency of micronutrient uptake, supporting plant growth and development, even in challenging soil conditions where essential elements might otherwise become unavailable [5].

Currently, aminopolycarboxylate (APCA) chelators, such as EDTA, DTPA, and EDDHA, are widely used in agriculture due to their stability and ability to efficiently complex micronutrients over a wide pH range. However, APCA chelators have a low biodegradation rate, leading to bioaccumulation in the environment. They can also continue to complex heavy metal ions like lead, cadmium, and mercury, remobilizing them into the environment and posing ecological risks [6].

In response to these challenges, increasing attention is being given to the development of innovative chelators. A promising alternatives to APCA chelators are organophosphorus compounds, which combine high efficiency in micronutrient stabilization in a wide pH range with improved biodegradability [7].

The role of zinc in plant nutrition

Zinc (Zn), present in plants in its ionic form (Zn^{2+}), is an essential micronutrient for plant growth and development, playing a crucial role as a catalytic, structural, and regulatory cofactor in numerous enzymatic processes. It is vital for chlorophyll synthesis, protein and carbohydrate metabolism, and the biosynthesis of growth hormones like indoleacetic acid. Despite its importance, Zn deficiency is one of the most widespread micronutrient deficiencies, particularly in calcareous, sandy, and peat soils, as well as soils high in phosphorus and silicon [8, 9, 10, 11].

Zn deficiency in plants leads to stunted growth, leaf chlorosis, shortened internodes and petioles, and the characteristic rosette symptom in dicotyledons. It can also reduce crop quality, increase susceptibility to high light or temperature stress, and make plants more vulnerable to fungal infections. The availability of Zn is influenced by soil type, pH, and interactions with other nutrients that may inhibit its uptake. Additionally, Zn applied as fertilizer often forms insoluble complexes, limiting its bioavailability to plants. Addressing Zn deficiency is crucial for maintaining plant health, productivity, and resistance to environmental stressors [8, 9, 10, 11].

Aim of work

Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 establishes requirements for fertilizing products, including the necessity for at least 80% of the declared micronutrient content in micronutrients fertilizers to be in a chelated form to ensure its effectiveness and bioavailability for plants [12].

Given these regulatory standards, the study aimed to evaluate the complexation degree of zinc with various organophosphorus compounds in an aquatic environment, in the presence of the supporting electrolyte. The research focused on assessing the impact of different pH and different chelat to zinc ions molar ratios on the formation of zinc complexes, providing insights into their potential as alternative chelators in agriculture.

Experimental

The determination of zinc in its ionic form was performed using differential pulse voltammetry (DPV) with a mercury electrode operating in Static Mercury Drop Electrode (SMDE) mode. The analysis was carried out with an AUTOLAB PGSTAT 12 potentiostat, equipped with GPES software and a 663 VA Stand mercury drop electrode. The experimental setup included a mercury working electrode, a silver chloride reference electrode, and a graphite auxiliary electrode. Measurements were conducted within a potential range of -1.2 V to -0.7 V, with a step size of 0.00495 V. Modulation amplitude was 0.00255 V and modulation time was 0.05 s. Equilibrium time was 5 s.The mercury drop size was set to 0.25 mm^3.

The test samples were prepared by adding 2.0 cm³ of $ZnSO_4$ (0.001M), 2.0 cm³ of KCl (0.01M), 1.0 cm³ of gelatin solution (1%), and an appropriate amount of a chelator solution (0.001M) to achieve final molar ratios of 0.5:1, 1:1, and 2:1 relative to the zinc ions concentration. The list of the tested chelating agents is presented in Table 1 and their chemical structures are presented at Fig. 1. A reference samples were also prepared without the addition of a chelating agent. The pH of the samples was adjusted to the desired level using NaOH and HCl solutions, and finally, the samples volume was 25 cm³.

Table 1

Full and abbreviated names of the studied organophosphorus componds.

Nitrilotris(methylenephosphonic acid)	NTMPA
Diethylenetriaminepenta(methylenephosphonic acid)	DETAPMPA
Ethylenediaminetetra(methylenephosphonic acid)	EDATMPA
1-Hydroxyethane-1,1-diphosphonic acid	HEDP
2-Phosphono-1,2,4-butanetricarboxylic acid	PBTCA

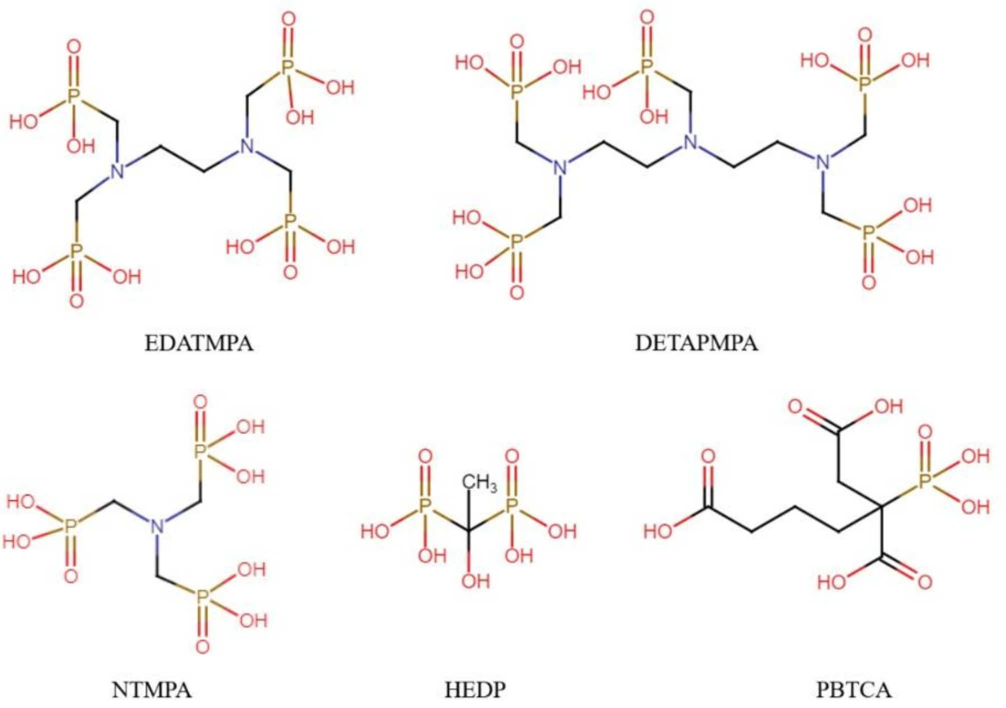

Fig.1. The structural formulas of the studied organophosphorus compounds.

The metal concentration is directly proportional to the intensity of the current signal. The degree of complexation was determined based on the difference between the metal ion concentration and the metal ion concentration in the presence of the chelating agent, according to the Eq. (1).

$$\alpha = \frac{c_0 - c_i}{c_0} \cdot 100\% \qquad (1)$$

where:

α – degree of Zn ions complexation [%],

c_0 – ions concentration of Zn before adding the chelator [mol/dm³],

c_i – ions concentration of Zn after adding the chelator [mol/dm³].

Results and discusion

The obtained results of zinc ions complexation degree by organophosphorus chelators, for the given pH values, are presented in Tables 2, 3, and 4.

At pH 3, the most effective chelator was EDATMPA, which achieved a zinc complexation degree of 78.1% at the highest concentration. NTMPA also performed well, yielding a similarly high result. In contrast, HEDP and PBTCA exhibited significantly lower complexation efficiencies, reaching 48.5% and 42.8%, respectively. The least effective chelator at this low pH was DETAPMPA, with a complexation degree of only 35.6% at a molar ratio of 1:2.

Table 2

Degree of zinc complexation [%] with different chelating agents at pH = 3

Molar ratio $C_{Zn2+} : C_{chelat}$	NTMPA	EDATMPA	DETAPMPA	HEDP	PBTCA
1 : 0.5	41.8	51.4	24.7	39.7	37.1
1 : 1	42.8	54.9	32.5	47.4	38.1
1 : 2	74.1	78.1	35.6	48.5	42.8

Table 3

Degree of zinc complexation [%] with different chelating agents at pH = 5

Molar ratio $C_{Zn2+} : C_{chelat}$	NTMPA	EDATMPA	DETAPMPA	HEDP	PBTCA
1 : 0.5	61.0	62.0	61.2	35.4	32.3
1 : 1	100.0	82.4	77.9	41.0	34.9
1 : 2	92.9	94.7	92.6	45.9	34.1

Table 4

Degree of zinc complexation [%] with different chelating agents at pH = 7

Molar ratio $C_{Zn2+} : C_{chelat}$	NTMPA	EDATMPA	DETAPMPA	HEDP	PBTCA
1 : 0.5	46.9	71.6	89.7	40.8	12.1
1 : 1	89.5	93.4	98.8	48.8	13.6
1 : 2	99.3	99.0	99.5	60.4	20.7

At pH 5, NTMPA and EDATMPA once again demonstrated excellent zinc ions complexation, reaching 92.9% and 94.7%, respectively, at the highest tested concentration. However, DETAPMPA also demonstrated a high complexation degree of 92.6% at a molar ratio of 1:2. This suggests that DETAPMPA's chelating ability significantly improves at higher pH levels. HEDP exhibited similar performance to results at pH 3, indicating that its complexation capacity remains relatively stable across different pH conditions. In contrast, PBTCA showed a noticeable decline in complexation efficiency compared to pH 3, achieving only 34.1% at the highest tested concentration. This trend suggests that PBTCA's ability to bind zinc ions decreases as pH increases, making it less effective under neutral to slightly alkaline conditions.

At the highest tested pH, the complexation dynamics shift once again. At the highest examined molar ratio of chelator to zinc ions, NTMPA, EDATMPA, and DETAPMPA achieved nearly complete zinc complexation, with values close to 100%. HEDP, in comparison, reached a moderate complexation degree of zinc ions 60.4%. However, differences between the chelators become more apparent at lower molar ratios. At a M:L ratio – 1:1, NTMPA showed a complexation degree of zinc ions of 89.5%, while EDATMPA and DETAPMPA displayed significantly higher values of 99.4% and 98.8%, respectively. The disparities become even more pronounced at a molar ratio of 1:0.5, where NTMPA, EDATMPA, and DETAPMPA achieved 46.9%, 71.6%, and 89.7%, respectively. PBTCA had much worse zinc ion complexing properties. At the appropriate molar ratio M:L, the degrees of complexation of the analyzed microelement ions were achieved equal to 12.1% at 1:0.5, 13.6% at 1:1, and 20.7% at 1:2. These results confirm that PBTCA has weak zinc-binding capabilities, particularly in higher pH environments, making it the least effective chelator among those studied.

Comparing the obtained results with literature data on aminopolycarboxylic acids (APCAs), particularly the findings presented by Borowiec et al. (2009) and Klem-Marciniak (2020), it can be concluded that the most effective organophosphorus chelators (NTMPA, DETAPMPA, and EDATMPA) exhibit complexation properties at higher pH values that are quite similar to those of commonly used APCAs [13, 14].

Despite the lower complexation efficiency observed at pH 3 compared to higher pH values, the results for organophosphorus chelators remain promising. The best-performing compounds, NTMPA and EDATMPA, still achieved notable zinc complexation, with values reaching nearly 80% at the highest tested molar ratio. These results indicate that, while organophosphorus chelators may be less effective in strongly acidic conditions than traditional APCAs, they still demonstrate significant potential for application in acidic environments.

Overall, while their performance is pH-dependent, the studied organophosphorus chelators show strong potential as zinc-binding agents. These initial results provide a foundation for further analyses of the properties of these substances, which represent a promising alternative to commonly used chelating agents. These initial results provide a foundation for further analyses of the properties of these substances, which represent a promising alternative to commonly used chelating agents.

Conclusions

The results indicate that generally the degree of zinc ion complexation increases with both rising pH and an increasing molar ratio of chelator concentration to zinc ion concentration. An exception to this rule is PBTCA, whose zinc complexation ability decreases as pH increases.

Among all the tested organophosphorus compounds, the best chelating properties were demonstrated by NTMPA, EDATMPA, and DETAPMPA. These compounds effectively complex zinc ions, indicating that the presence of at least one nitrogen atom in the molecular structure enhances their chelating ability.

The number of phosphonate groups in the chelator's structure also plays a significant role in its effectiveness. Compounds with a higher number of phosphonate groups show better chelating properties in higher pH environments.

When comparing the results obtained in this study with literature data on aminopolycarboxylic acids (APCAs), organophosphorus compounds like NTMPA, EDATMPA, and DETAPMPA exhibited chelation efficiency similar to commonly used APCAs, especially at higher pH values, which could make them a potential alternative with lower environmental toxicity.

Although the results at pH 3 were not as optimal as those at higher pH values, satisfactory zinc complexation was still achieved, suggesting that using higher molar ratios of chelator to metal could improve the effectiveness of these compounds at this pH.

The findings demonstrate that under specific conditions, certain organophosphorus chelators meet the requirements outlined in Regulation (EU) 2019/1009, which mandates a minimum of 80% complexation for chelating agents in micronutrient fertilizers. At higher pH values, NTMPA, EDATMPA, and DETAPMPA successfully fulfilled this requirement at molar ratios of 1:1 and 1:2. At pH 3, NTMPA and EDATMPA were close to compliance at a molar ratio of 1:2, suggesting that a further increase in the molar ratio would be necessary to fully meet the regulatory criteria.

References

[1] P. D. United Nations Department of Economic and Social Affairs, „World Population Prospects 2024: Summary of Results", 2024.

[2] Kehoe L., Romero-Muñoz A., Polaina E., Estes L., Kreft H., & Kuemmerle T. (2017). Biodiversity at risk under future cropland expansion and intensification. Nature Ecology & Evolution, 1(8), 1129–1135. DOI: 10.1038/s41559-017-0234-3

[3] Tang J., & Riley W. J. (2021). Finding Liebig's law of the minimum. Ecological Applications, 31(8), 1–10. DOI: 10.1002/eap.2458

[4] Zaib, M., Abbas, Q., Hussain, M. S., Mumtaz, S., Khalid, M. U., Raza, I., Abbas, S., Danish, M., Abbas, R., Muhammad, N. G., & Bano, S. (2023). Micronutrients and their significance in agriculture: a mini review with future prospects. International Research Journal of Education and Technology, 5(4), 234–252.

[5] Souri, M. K. (2016). Aminochelate fertilizers: the new approach to the old problem; a review. Open Agriculture, 1(1), 118–123. DOI: 10.1515/opag-2016-0016

[6] Bucheli-Witschel, M., & Egli, T. (2001). Environmental fate and microbial degradation of aminopolycarboxylic acids. FEMS Microbiology Reviews, 25(1), 69–106. DOI: 10.1111/j.1574-6976.2001.tb00572.x

[7] Knepper, T. P. (2003). Synthetic chelating agents and compounds exhibiting complexing properties in the aquatic environment. Trends in Analytical Chemistry,, 22(10), 708–724. DOI: 10.1016/S0165-9936(03)01008-2

[8] Hafeez B., Khanif Y. M. & Saleem M. (2013). Role of zinc in plant nutrition- a review. American Journal of Experimental Agriculture, 3(2), 374–391. DOI: 10.9734/AJEA/2013/2746

[9] Nandal V., & Solanki M. (2021). Zn as a vital micronutrient in plants. The Journal of Microbiology, Biotechnology and Food Sciences, 11(3), 1–9. DOI: 10.15414/jmbfs.4026

[10] Rudani K., Patel V., & Prajapati K. (2018). The importance of zinc in plant growth – a review. International Research Journal of Natural and Applied Sciences, 5(2), 38–48.

[11] Montalvo D., Degryse F., da Silva R. C., Baird R., & McLaughlin M. J. (2016). Agronomic effectiveness of zinc sources as micronutrient fertilizer. In Sparks D. L. Editor, Advances in Agronomy (pp. 215–267). Academic Press. DOI: 10.1016/bs.agron.2016.05.004

[12] Regulation (EU) 2019/1009 of the European Parliament and of the Council of 5 June 2019 laying down rules on the making available on the market of EU fertilising products and amending Regulations (EC) No 1069/2009 and (EC) No 1107/2009 and repealing Regulation (EC) No 2003/2003, ELI: http://data.europa.eu/eli/reg/2019/1009/2024-11-20

[13] Borowiec M., Hoffmann K., & Hoffmann J. (2009). The determination of the degree of zinc

complexation by chelating agents with differential pulse voltammetry. International Journal of Environmental and Analytical Chemistry, 89(8), 717–725. DOI:10.1080/03067310802691672

[14] Klem-Marciniak E. (2020) EDDHA and EDDHSA micronutrient chelate technology for fertilizing purposes, Doctoral dissertation