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ZINC DEFICIENCY IN SOILS OF UKRAINE: POSSIBLE CAUSES AND REGULATORY MECHANISMS

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ABSTRACT

In the context of global pollution, zinc is generally considered a heavy metal that can harm human health and other living organisms. However, it is known that zinc is a necessary micronutrient that is involved in many important metabolic processes. In a coronavirus pandemic, the positive role of zinc in controlling COVID is important. Zinc is one of the priority micronutrients that are deficient for most regions of the planet and its deficiency can lead to serious diseases and Ukraine is no exception. It is established that zinc is in short supply for most regions of Ukraine and products that are part of the diet of Ukrainians do not contain enough of it and do not provide the daily physiological needs of people. One of the reasons for such an unsatisfactory situation may be the insufficient amount of zinc in the soils of Ukraine, or the low level of its mobility. It is shown that Zn was characterized by a low level of transition from soil to crop production - the average transition coefficient ranged from 0.10. The reason for this phenomenon could be the low content of zinc in the soils of Ukraine. The grouping of soils of Ukraine by the potential ability to provide plants with a sufficient amount of Zn, taking into account the physiological needs of man was carried out. Using Zn transition coefficients in the soil-plant system and potential mobility of the element in soils of different soil-climatic zones of Ukraine, the division into groups was made: very low potential $\leq$ 21 mg Zn kg^{-1}, low potential from 22 to 48 mg Zn kg^{-1}, average potential from 49 to 77 mg Zn kg^{-1}, high potential $\geq$ 78 mg Zn kg^{-1}. According to the division, an assessment was made and it was found that the population of most of Ukraine cannot get enough zinc naturally through food of plant and, accordingly, animal origin. It is shown that one of the effective mechanisms of regulation of zinc inflow into the soil and increase of its mobility is the system of fertilization of agricultural plants. The analysis of traditional fertilizers of Ukraine and phosphorites from deposits of Ukraine is presented. It was found that the highest content of Zn was in phosphorites - it ranged from 7.8 to 14.2 mg kg^{-1}. It is shown that, depending on the peculiarities of the technology of growing crops, the soil can be annually introduced from 200 to 20.000 and more mg kg^{-1} of Zn. It is proved that it is possible to increase the content of zinc in soils by applying agrochemicals, first of all, phosphorus fertilizers, and to increase its mobility and transition to plants - by introduction of technological operations of cultivation of crops, especially in conditions of low level of natural mobility Zn (south and east of Ukraine).

Key words: Zinc, Micronutrient, Deficiency, Soil, Agricultural plants.

INTRODUCTION

Zinc (Zn) is a micronutrient whose positive role is difficult to overestimate. It is involved in the regulation of many biological processes of living organisms, including humans. Zn has a structural and catalytic role and binds to a large number of proteins (Maret, 2012). Zn deficiency leads to many serious diseases, especially it affects the development of children (Makarenko, et al., 2020). It is established that Zn deficiency reduces the body's immunity. This property is especially important in the context of the COVID pandemic. It is known that Zn has many direct and indirect antiviral properties, which are realized through various mechanisms. Many studies have shown that the introduction of Zn supplements can strengthen the body's antiviral immunity (Kuma, et al., 2020; Finzi, 2020; Skalny, et al., 2020). Zn^{2+} has been shown to inhibit coronavirus RNA polymerase activity, and zinc ionophores block replication of these viruses (Aartjan, et al., 2010).
However, zinc excess can also be dangerous. In particular, it can cause copper deficiency with subsequent irreversible hematological effects and potentially irreversible neurological manifestations (Official site of the US government, 2019; Wong, et al., 2019).
Zinc enters the human body with air, water and food. It is accepted to take into account the inflow of zinc on the indicator of the total daily load (SDN, mg), which is calculated as the sum of aerogenic, water and food daily intake (State sanitary norms and rules No. 400, 2010).
International standards set the daily dietary norm of elemental zinc for men - 11 mg, for women - 8 mg (State sanitary norms and rules No. 400, 2010). Ukrainian standards define a higher level of daily requirement: for men - 15 mg, for women - 12 mg, children aged 1 to 10 years - 10 mg (Order of the Ministry of Health of Ukraine of September No. 1073, 2017).
The diet determines the level of zinc intake in a particular person. But it is established that in general for Ukraine insufficient intake of zinc in the body of adults and especially children is characterized. Domestic scientists emphasize that the level of Zn is less than the established norm of human physiological needs (Lyubarska, et al., 2015; Lyubarska, et al., 2014; Biletska, et al., 2017).
Vegetable products obtained in Ukraine contain zinc in the range of 1.5-6.9 mg kg^{-1}, fruits and berries - 0.7-3.9, cereals, pasta and bread - 4.2 -15.0, nuts, seeds - 33.9-81.9, meat - 13.4-27.7, eggs - 4.7 mg kg^{-1} (Lyubarska, et al., 2015). For comparison: vegetables grown in China contain 3.87 - 25.50 mg kg^{-1} of zinc, in Ethiopia - 56.9-129.0 mg kg^{-1} of zinc, in Pakistan - 172-400 mg kg^{-1} of zinc (Wong, et al., 2019).
The low content of zinc in plant products, and, accordingly, in livestock products, may be associated with its content in the soils of agricultural lands of Ukraine. Thus, in Polissya the zinc content in soils is 8-90 mg kg^{-1} of soil, in the Forest-Steppe - 20-90, and in the Steppe - 33-100 mg kg^{-1} of soil (Balyuk, et al., 2008; Kabata-Pendias, et al., 1989). For comparison: in China, the zinc content in soils ranges from 54-570 mg kg^{-1} (Balyuk, et al., 2008). The transition of zinc from the soil to plants can also be complicated by their physicochemical properties, namely pH, high content of organic matter and physical clay, which reduce the mobility of zinc and prevent its entry into plants (Makarenko, et al., 2020; Makarenko, et al., 2019).
Given the above, it is important to assess the zinc content in soils of different regions of Ukraine from the standpoint of meeting human needs in this trace element. Also, the issue of regulating the mechanisms of zinc entry into the soil is relevant. With the subsequent transition to plants through separate technological operations of cultivation of agricultural plants. One of the most effective mechanisms of influence on these processes is the use of agrochemicals that contain zinc or can indirectly affect the physicochemical properties of the soil and thus increase the activity of the transition of zinc to plants.

MATERIALS AND METHODS

To establish the total content of zinc, as well as its various forms of mobility in the soil, we studied the soils common in the main soil-climatic zones of Ukraine: sod-medium-podzolic, dark-gray podzolic, chernozem typical, chernozem ordinary, dark-chestnut saline. Soil samples were taken in the research fields of scientific institutions of NAAS of Ukraine: NSC "Institute of Agriculture of NAAS", Institute of Agricultural Microbiology and Agroindustrial Production, Rivne State Agricultural Research Station, Zaporizhzhia Agricultural Research Station of the Institute of Oilseeds, as well as in the research fields Separate subdivision of the National University of Life and

Environmental Sciences of Ukraine "Agronomic Research Station". To characterize the total zinc content, it was used a mixture of H_2SO_4 + HF, potentially mobile - 1.0N HCL, mobile - 0.1N HCL.

The transition of zinc from the soil to winter wheat plants was studied in the conditions of stationary experiments of these scientific institutions according to the following scheme:

- ✓ *soil – dark-gray podzolic (Polissya zone of Ukraine):* Option 1 - control (without the use of agrochemicals), Option 2 - manure 10 t ha^{-1}; Option 3 - $N_{90}P_{60}K_{60}$ + straw + green manure (Rivne State Agricultural Research Station);
- ✓ *soil - typical medium loam chernozem (Forest-Steppe zone of Ukraine):* Option 1 - control; Option 2 - $N_{60}P_{60}K_{60}$ (Separate subdivision of the National University of Life and Environmental Sciences of Ukraine "Agronomic Research Station");
- ✓ *soil - chernozem ordinary low humus (Steppe zone of Ukraine):* Option 1 – control; Option 2 - $N_{75}P_{50}K_{25}$; Option 3 - manure 5.7 t ha^{-1} (Zaporizhzhia Agricultural Research Station of the Institute of Oilseeds);

To determine the level of zinc in the soil with agrochemicals we studied traditional phosphorus fertilizers (superphosphate simple and double, amophos, diamophos, nitrophosphate) and phosphorus-containing ores of Ukrainian deposits: Novo-Amvrosiivske - phosphorite concentrate (25% P_2O_5), South Osykove - phosphorite concentrate (28% P_2O_5), Osykove - phosphorite concentrate (19% P_2O_5), Manevychi-Klevan phosphorite-bearing site (MKS) - phosphorite concentrate (25% P_2O_5), Ratne - phosphorite concentrate (28% P_2O_5), Volyn - phosphorite grains % P_2O_5), Zdolbuniv - phosphorite (12.6% P_2O_5).
Sampling of soil was carried out in accordance with DSTU ISO 10381-1: 2004, DSTU ISO 10381-2: 2004. The zinc content in soil samples and phosphorus fertilizers was determined by atomic absorption spectroscopy.

Statistical analysis

The significance of the experimental data was estimated by the analysis of variance (two-factor, ANOVA).

RESULTS AND DISCUSSION

Zinc is one of the priority micronutrients that are deficient for most regions of the planet and its deficiency can lead to serious diseases. Ukraine is no an exception. Works (Lyubarska, et al., 2015; Lyubarska, et al., 2014) show that the products included in the diet of Ukrainians do not contain enough zinc and do not provide its daily physiological needs, which is for men - 15 mg, women - 11 mg, children aged 1 to 10 years - 10 mg. One of the reasons for this unsatisfactory situation may be the insufficient amount of zinc in the soils of Ukraine.

The following data were used to determine the level of zinc supply of the soils in Ukraine, taking into account human needs in this micronutrient:

- zinc content in basic foodstuffs of plant origin,
- average zinc content in the soils of Ukraine,
- coefficients of zinc transition from soil to plants (food of plant origin).

Using this information, the minimum level of zinc concentration in the soil that can meet the physiological needs of zinc for humans was calculated. The standard for men was 15 mg day^{-1}.
The calculation of the average zinc transition coefficients (CtZn) in the soil-plant system was based on the use of the ratio between the average zinc content in basic food products of plant origin (Lyubarska, et al., 2015) and the average Zn content in the soils of Ukraine (54 mg kg^{-1} of soil). The transition coefficients were set using the following ratio:

$$\text{CtZn} = \frac{Zn \text{ content in food}}{Zn \text{ content in the soil}}$$

It was found that for vegetable crops CtZn ranged from 0.03 to 0.09, with an averaged indicator of 0.05. Dill, lettuce, and beets were characterized by the greatest ability to accumulate zinc (Fig. 1).

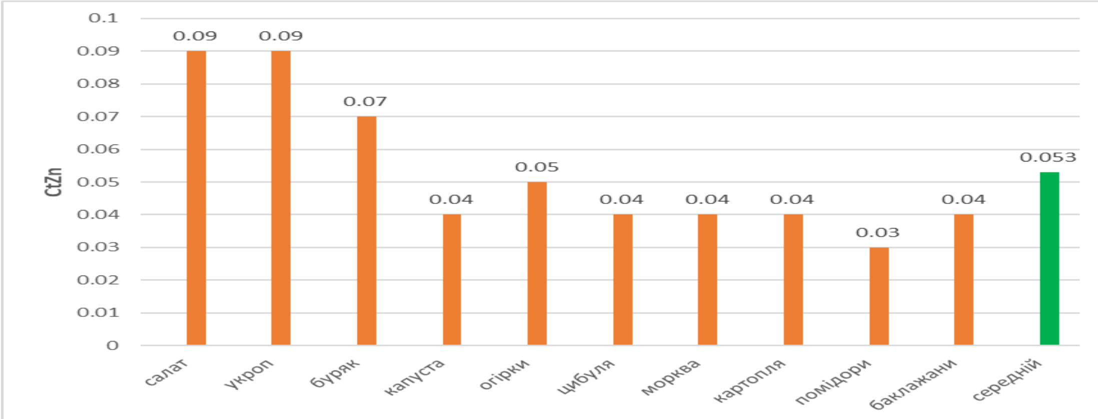


Figure1. Coefficients of Zn transition from soil to vegetable crops

The vast majority of fruit and berry crops had a low ability to accumulate zinc, the transition coefficients ranged from 0.01 to 0.07, the averaged indicator was 0.03 (Fig. 2).

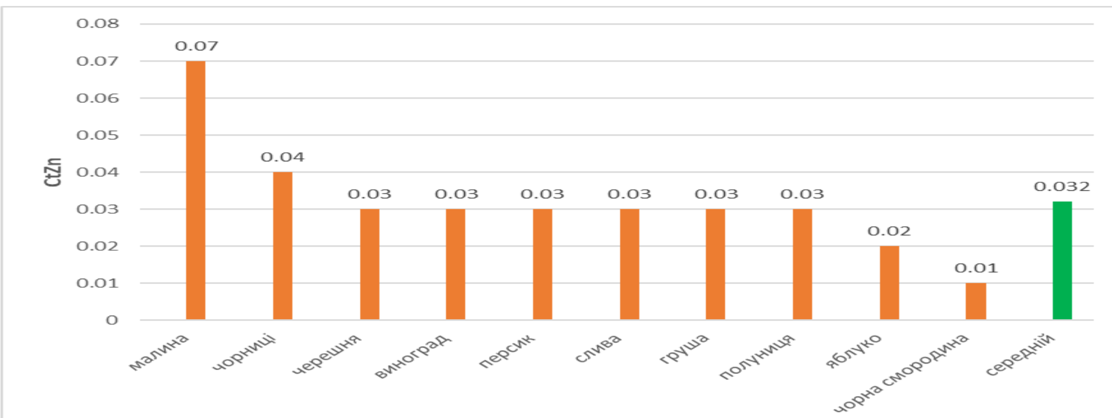


Figure 2. Coefficients of Zn transition from soil to fruit and berry crops

Cereals were characterized by a higher level of zinc absorption, transition coefficients ranged from 0.18 to 0.28, the averaged indicator was 0.22. The highest level of zinc absorption was characterized by buckwheat, wheat, rice (Fig. 3).

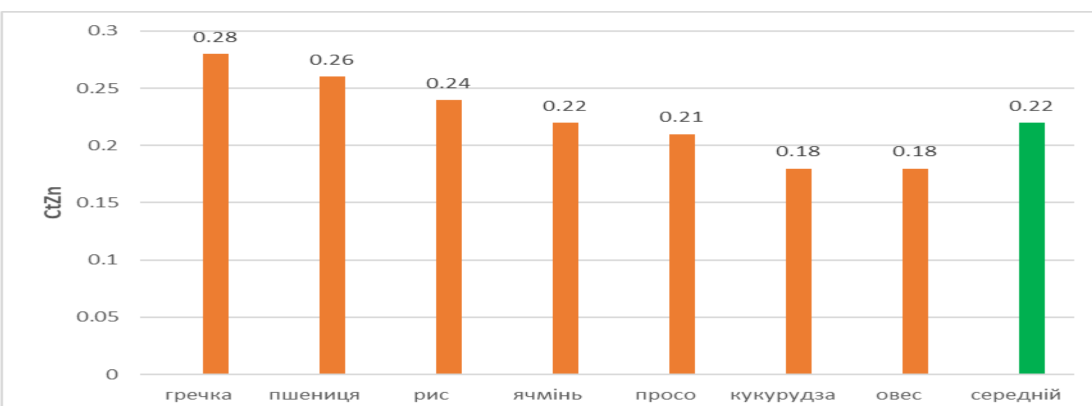


Figure 3. Coefficients of Zn transition from soil to cereals

In general, it should be noted the low level of transition of zinc from soil to crop products. The results of estimating the zinc transition coefficients in the soil-plant system revealed that the average coefficient ranged from 0.10. The reason for this phenomenon may be the low content of zinc in the soils of Ukraine, as well as physical and chemical properties of soils in the zonal section, which affect the mobility of the element. Therefore, to assess the potential ability of soils to provide the required amount of zinc in plants, not only the total content of the element in the soil, but also its mobility (mobility) was taken into account. It is the mobile forms of zinc, as a rule, that are a potential source of the element for plants. Zinc mobility depends on the physicochemical properties of soils and, above all, on the content of humus, physical clay and pH (Makarenko, et al., 2020). It was found that the soils common in the Polissya zone (sod-podzolic, gray forest) are characterized by a fairly high content of mobile zinc compounds - more than 30%, chernozem-type soils common in the Forest-Steppe zone - 15-22%, and Steppe soils (chestnut) - 17% (Fig. 4).

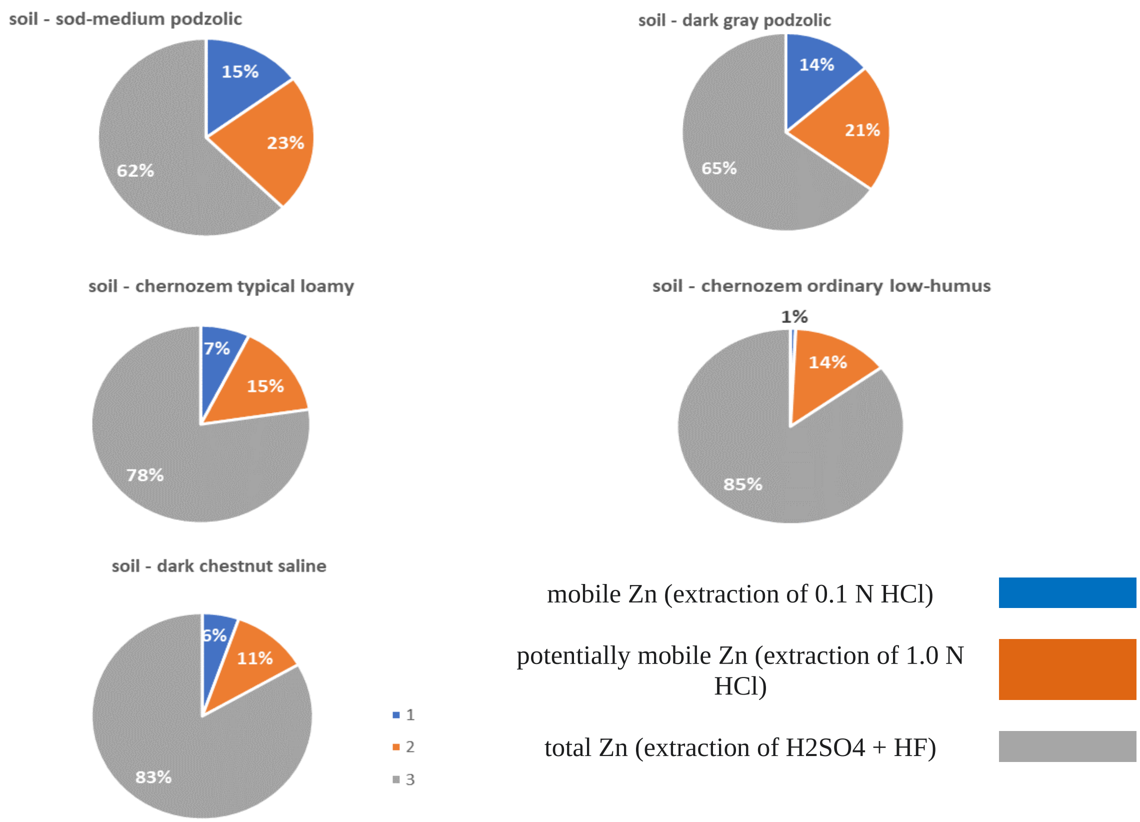


Figure 4. The content of various forms of zinc in the soils of Ukraine

Given the above, we can predict that the potential ability of soils in Polissya to provide plants with sufficient zinc may be higher by about 30%, in Forest-steppe - by 20%, in Steppe - by 15%.

Using the obtained data, the soils of Ukraine were grouped according to the potential ability to provide plants with a sufficient amount of Zn with subsequent visualization of the results in the form of a map (Fig. 5).

To create it, the information presented in a project "Nature of Ukraine" of A. Grachev on the website https://nature.land.kiev.ua/projekt.html was used. Using this information, as well as taking into account the potential mobility of the element in soil, the following grouping of soils by their potential ability to ensure the transition of Zn into plants with the subsequent provision of physiological human needs:

very low potential ≤ 21 mg kg^{-1},
low potential from 22 to 48 mg kg^{-1},
average potential from 49 to 77 mg kg^{-1},
high potential ≥ 78 mg kg^{-1}.

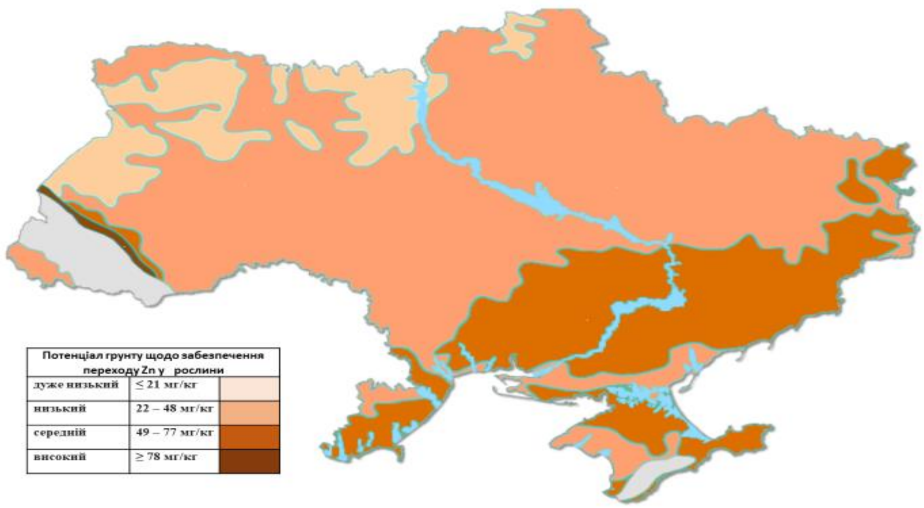


Figure 5. Potential ability of Ukrainian soils to meet the physiological human needs in Zn, taking into account its transition in the soil-plant system

The results show that the population of most of Ukraine cannot get enough zinc naturally through foods of plant and, accordingly, animal origin. The conclusions are based on averaged data and make it possible to characterize only the general picture and outline certain problems in the zonal context of Ukraine. For more accurate information, additional research in specific soil and climatic conditions is needed. However, even such information should draw attention to an important problem, the solution of which will make it possible to avoid many diseases, especially in children. One of the effective mechanisms for regulating the inflow of zinc into the soil and increase its mobility is a system of fertilization of agricultural plants. It is known that agrochemicals, in particular mineral fertilizers, as well as their combination with organic fertilizers and other technological operations can: a) increase the amount of zinc in the soil, because they contain this micronutrient and are introduced during plowing or cultivation into the soil, b) lead to an increase in zinc content in plants during foliar feeding, c) change the physicochemical properties of the soil and thus increase the mobility of zinc in the soil and intensify its transition to plants.

Studies have shown that Zn is mainly found in phosphorus fertilizers. Its content in traditional fertilizers (superphosphate, amophos, nitrophosphate, etc.) ranged from 1.8 to 7.2 mg kg^{-1}. Phosphorites from the following deposits of Ukraine were characterized by the highest zinc content: Novo-Amrosiivske, South Osykove, Osykove, Volyn, Zdolbuniv, Ratne, Manevychi-Klevan phosphorous-bearing site (MKS). The Zn content in phosphorites ranged from 7.8 to 14.2 mg kg^{-1} (Fig. 6).

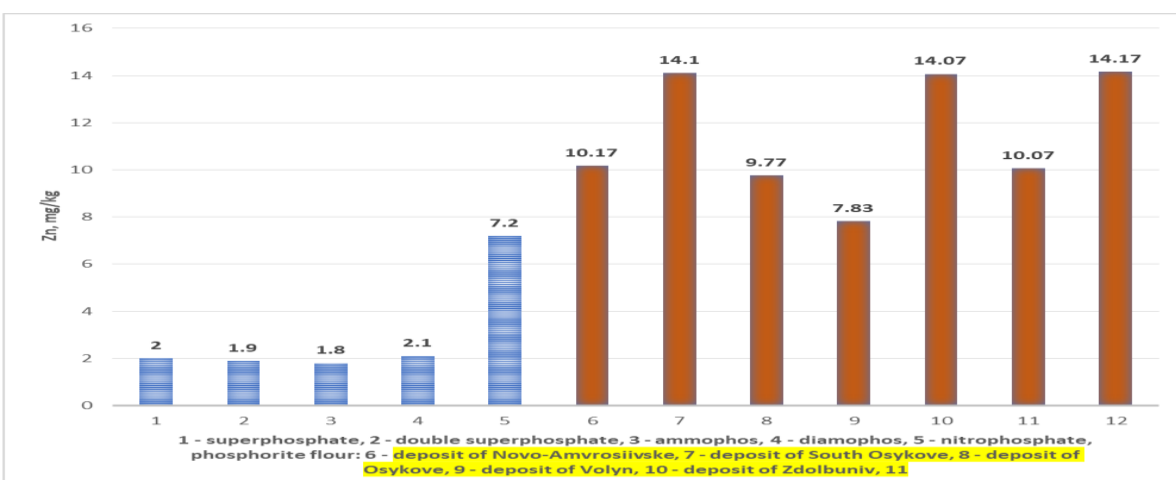


Figure 6. Zinc content in agrochemicals (mineral fertilizers and phosphorites of Ukrainian deposits)

However, the amount of zinc entering the soil depends not only on its content in the agrochemical, but also on the dose of its application, which is determined by the content of active substance (active substance - the main element of plant nutrition, which is used to calculate the application dose). The dose of agrochemical is determined by the technology according to which the crop is grown. The amount of zinc entering the soil with the agrochemical (G) is calculated using the following formula (Makarenko, 2002):

$$G = \frac{d\ g2\ 100}{g1},$$

Where: d - recommended dose of agrochemical according to the active substance, kg ha^{-1}; g2 - the concentration of Zn in the agrochemical, mg kg^{-1}; 100 - conversion to the physical mass of the agrochemical, %; g1- the concentration of the active substance in the agrochemical, %.

Analysis of traditional phosphate fertilizers and phosphorites of Ukrainian deposits, taking into account the peculiarities of technologies for growing crops on the example of winter wheat, showed that Zn can be introduced into the soil annually from 200 to 20,000 and more mg kg^{-1} (Table 1). It was found that the largest amount of Zn can enter the soil with Zdolbuniv phosphorite with intensive technology of growing winter wheat, which involves the use of 180 kg ha^{-1} P_2O_5 - 20100 mg ha^{-1} (Fig. 7).

Table 1. The entry of Zn into the soil from agrochemicals in the cultivation of winter wheat by different technologies

№	Agrochemical	Dose application according to the content of P_2O_5 kg ha^{-1} (d)			P_2O_5 content, % (g1)	Zn content, mg kg^{-1} (g2)	Inflow of Zn into the soil, mg ha^{-1} (G)		
		I*(it)	II (rt)	III (at)			I (it)	II (rt)	III (at)
1	Simple superphosphate	180	120	60	20,0	2,00	1800	1200	600
2	Double superphosphate	180	120	60	46,6	1,90	734	489	241
3	Amophos	180	120	60	51,2	1,80	633	422	211
4	Diamophos	180	120	60	51,2	2.10	738	492	246
5	Nitrophosphate	180	120	60	62,9	7,20	2060	1373	687
6	Phosphorite of Novo-Amvrosiivske	180	120	60	25,0	10,17	7322	4881	2441
7	Phosphorite of South Osykove	180	120	60	28,0	14,1	9064	6043	3021
8	Phosphorite of Osykove	180	120	60	19,0	9,77	9256	6170	3085
9	Phosphorite of Volyn	180	120	60	8,6	7,89	16514	11009	5505
10	Phosphorite of Zdolbuniv	180	120	60	12,6	14,07	20100	13400	6700
11	Phosphorite of Ratne	180	120	60	28,0	14,17	9109	6073	3036
12	Phosphorite of MKS	180	120	60	25,0	10,07	7250	4833	2417

*- technologies of growing winter wheat: I - intensive (it), II - resource-saving (rt), III - adaptive (at)

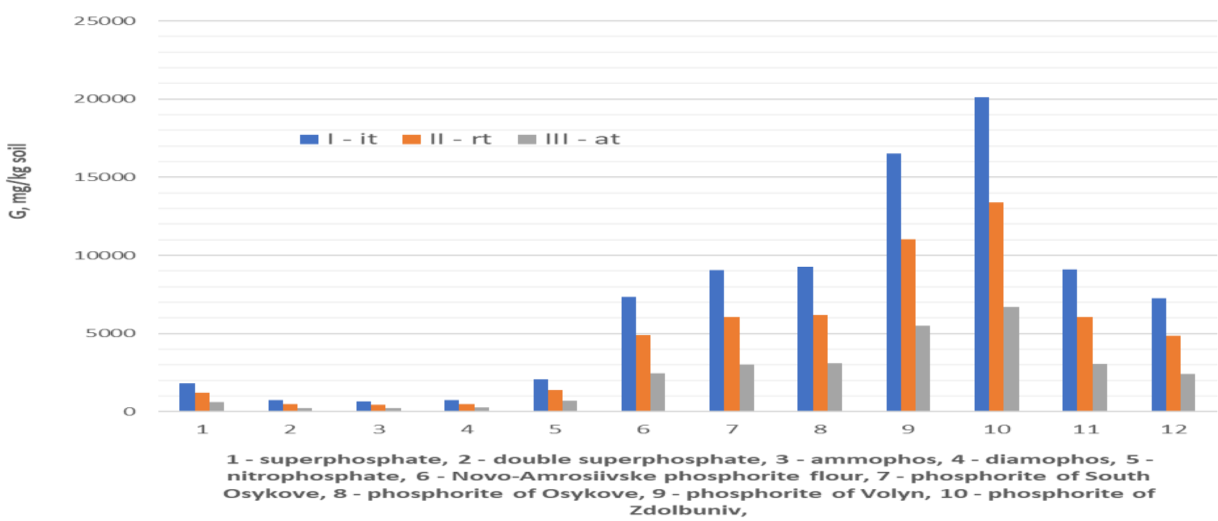
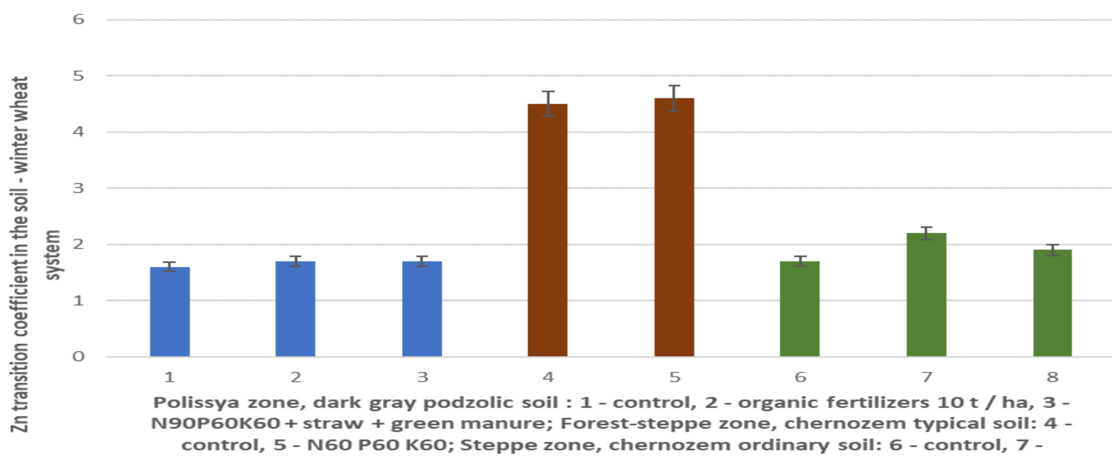


Figure 7. Inflow of Zn into the soil by different technologies of winter wheat cultivation: I - intensive (it), II - resource-saving (rt), III - adaptive (at)

Previous work has shown that crop production technologies can affect the transfer of Zn from soil to plants (Makarenko, et al., 2020). Agrochemicals, along with soil enrichment with zinc, can increase its mobility, which, in turn, affects the translocation of the element in plants. It was found that under the influence of various technological techniques in the Polissya zone on dark gray podzolic soil the number of mobile Zn compounds increased by 3-67%, in the Forest-Steppe zone on typical chernozem by 10%. At the same time, a tendency to intensify the transition of zinc from the soil to plants was recorded, as evidenced by the coefficients of the transition of zinc in the soil-plant system of winter wheat. It should be noted that the use of mineral and organic fertilizers on the soils of Polissya and Forest-Steppe zone did not lead to a significant increase in the transfer of zinc to plants (we can only talk about the trend), which may be due to their high natural ability to mobility and translocation. Instead, the use of agrochemicals on the soils of the Steppe zone has led to an increase in the conversion coefficients of Zn in plants, which indicates an increase in the mobility of the element under the influence of these technological operations of growing crops (Fig. 8).



Figbre 8. Zn transition coefficients in the soil- winter wheat system under the influence of different technological methods of cultivation

Thus, it can be argued that in soils it is possible to increase the zinc content through the use of agrochemicals, primarily phosphorus fertilizers, and increase its mobility - through the introduction of technological operations for growing crops, especially in conditions of low natural mobility Zn (south and east of Ukraine).

CONCLUSIONS

It is established that zinc is in short supply for most regions of Ukraine and products that are part of the diet of Ukrainians do not contain enough of it and do not provide the daily physiological needs of people. One of the reasons for such an unsatisfactory situation may be the insufficient amount of zinc in the soils of Ukraine, or the low level of its mobility.

It is shown that Zn was characterized by a low level of transition from soil to crop production - the average transition coefficient ranged from 0.10. It was assumed that the reason for this phenomenon could be the low content of zinc in the soils of Ukraine, as well as their physicochemical properties: soils common in the Polissya zone were characterized by a fairly high content of mobile zinc compounds - more than 30%, soils of chernozem common type in the forest-steppe zone - 15-22%, and the soils of the Steppe zone - 17%.

The soils of Ukraine were grouped according to their potential ability to provide plants with a sufficient amount of Zn. We took into account the physiological needs of human, the coefficients of transition in the soil-plant system and the potential mobility of the element in the soils of different soil-climatic zones of Ukraine. The division into groups was as follows: very low potential ≤ 21 mg kg^{-1}, low potential from 22 to 48 mg kg^{-1}, average potential from 49 to 77 mg kg^{-1}, high potential ≥ 78 mg kg^{-1}.

It is shown that one of the effective mechanisms of regulation of zinc inflow into the soil and increase of its mobility is the system of fertilization of agricultural plants. It is established that Zn is mainly contained in phosphorus fertilizers. Its content in traditional fertilizers (superphosphate, amophos, nitrophosphate, etc.) ranged from 1.8 to 7.2 mg kg^{-1}. Phosphorites from Ukrainian deposits were characterized by the highest zinc content: Novo-Amrosiivske, South Osykove, Osykove, Volyn, Zdolbunivsky, Ratne, Manevychi-Klevan phosphorous-bearing sites. The Zn content in phosphorites ranged from 7.8 to 14.2 mg kg^{-1}. Depending on the characteristics of the technology of growing crops Zn can be introduced from 200 to 20,000 or more mg kg^{-1} into the soil annually.

It is proved that it is possible to increase the content of zinc in soils by applying agrochemicals, first of all, phosphorus fertilizers, and to increase its mobility - by introduction of technological operations of cultivation of crops, especially in the conditions of low level of natural mobility Zn (south and east of Ukraine).

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