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Review

Soil Properties and Microelement Availability in Crops for Human Health: An Overview

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Abstract

Microelement deficiencies, often termed "hidden hunger", represent a significant global health challenge. Optimal human health relies on adequate dietary intake of essential microelements, including selenium (Se), zinc (Zn), copper (Cu), boron (B), manganese (Mn), molybdenum (Mo), iron (Fe), nickel (Ni), and chlorine (Cl). In recent years, there has been a growing focus on vitality and longevity, which are closely associated with the sufficient intake of essential microelements. This review focuses on these nine elements, whose bioavailability in the food chain is critically determined by their geochemical behavior in soils. There is a necessity for an understanding of the sources, soil–plant transfer, and plant uptake mechanisms of these microelements, with particular emphasis on the influence of key soil properties, including pH, redox potential, organic matter content, and mineral composition. There is a dual challenge of microelement deficiencies in agricultural soils, leading to inadequate crop accumulation, and the potential for localized toxicities arising from anthropogenic inputs or geogenic enrichment. A promising solution to microelement deficiencies in crops is biofortification, which enhances nutrient content in food by improving soil and plant uptake. This strategy includes agronomic methods (e.g., fertilization, soil amendments) and genetic approaches (e.g., marker-assisted selection, genetic engineering) to boost microelement density in edible tissues. Moreover, emphasizing the need for advanced predictive modeling techniques, such as ensemble learning-based digital soil mapping, enhances regional soil microelement management. Integrating machine learning with digital covariates improves spatial prediction accuracy, optimizes soil fertility management, and supports sustainable agriculture. Given the rising global population and the consequent pressures on agricultural production, a comprehensive understanding of microelement dynamics in the soil–plant system is essential for developing sustainable strategies to mitigate deficiencies and ensure food and nutritional security. This review specifically focuses on the bioavailability of these nine essential microelements (Se, Zn, Cu, B, Mn, Mo, Fe, Ni, and Cl), examining the soil–plant transfer mechanisms and their ultimate implications for human health within the soil–plant–human system. The selection of these nine microelements for this review is based on their recognized dual importance: they are not only essential for various plant metabolic functions, but also play a critical role in human nutrition, with widespread deficiencies reported globally in diverse populations and agricultural systems. While other elements, such as cobalt (Co) and iodine (I), are vital for health, Co is primarily required by nitrogen-fixing microorganisms rather than directly by all plants, and the main pathway for iodine intake is often marine-based rather than soil-to-crop.

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1. Introduction

Agriculture provides the essential nutritional elements required for sustaining human life. However, it is worth noting that the food produced may not always contain all the necessary nutrients. Therefore, it is crucial for global agricultural institutions to acknowledge that the nutritional well-being of people worldwide heavily relies on the delivery of nutrients produced by agricultural systems [1]. Consuming a diverse range of dietary elements is vital for the optimal functioning of the human body and maintaining good health. In recent times, there has been a growing focus on microelements due to the widespread deficiency in them among people [2–4]. Microelements are essential substances found in food that the human body requires in small quantities to maintain health, ranging from well-known vitamins to crucial trace elements. Microelement malnutrition, also known as "hidden hunger," arises when the body's demands for bioavailable microelements are not met due to inadequate, low doses of consumption [5]. Malnutrition, including both evident nutrient deficiencies and chronic diet-related diseases, such as heart disease, cancer, stroke, and diabetes, is a leading cause of death globally. In fact, it is responsible for more deaths annually than any other cause, with over 20 million deaths attributed to it each year [6]. Microelement deficiencies also can lead to serious illnesses such as stunted growth, intellectual impairments, and perinatal complications [7]. While other elements, such as cobalt (Co), iodine (I), and fluorine (F), are also vital for human and animal health, this review focuses on nine microelements that are essential for plants and whose pathways are critically governed by soil–plant interactions: zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), molybdenum (Mo), boron (B), chlorine (Cl), and nickel (Ni) [4]. Additionally, selenium (Se) is included due to its essentiality for humans and its strong linkage to soil chemistry [8,9]. One effective approach to tackle this issue is through biofortification. Biofortification is a potential solution to microelement malnutrition, relying on the plant's biosynthesis of vitamins or physiological abilities to produce or accumulate desired nutrients [10]. Biofortification aims to enhance the nutritional content of food crops and increase the bioavailability of nutrient-deficient elements in the human population. It is developed using modern biotechnology, conventional plant breeding, and agronomic practices [11–13]. Despite the potential benefits of biofortification, there are cases where microelements may exist in toxic concentrations in the soil, posing a risk to plant growth and human health [13]. However, the more significant challenge remains to be the inadequate levels of microelements in soils, which translates to insufficient dietary intake in populations dependent on food crops grown in these soils [14]. The bioavailability of microelements from soil to crops is determined by a multitude of soil factors, including pH, organic matter content, soil aeration, moisture, and interactions with other soil elements, as well as by the crop variety itself, which governs plant uptake physiology and specific root–soil interactions [15–18]. The source of microelements in soil is a primary determinant of their subsequent behavior and bioavailability. These sources can be broadly categorized as lithogenic (geogenic) and anthropogenic. Lithogenic microelements are derived from the weathering of parent rock material, where they exist within the crystal lattice of parent and soil-formed minerals [19]. Their release into the soil solution is a slow process governed by weathering rates, making their availability long-term, but often limited. In contrast, anthropogenic sources, such as fertilizers, pesticides, industrial emissions, and sewage sludge application, introduce microelements in forms that are often more mobile and immediately available, but can

also pose a risk of toxicity if mismanaged [13]. Lithogenic elements are either bound to minerals inherited from the parent material (e.g., silicates) or those formed through pedogenesis, such as clay minerals and oxides. Their mobility is mainly affected by the weathering process, and subsequently, by the anion and cation exchange capacity of the minerals. While microelements can arise from lithogenic and anthropogenic sources, their distribution and speciation are subject to various pedogenetic processes, such as fixation by clay minerals and binding/complexation with soil organic matter [13]. The bioavailability of soil microelements has been a topic of discussion in relation to climate change. Aridity can affect the soil elements in drylands both directly and indirectly. This can alter global biogeochemical cycles and ecosystems under climate change [20]. Microelements play a crucial role in the growth and development of plants and their subsequent nutritional value for human consumption. In particular, soil nutrient availability, salinity, and permeability can influence plant phytochemistry by modulating the costs associated with their production and deployment of phytochemicals, through physiological constraints on metabolism [21,22]. The development of regional soil micronutrient management strategies increasingly relies on advanced predictive modeling techniques. Among these, portable X-ray fluorescence (pXRF) spectrometry, combined with ensemble learning-based digital soil mapping, offers a powerful tool for the rapid assessment of micronutrient distribution. These techniques are versatile, applicable from broad regional scales to identify large-scale deficiency zones down to the field level for precision agriculture [23]. However, it is crucial to understand that pXRF measures total elemental concentrations in the soil, which must be calibrated against plant-available fractions and actual plant tissue concentrations to be meaningful for agriculture. While these methods do not directly yield specific fertilizer recommendations, they are instrumental in developing targeted regional management strategies. By identifying potential "hotspots" of deficiency or toxicity, they guide more detailed soil and plant analyses, ultimately supporting a more precise and efficient approach to soil fertility management and sustainable agricultural practices [24]. Furthermore, recent research underscores the potential of pXRF spectrometry for predicting micronutrient availability in highly weathered soils, particularly in regions such as Brazil, where the degree of weathering plays a critical role in shaping soil composition [23–25]. Comprehensive understanding of the mechanisms behind crop production and microelement uptake in the soil–plant system is necessary to ensure the production of high-quality food. This review paper will focus on the impact of microelement bioavailability, including Se, Zn, Cu, B, Mn, Mo, Fe, Ni, and Cl, in relation with physico-chemical soil properties. By understanding the relationship between soil microelement content and bioavailability, we can develop strategies to improve crop yield and the nutritional quality of our food.

2. Microelement Deficiency in Agriculture Hinders Global Food Security and Human Health

To avoid the widespread incidence of hunger, the agricultural sector must once again replicate the success achieved during the "Green Revolution" in augmenting food production [1]. With the global population projected to continue its expansion, agricultural systems face the immense challenge of increasing food production to meet future demands. This challenge is not only about quantity, but also about nutritional quality. However, in developing countries, most agricultural systems currently fail to provide sufficient nutrients, with many lacking the requisite microelements (14 trace elements and 13 vitamins) to meet the demands of human nutrition, notwithstanding that energy production from grains appears to meet global protein needs [12,26,27]. The lack of microelements in the soil not only disturbs crop production, but also adversely affects human nutrition and health, as an estimated 3 billion people suffer from microelement deficiencies, according to

the World Health Organization [14]. The intricate relationship between soil quality and human health is a cornerstone of environmental and nutritional science, establishing that the health of populations is fundamentally linked to the pedological characteristics of their environment [19]. This connection is not merely incidental, but is established through a direct and vital pathway: the transfer of essential trace elements from the soil, as an abiotic medium, into the biotic systems of plants and animals that constitute the human diet [27,28]. Microelements are used in relatively small amounts and constitute less than 0.1% of dry plant tissue, and some of the microelements may be toxic when consumed at high amounts in the human diet [29]. Microelement malnutrition poses a serious global challenge that undermines people's productivity and seriously hinders economic development [1]. The crucial role played by microelements in all ecosystems is beyond dispute, and a deficiency or excess of any one can cause an imbalance. Microelements play a crucial role in longevity and vitality, significantly contributing to overall health and well-being, as explored in a few recent studies [30–32]. However, they are also today's biggest global problem, contributing to increased mortality, disability, impaired cognitive and physical development, and reduced national socioeconomic growth. Microelement deficiencies are associated with over five million deaths annually during childhood [6,28]. Microelements, although required in small quantities (i.e., milligrams per day), have a significant impact on human health and well-being. Inadequate intake of these essential nutrients through the diet can impair brain function, immune and reproductive systems, and energy metabolism, resulting in learning difficulties, reduced work capacity, severe illness, and even death. Several nutrients and dietary components, including macroelements and microelements, can potentially influence bone health. In addition to calcium (Ca) and vitamin D, there is increasing interest in the role of microelements in bone health [33]. In research, it was determined that certain microelements play crucial roles in promoting dental health and supporting human development [34]. A recent study [3] demonstrated that microelement intake, especially of Se, Zn, Fe, and Cu, is essential during the first trimester of pregnancy. High concentrations of essential metals, such as Co, Mn, Se, and Zn, can affect different stages of male and female reproduction [35]. In response to this challenge, scientific intervention evolved from merely identifying the problem to developing targeted solutions. One of the most promising strategies is agronomic biofortification, which involves deliberately increasing the content of essential micronutrients in staple crops during their cultivation [36]. This approach represents a paradigm shift, transforming agriculture into a direct vehicle for public health improvement. As reviewed by Cakmak and Kutman [36], the agronomic biofortification of cereals with Zn emerged as a robust and effective method to enhance the zinc content of staple foods, addressing a widespread global deficiency. This strategy has been successfully applied to other critical micronutrients as well. Early research by Lyons, Stangoulis, and Graham [37] demonstrated the efficacy of producing high Se wheat, proving that targeted agricultural practices could effectively biofortify a major food staple and contribute to better health outcomes. The functional integrity of soil ecosystems constitutes a critical determinant of public health, directly governing nutritional security and the mitigation of disease [19]. Addressing this issue will require a concerted effort from governments, organizations, and individuals alike to ensure adequate access to essential vitamins and minerals for all.

Mechanisms of Microelements Absorption and Plant Physiology

Microelements play diverse roles in plants. Apart from being a vital component of enzymes, certain microelements also aid in enzyme activation and participate in oxidative-reductive reactions in plant metabolism [4,38]. Inadequate levels of microelements in plants not only disturb agricultural production, but can also impact human nutrition since

plant-based foods serve as a primary source of dietary intake for humans [4]. Microelements are essential for plants in relatively small amounts, as achieved biological yield typically removes only a few tens or hundreds of grams per hectare from the soil [39]. Microelements are absorbed by plants in different forms and various oxidative states. Plants absorb microelements in various forms. For instance, Fe is absorbed as Fe^{2+}, Fe^{3+} ions, or as Fe chelates [40,41]. Mn is taken up as water-soluble or exchangeable Mn^{2+} ions [42]. Boron is primarily absorbed as undissociated boric acid (H_3BO_3) [43], while Zn is absorbed as the Zn^{2+} cation or as various complexes [44]. Copper is also absorbed as the Cu^{2+} cation or as Cu chelates [45]. Molybdenum is taken up as the molybdate anion (MoO_4^{2-}) [40]. Finally, plants absorb Cl as the Cl^- anion, Ni as Ni^{2+}, and Se as selenate (SeO_4^{2-}) or selenite (SeO_3^{2-}) [40,42–44]. From a physiological perspective, microelements play various roles and have a crucial impact as regulatory or structural components. Iron is necessary for the synthesis of chlorophyll, the reduction in nitrate and sulfate, N_2 assimilation, nodulation in *Bradyrhizobium*, and many other constitutive roles [41,46]. Manganese is not a structural element, except in manganin, but it plays significant roles in redox processes [47,48]. Furthermore, B has numerous physiological roles, including carbohydrate transport, participation in sucrose synthesis, acid metabolism, photosynthesis, protein metabolism, cell membrane stabilization, regulation of meristematic activity, cytokinin synthesis, and more [44]. Additionally, Zn has a vital and extensive physiological role, as it affects the metabolism of many substances, mainly proteins. It is a constituent of many enzymes where it acts as a divalent cation that forms tetrahedral chelates, connecting the enzyme to the substrate [44,46,49,50]. Copper plays a crucial physiological role as it is a component or activator of enzymes that primarily participate in oxidation processes. It participates in the synthesis of many pigments and acts as a stabilizer of proteins, especially chlorophyll [51]. On the other hand, Mo is essential for the oxidation of sulfite to sulfate and the reduction in nitrate, which are key processes for plant growth. A deficiency of Mo can reduce the activity of nitrate reductase, leading to slower growth [52]. Moreover, Cl is required in very small concentrations for plants, but has important functions, including osmoregulation, stomatal opening, and photosynthesis. Nickel is a critical component of enzymes such as urease and hydrogenases, which are necessary for sulfate reduction, photosynthesis, and hydrogen oxidation in bacteria such as *Rhizobium* and *Bradyrhizobium*. Finally, Se is necessary for the synthesis of selenomethionine (SeMet) and selenocysteine (SeCys), which play important roles in various physiological processes [50,53,54]. Furthermore, soil microorganisms, such as PGPR bacteria and AMF fungi, are crucial for better absorption of micronutrients by plants. They do this through various mechanisms, and this represents a sustainable way to improve the nutritional value of crops and reduce the use of synthetic fertilizers [27–29].

3. Microelement Cycling in Agroecosystems: Processes and Factors from Rocks to Fertile Fields

The journey of microelements from soil to crops is governed by the critical distinction between total concentration and bioavailability. While soil parent material dictates the total elemental pool (the lithogenic source), only a small fraction is typically in a chemical form that plants can absorb [4]. This bioavailable fraction is controlled by a complex interplay of soil properties, primarily soil pH, organic matter content, and redox potential [15,16]. Anthropogenic inputs, such as fertilizers, manure, and atmospheric deposition, can further alter these dynamics [55,56]. Understanding these controlling factors is the first step in diagnosing and managing microelement deficiencies in agroecosystems. The cycling of microelements in agroecosystems is a complex set of processes that involve the content and removal of microelements from the soil, as well as their chemical transformation, solubility,

and availability to plants caused by changes in the ecosystem [27]. Microelements in soils result from alluvial or atmospheric deposits and the application of fertilizers, manure, or compost [56]. The characteristics of the distribution and migration of microelements in the environment are influenced by the components of the parent rock and substrate, as well as geochemical processes [57–60]. Elements can be categorized as lithophilic, chalcophilic, and siderophilic based on their affinity for different minerals. Lithophilic elements, such as B, Zn, Mn, and Fe, tend to associate with silicate minerals, while chalcophilic elements, including Zn, Cu, and Ni, prefer sulfide minerals, and siderophilic elements, such as Fe, Cu, Mo, and Ni, are commonly associated with iron oxides and hydroxides [4,61]. Some elements may exhibit a secondary affinity for silicate and sulfide minerals. However, among essential microelements, Co, Cu, and Zn, which are also classified as heavy metals, are typically present in lower concentrations in soils than in the parent material from which they are derived [4]. All essential elements originate not only from soil minerals, but also from trace elements, such as B, I, and Se, which are delivered in significant amounts to soil through atmospheric transport from marine environments [4]. Another important factor to consider, especially regarding organic matter, is the effect of adding organic matter, which can affect the availability of mineral elements in the soil. The general preference order for the formation of organic complexes in soils (both in solid and soluble forms) is as follows: $Fe^{3+} > Cu^{2+} > Co^{2+} > Zn^{2+} > Fe^{2+} > Mn^{2+}$ [62]. The efficient bioavailability of minerals in soil can be reduced by dissolved organic matter, which is released as organic amendments are degraded, forming complexes that sequester nutrients and reduce their availability for plants [63]. The geochemical action of biological organisms leads to the redistribution of microelements in the landscape. The series of biological enrichment is Ni > Zn > Cu > Ba > Co > Cr > Pb > Be > Ti > V [64]. It is important to clarify that this series describes the general tendency for biological accumulation of various elements, including both essential micronutrients and potentially toxic heavy metals such as lead (Pb). The inclusion of Pb highlights that accumulation processes are not always selective for beneficial elements, posing a potential risk for food chain contamination [64,65]. It is evident that elements with high biological enrichment coefficients, such as Ni and Zn, exhibit accumulation characteristics in soil formation, except for specific elements, such as Cu. This exception is likely associated with the selective absorption of different parts of the organism. For aquatic ecosystems, factors such as water pH and ion composition, sediment type, water flow, etc., influence the bioavailability of microelements. Some studies have shown that the concentration of microelements in fish is a more informative indicator of water pollution compared to the concentration of microelements in water [66]. Microorganisms play a pivotal role in the natural cycling of microelements, significantly contributing to the ecological equilibrium on Earth through the process of biological decomposition [67,68]. This intricate process involves the degradation of plant and animal remnants into simpler elements, thereby facilitating their circulation. The absence of this process would leave numerous elements "locked" and unavailable for plant and human nutrition [69]. Harvesting and erosion of the soil surface increase the losses of microelements from agricultural soils [56]. Soil represents the primary source of microelements for plants, with few exceptions, such as the occurrence of atmospheric depositions or floodwaters contaminated with pollutants [4]. To sum up, the most critical factors implicated in the sorption of heavy metals in soils are predominantly inorganic colloids, including clay minerals, metal oxides and hydroxides, and carbonates. Additionally, organic colloidal matter derived from detritus and living organisms, such as algae and bacteria, provide a substrate for the sorption of heavy metals [70]. In conclusion, microelements are found throughout nature and within us; therefore, we have summarized Table 1, which presents the concentrations of individual microelements in the biosphere (Earth's crust, soil, plants, and the human body).

Table 1. Mean values (mg/kg) of microelements in the Earth's crust, soil (top meter), plants, and the human body.

Element	Earth's Crust	Soil	Plant	Human Body
Selenium (Se)	0.083	0.01	0.05	0.11
Zinc (Zn)	52	50	100	33.0
Cooper (Cu)	14	20	14	1.0
Boron (B)	17	10	50	0.30
Manganese (Mn)	530	800	630	0.17
Molybdenum (Mo)	1.4	3	0.05	0.08
Iron (Fe)	31,000	40,000	140	60
Nickel (Ni)	75	40	3	0.14

Source: Nieder et al. 2018 and Iyaka 2011.

3.1. Selenium

Selenium (Se) is a chalcogen element belonging to group 16 and shares similar chemical properties with sulfur (S). While it is an essential mineral nutrient for humans and livestock, excessive intake of Se can lead to toxicity [71,72]. The concentration of Se in soils across the globe ranges from 5 to 3500 μg kg^{-1}, with an average of 383 μg kg^{-1} [73]. Selenium can be found in all rocks and soils. Its concentration in igneous rocks averages around 90 μg kg^{-1}, while in sedimentary rocks and sandstones, it is typically around 1000 μg kg^{-1}. Limestone has a Se concentration of 80 μg kg^{-1}. The highest concentration of Se is found in shales, with levels reaching up to 675,000 μg kg^{-1}. Phosphate rocks, on the other hand, contain Se levels between 1000 and 300,000 μg kg^{-1} [74]. The amount of Se present in parent rocks generally varies significantly: tertiary sand eluvium: 50–80 μg kg^{-1}; limestone: 30–100 μg kg^{-1}; and clay: 400–600 μg kg^{-1} [75]. The forms and concentrations of Se in soil solution depend on various physico-chemical factors, such as pH, dissociation constant, solubility of products, and oxidation–reduction potential [76]. Selenium is naturally present in one of four oxidation states: +6 (selenate), +4 (selenite), 0 (elemental Se), and −2 (selenide) [9]. Plants can absorb Se in the form of selenates, selenites, and organic compounds containing Se, such as SeCys and SeMet, but they cannot absorb selenides and colloidal elemental Se [9,72]. Selenate (SeO_4^{2-}) is the primary water-soluble form of Se in oxidic soils, whereas selenite (SeO_3^{2-}, $HSeO^{3-}$, and H_2SeO_3) predominates in anaerobic soils with neutral to acidic pH. Selenate is relatively mobile in soil solution, while selenite strongly adheres to iron and aluminum oxides/hydroxides, and to a lesser extent, to clay and organic matter [77]. Selenate's solubility is very high, which makes it unsuitable for long-term persistence in agricultural soils [37]. In contrast, selenite is only mobile when associated with iron selenite in acidic soils, and selenide has extremely low solubility [74]. Research has shown that plant uptake of added Se increased with liming when soil pH was adjusted to between 5 and 8, and regardless of the added Se form in alkaline soils, Se eventually converted to the more soluble selenate. Furthermore, the Se content was mainly dependent on the parent substrate, and a high correlation was observed between total Se and organic carbon, especially in the upper soil horizons [78]. It has been shown that adding Se as Na_2SeO_3 is less effective as it strongly adsorbs to soil oxides, whereas moderate addition of selenate should not affect levels of other essential trace elements, yield, and plant health [79]. Surface organic layers of soil have higher Se content than deeper horizons due to the reflection of seleno-organic binding [80], and such soil fractions relate to organic compounds, likely amino acids, bound to selenoproteins and selenate or selenite adsorbed in organic compounds [71]. A study conducted on three different soil types found that

Chernozem had the highest Se concentrations, followed by Gleysol, and finally, Luvisol and Cambisol, which may be related to varying organic matter content [75]. Elrashidi et al. determined that only a very small percentage of Se is actually in the water-soluble fraction in 500 soil samples from the seleniferous area of the United States [74].

3.2. Zinc

Zinc, a heavy metal, is one of the eight trace elements necessary for normal healthy growth and crop reproduction [81]. Zinc's ionic radius (0.83 Å) is identical to that of divalent Fe (0.83 Å) and almost the same as that of Mg (0.78 Å), suggesting that Zn is mineralogically closely related to Fe and Mg. However, it is well known that this is not the case [82]. The average Zn content in the lithosphere is approximately 80 mg kg^{-1}. Zinc content in soils generally ranges from 10 to 300 mg kg^{-1}, and Zn is considered a trace element in soil due to its low concentration [83]. Zinc content in limestones is 20 mg kg^{-1}, in sandstones is 30 mg kg^{-1}, in clay and shale, the Zn content is on average 120 mg kg^{-1}, and bituminous shales are the richest in Zn, with a concentration of 200 mg kg^{-1} [81]. Zinc deficiency in agricultural crops is one of the most common deficiencies among microelements. Zinc deficiency is particularly pronounced in calcareous and high-pH soils, where critical deficiency thresholds in many cereal crops fall below 15–20 mg/kg in dry leaf matter [36]. This often results in significant yield penalties, including stunted growth ("dwarfism"), delayed maturity, and poor grain filling, a phenomenon known as P-induced Zn deficiency when exacerbated by high phosphorus application [62]. Since 1957 Thorne [83] studied Zn deficiency and its control, and Zn deficiencies have become even more widespread [83]. There are many geochemical factors that can affect the concentration of Zn in the biosphere. Geochemical factors that directly affect solubility and sorption are temperature, pressure, pH, redox potential, concentrations of other elements in the soil, ions, or compounds that complex with Zn (e.g., Cl^-, HS^-, SO_4^{2+}, and more), and partial pressure of gases (e.g., O_2, CO_2, H_2S, S_2, and NH_3) [81,84]. The interaction of Zn with organic matter is somewhat unclear because the content of organo-Zn compounds is common where there is little humus, but zinc acetate $Zn(CH_3COO)_2$ and Zn–arginine can be formed in peat soil [85]. Zinc is stable in the form of Zn^{2+} at pH below 6 [70]. Worldwide trends show low concentrations in sandy soils and higher concentrations of Zn in soils with higher clay content. This is due to the higher concentration of Zn in parent materials of clay and shale, as well as the greater ability of clay-rich soils to adsorb and retain Zn and other elements compared to soils with a lower percentage of clay and a higher percentage of sand [81]. Dere et al. found a strong correlation between organic carbon and Ca carbonate in leached soil, suggesting a common origin [86]. It has been noted that (over)application of phosphorus limits Zn concentrations in shoots and leads to reduced growth and yield [36]. This phenomenon is called P-induced Zn deficiency. It is still a subject of debate whether the interaction between P and Zn occurs in the soil or in the plant [87]. Liang et al. [88] reported that using groundwater can pick up Fe phases, clay minerals, and disrupt their interaction with Zn. Moreover, low organic matter content and Mn concentration are very limited in affecting the isotopic fractionation of Zn in low-humus Gleysols [88]. Previous studies have shown that clay can adsorb heavy metal ions through one or more of the following mechanisms: specific binding, hydrolysis, and exchange processes. It has also been observed that the specific maximum sorption for Zn is lower than the fraction of CEC and (Ca–Mg) for all studied Gleysols. This could indicate that exchangeable cations, primarily Ca and Mg from the cation exchange capacity, are competitive with Zn for sorption sites [89]. Reactions between Zn and organic matter have also been widely studied due to the frequent occurrence of Zn deficiency in soils rich in organic matter [90]. Interestingly, Se has been found to enhance Zn uptake in lamb's

lettuce plants in vermicompost where the pH was 9.23, while in commercial substrate, Se reduced Zn uptake where the pH was 6.34 [91]. The research conducted by Vahedi et al. [92] concluded that amending soil with biochar and microorganisms can effectively maintain organic carbon, improve soil fertility, increase nutrient availability, such as Zn, P, and Fe, and ultimately lead to better wheat yield [92].

3.3. Cooper

Copper (Cu) is listed in the periodic table under group 4, with an atomic number of 29, atomic weight of 63.5, and a density of 8.96 g cm^{-3} [93]. Copper is widely used in various technical fields, such as transportation, production, and transmission of electricity, as well as in agriculture for fungicides and herbicides. Copper is intentionally used in agriculture in both inorganic forms (copper (II) sulfate; copper oxychloride, copper (II) hydroxide) and organic forms (copper salt with naphthenic acid; 8-hydroxyquinoline copper (II), etc.). Despite being an essential element, Cu toxicity cannot be ignored [94]. While the average content of Cu in the Earth's crust is low, its concentration in soils can vary widely, typically ranging from 20 to 60 mg kg^{-1} depending on the parent material and anthropogenic inputs. The maximum allowed concentration in many agricultural soils is regulated, for instance, at 55 mg kg^{-1} in some regions [95], indicating that soils in certain areas, particularly those with a long history of fungicide use, can approach or exceed toxic levels. The interaction of metal ions such as Cu (II) with soil is usually considered an ion exchange, but it has been observed that Cu (II) binds to free Fe and Mn oxides, clay minerals, and soil organic matter, thus exceeding the capacity of ion exchange [96]. Vlček and colleagues [94] identified key soil parameters responsible for their ability to bind free Cu. It seems that the content of P and Mg is a critical factor, while clay is also a factor. Soils that contain Mg retain copper more effectively, while soils with P do not have as much affinity. This should be taken into account when applying agricultural preparations such as fungicides. The results can be generalized to other similar types of soil [94]. The research on Pb, Cu, and Zn concluded that these elements interact with soil organic matter when applied to ordinary Chernozem in pot experiments. Two years after treatment, a significant portion of applied metals was found in organic matter, mainly in a weakly bound state. These organic matters were supposed to be organo-mineral complexes whose formation resulted in the partial destruction of humic acid molecules. These processes increased the content of aliphatic structures and the proportion of fulvic acid and decreased the content of humic acids in Chernozem organic matter [97,98]. Copper in soil can bind to organic matter and other components such as sand, clay, etc. High levels of Cu in soil are non-degradable and become toxic to microorganisms, disrupting the nutrient cycle and inhibiting the mineralization of essential nutrients such as N and P. Soil microorganisms (including those that provide nitrification) are also sensitive to changes in the soil environment and are early indicators of changes in soil ecology [93]. The mobility of Cu in carbonate Chernozems is very low due to colloid peptization and moderately elevated pH values [99]. The binding of Cu to soil particles is greater than that of Pb and Zn, which may be related to its poor mobility in Chernozem [100]. Rice fields are affected by Cu contamination due to stagnant surface water and rice cultivation methods, as Cu is poorly mobile in the soil and remains immobilized by organic matter or clay in surface soil layers [93]. An increase in soil Cu content reduces the amount of plant-available P. Similarly, some microelements are also affected, such as Zn, Mn, and Fe, due to the increased content of Cu in vineyard soils resulting from the continuous application of Cu fungicides in the form of a Bordeaux mixture [93]. Vlcek and colleagues (2018) found the strongest positive correlation between Cu and Mg, and the strongest negative correlation with P in Chernozem [94]. In a study of leached soil, the clay mineral content in the B1 horizon was found to be 30% higher than

in the E horizon, explaining why the B1 horizon adsorbs one third more Cu than the E horizon [94]. However, Cu uptake, even in the B1 horizon, is lower than that of smectite clay studied in the same area [101]. Clay adsorbs large amounts of Cu, and enhanced vermiculitization of chlorite increases copper sorption, while fixation and illitization of K, as well as initial Al–hydroxy layering of vermiculite, make Cu uptake more difficult, and on the other hand, iron coatings can also be an important factor that increases Cu sorption on clay minerals in leached soils [102]. In research by Gudzic et al. [103], no toxic doses of Cu were found in Stagnosols [103], while accumulation of Cu and heavy metals on Stagnosols under forest vegetation was found in the areas around the rivers [104]. Copper can accumulate on the surface of microorganisms at acidic pH, which can also contribute to the retention of copper in organic soil horizons during organic matter transport [105].

3.4. Boron

Boron is a lightweight non-metal that occurs mainly as an oxoanion in silicate minerals. Boron content in the Earth's crust is approximately 10 mg kg^{-1}, and in igneous rocks, it varies from 5 to 15 mg kg^{-1}, while in sedimentary rocks, it is found in concentrations of 20 to 100 mg kg^{-1}, and marine sediments it averages at 100 mg kg^{-1} [106]. Although it has been found that B availability is reduced in many cases due to excess Ca, the areas with the greatest B deficiency are still in moist areas where soils are generally acidic, so B deficiency will be largely prevalent in humid regions. In areas with low rainfall, soil B content is high. Boron in such soils likely exists mainly as sodium–calcium borates, and both are highly soluble. In these regions, B content in water is sometimes high enough that the water cannot be used for irrigation purposes [107]. Compared to other nutrients, soil B chemistry is very simple. Boron does not undergo redox reactions or volatilization. Boric acid is a very weak, monobasic acid that acts as a Lewis acid by accepting hydroxyl ions to form a borate anion. Boron is found in minerals that are either very insoluble (tourmaline) or very soluble (hydrated B minerals) and generally do not control B solubility in soil solution [108]. Boron deficiency in agricultural soils may result from low B levels in the parent substrate or limited availability as a result of factors such as soil pH, texture, moisture, and organic matter content. Deficiency is found in soils derived from various parent substrates that differ greatly in physical and chemical characteristics [109]. Data have also shown that available B decreases with increasing acidity, probably because organic matter also decreases with increasing acidity. The effect of soil organic matter is to keep B in a more available form. However, the final effect of organic matter on B availability is not as great as the pH value. This is especially true when the pH is above 7.0. In these cases, a very significant negative correlation was obtained between pH value and available B [108,110,111]. Increased soil moisture could stimulate the accumulation of soil organic matter and the formation of clay, further affecting B availability. Compared to other elements, B availability is more sensitive to soil moisture [112]. Lower concentrations of water-soluble B fractions were found in Gleysols compared to total fractions because this soil had the highest content of organic C and clay content, which can affect total B [113]. The adsorption of B onto clay minerals is influenced by soil pH, Al and Fe hydroxides, clay minerals, calcium carbonates, and organic components [114]. Paradoxically, less B is needed to correct B deficiency in soils with coarse texture than in soils with fine texture due to stronger B adsorption in such soils [115]. Most studies related to B globally focused on its agronomic trials and delineation. Only a few studies investigated the impact of different fractions of B on its availability in soil using various extractants, considering soil properties such as clay mineralogy [116].

3.5. Manganese

Manganese is a heavy metal (ρ = 7.440 g cm^{-3}) found in plants as Mn^{2+} and Mn^{3+} cations, and in soil as Mn^{4+} and Mn^{6+}. It is the tenth most abundant element in the lithosphere. The total content of Mn in soils ranges from 200 to 3000 mg kg^{-1}, of which 0.1 to 1.0% is available to plants. Most of the Mn in soil comes from MnO_2, and many minerals contain Mn. Different oxides with oxidation states of +2 to +7 (such as MnO_2 pyrolusite, [MnO(OH)] manganite, Mn_2O_3 braunite, Mn_3O_4 hausmannite, etc.) contribute to its chemistry [38]. Manganese is abundant in the soil environment and plays an important role as a component of soil. In its oxidized forms, Mn (MnIII, IV) is insoluble in water, immobile, and due to its pigmentation, it is easily identifiable in the oximorphic horizons of soil. However, in the absence of O_2, minerals participate in reversible electron transfer reactions and can be released into soil solution as Mn^{2+}. The chemistry of Mn in Gleysols is affected by water saturation due to the presence of groundwater, while Planosols, Plinthosols, and soils with stagnic properties (Stagnosols) show Mn reduction due to temporary watering [117]. The initial increase in Fe, Mn, Cu, and Zn content after soil irrigation may be related to the reduction in Fe and Mn oxides and the formation of organic complexes. Conversely, reduced levels of Fe, Mn, Cu, and Zn may be caused by an increase in pH and the formation of sulfides [118]. The development of Stagnosols is a consequence of accumulated groundwater, which induces periodic oxidation and reduction conditions, causing the spatial distribution of Fe and Mn between the soil matrix and ferromanganese concretions or nodules. In research by Rennert et al. [119], a positive correlation has been found between soil organic matter, Fe, and Mn. Processes that occur under weakly reducing soil conditions, such as denitrification and trace metal mobilization, are associated with the reductive dissolution of Mn oxides, which can be identified when Mn oxide is removed along the redox gradient, while the Fe oxide coating remains stable [117]. Nodules that form in soils on Chernozem differ in their morphology and chemical composition depending on the degree of hydromorphism. The highest accumulation coefficients of Mn are found in nodules in such soils [47]. In the study by Van Groeningen et al. [120], it was discussed that it is crucial to understand the effects of Mn(II) oxidation on trace metal retention in soils and the involvement of clay minerals in the transformation processes in order to fully grasp the dynamics of trace metals in different environmental contexts. Specifically, it is important to examine how Mn(II) oxidation affects the retention of trace metals during re-aeration and whether clay minerals alter these effects [120].

3.6. Molybdenum

Molybdenum belongs to the VI group of the periodic table, alongside Cr and tungsten (W). It is not found in nature in its pure metallic form and exists in five oxidation states (2–6), with Mo(IV) and Mo(VI) being the most common species [121]. As a trace element, Mo is essential in the cycling of N, C, and other elements crucial for life. Molybdenum is essential as a co-factor in nitrogenase, and its deficiency can limit nitrogen fixation [122]. It is not found in a pure form in nature, but occurs in minerals such as molybdenite, powellite, and wulfenite, often combined with elements such as sulfur, oxygen, and lead [123]. While the average concentration of Mo in soil is around 1–2 mg kg^{-1}, the level of Mo varies considerably depending on the specific types of geological materials present in the soil. For example, sedimentary materials such as shale contain high concentrations of Mo, while they are often lacking in acidic soils. In general, Mo-deficient and Mo-excessive soils are defined by concentrations of 0.2 mg kg^{-1} and 0.7 mg kg^{-1}, respectively. At a pH of 7.5, there is low absorption of Mo, and plants mainly take up Mo from alkaline or neutral soils. Municipal waste sludge is typically contaminated with Mo, with average concentrations around 15 mg kg^{-1} and ranging from about 1 to 40 mg kg^{-1} of Mo [121]. The concentration

of Mo in agricultural soils varies between 0.2 and 5.0 mg kg^{-1}. Plants absorb Mo in the form of molybdate anions, which are the predominant species in soil solution [124]. The release of Mo from solid mineral forms into soil solution depends on various soil properties, such as soil pH, and the content of Fe, Mn, Al oxides, clay minerals, and organic carbon. Among these factors, soil pH has the most significant impact on the processes of adsorption and release of molybdate ions into soil solution. Molybdenum occurs in the soil as oxoanions in alumisilicates and organic matter. In the soil environment, the presence of Fe, Al, and organic carbon is positively correlated with Mo^{5+}, while it has an antagonistic relationship with Cu^{2+}. In acidic soils, the primary soluble form of Mo^{5+} is the $MoO_4{}^{2-}$ anion. In neutral and alkaline media, Mo^{5+} forms mobile anionic complex compounds [124]. Molybdenum has the maximum adsorption on positively charged metal oxides between pH 4 and 5. In acidic soils, molybdate anions are adsorbed onto positively charged Fe, Mn, and Al oxides, clay minerals, and organic colloids. The availability of Mo to plants increases as soil pH increases. For every unit of pH value above 3, the solubility of molybdate ions increases approximately 100 times, mainly because of the reduced adsorption of metal oxides [125]. Sedimentary materials, particularly shales, are generally associated with high Mo concentrations in soils. Ancient alluvial sands and sandy loams from Belarus had Mo concentrations ranging from 0.28 to 0.90 mg kg^{-1}, while moraine loams and loessial loams had concentrations between 0.9 and 4.9 mg kg^{-1}. Clays had an average concentration of 2.8 to 3.7 mg kg^{-1} [123]. It has been observed that Mo adsorbs onto all solid phases of soil, and this adsorption generally decreases as pH increases [126].

3.7. Iron

Iron is a dense metal that easily undergoes changes in its valence states and can form various complexes. Its presence in the soil is linked to several lithogenic and pedogenic minerals, and the reserves of Fe in the soil are primarily in inorganic form, with a total content typically ranging between 0.5% and 5.0%, but it can be significantly higher in iron-rich soils [38]. Iron can be found in most rocks in the Earth's crust. The different pathways of formation of various Fe oxides in soils can be understood by observing the environmental conditions under which a specific phase or association of phases occurs in a given soil or soil sequence [127]. Iron can be found in carbonates, oxides, silicates, and sulfides, and the most significant ones are hematite (α–Fe_2O_3) and goethite (α–FeOOH). In soils with a high amount of organic matter, the organic iron reserves can be significant, such as Fe oxy–hydroxide compounds and Fe chelates [38]. Several types of microorganisms, mainly anaerobic bacteria, are capable of reducing Fe oxides. The degree of crystallinity is a characteristic of Fe oxides that varies greatly among different soil types. One of the most critical properties of different Fe oxides in soil is their surface structure and the dependence of surface charge on pH as their surface area interacts with soil solution, other solid phases, plant roots, and soil biota [127]. The availability of Fe in soils seems to depend on the chemical nature and reactivity of Fe forms, physiological and morphological properties of plant roots, and surface interactions of roots with soil [128]. The primary pool of Fe(III) consists of different forms of Fe oxides, hydroxides, and oxyhydroxides. Reduction in Fe(III) results in the release of reduced Fe or Fe(II). Under reducing conditions at acidic to neutral pH, Fe(II) is present as soluble Fe^{2+} in water. Upon reintroduction of O_2 to lowland soils, Fe^{2+} is rapidly oxidized, resulting in simultaneous precipitation as Fe oxide [129]. The solubility of Fe in soils is controlled by $Fe(OH)_3$ in well-oxidized soils, $Fe_3(OH)_8$ in moderately oxidized soils, and $FeCO_3$ in strongly reduced soils. The main forms of inorganic Fe in soil solution are Fe(III), $Fe(OH)_2$, and $Fe(OH)_3$ [128,130]. Soil genesis is commonly investigated through the analysis of Fe forms, which can provide valuable information on the direction, type, and intensity of soil formation processes [131]. In gleyed soils, which are waterlogged, Fe

(hydr)oxide concentration exhibits highly localized patterns that result in a reduction in complex redox conditions in the soil. The distribution of oxidative and reductive conditions in these soils is influenced by factors such as groundwater and soil water chemistry, microbial activity, organic matter distribution, soil aggregation, and pore structure [132]. In a study of leached soil, the presence of Fe (hydroxide) oxides primarily affected the stability of small soil microaggregates by cementing them into smaller sizes within small pores [133]. On the other hand, the effect of organic carbon was limited to the size of colloids, causing them to stick together into small soil microaggregates within specific size ranges in the presence of organic carbon, but releasing them in its absence [133]. Soil organic matter particles were present in all soils (Gleysolic, Stagnosols, and Cambisolic), and their degree of impregnation increased with depth. A strong correlation was also observed between soil organic matter and Fe forms in all soils [132]. The degree of hydromorphism in Chernozem soil type is most clearly reflected by the coefficient of saturation, which is the ratio of Fe and Mn in the extract of 1N H_2SO_4, and is influenced by surface and groundwater [47].

3.8. Nickel

Nickel is a metallic element that belongs to Group X of the periodic table. It has a silver–white color, is hard, ductile, and an excellent conductor of heat and electricity. It can exist in various oxidation states and is insoluble in water, but soluble in diluted nitric acid (HNO_3), slightly soluble in hydrochloric acid (HCl) and sulfuric acid (H_2SO_4), and insoluble in ammonium hydroxide (NH_4OH) [134]. Nickel is typically found in oxidation states 0 and +2, but can occasionally occur in −1, +1, +3, and +4. Due to its high electrical and thermal conductivity, Ni is resistant to electrical erosion, oxidation, and corrosion, even at temperatures ranging from −20 to +30 °C [135]. The most important Ni ores are pentlandite (nickel–iron sulfide) and garnierite (nickel–magnesium silicate). Nickel is a naturally occurring metal that is widely distributed throughout the earth's crust. Its status in soil is largely dependent on the concentration of Ni in parent rocks. However, in surface soils, its content is also influenced by soil formation processes and pollution [135]. Nickel is present in soil, water, air, and biological materials. Although Ni occurs naturally, concentrations found in the environment can also be caused by human activities, such as deposition from burning fossil fuels. Under anthropogenic influence, approximately 180,000 tons of Ni are globally released annually, with 150,000 tons being redistributed by natural processes [134]. The Ni concentration in soils exhibits a significant degree of variability and can range from 3 to 1000 mg kg^{-1}, while the global average ranges between 0.2 and 450 mg kg^{-1}, with an average of 22 mg kg^{-1} [135]. Nevertheless, young soils that are rich in clay, minerals, and saprolitic materials tend to have a higher proportion of Ni that is available to plants. The factors that have the greatest influence on the phytoavailability of Ni include (i) the original characteristics of the parent material and its weathering history; (ii) soil composition, such as organic matter and clay content, as well as thermodynamic factors, including pH and redox potential; and (iii) rhizosphere effects, which include root exudates [21]. Nickel is commonly associated with Fe and Co, and soils that contain high levels of these elements often contain elevated amounts of Ni as well. The mobility of Ni in soil is dependent on the texture composition and mineralogical structure of the soil. In addition to soil minerals, amorphous Fe and Mn oxides are the most important sinks for Ni in soil [136], with such formations accounting for approximately 50% or more of Ni in soil [21]. The increased mobility of Ni in the presence of chloride ions is apparently due to the formation of chloride complexes. It has been experimentally shown that sulfate (SO_4) and the formation of nitrate (NO_3) complexes have predictable effects in reducing Ni sorption by kaolinite. Based on known stability constants of metal chelate species, Ni(II) should bind with various chelates, excluding competitive cationic species at typical soil pH

values [137]. A study found that adding 50 mg kg^{-1} to acidic sandy soil caused damage to several plant species, while adding 100 mg kg^{-1} of Ni to neutral leached soil did not result in toxicity to plants [138]. In most soils, Ni is bound to ion exchange sites, particularly adsorbed or co-precipitated with Al and Fe oxyhydroxides. These are dominant processes in neutral to alkaline soils. In acidic, organic-rich soils where fulvic and humic acids are formed by organic material degradation, Ni can be quite mobile, probably because it complexes with these ligands [136].

3.9. Chlorine

Chlorine exists in terrestrial environments in the form of both inorganic chloride and organic chlorine, and its biogeochemical cycling in soil involves a complex series of processes. The primary source of chloride in soil is deposition from the atmosphere, which originates from the sea. The influence of this source depends on the distance from the sea and the amount of rainfall in the area. The amount of chloride stored in soil varies significantly between different locations and is largely dependent on the balance between deposition and evapotranspiration, as well as the amount of chloride deposited in the area [139]. Chlorine, in the form of Cl^- ions, is ubiquitous in the soil environment and is introduced through a variety of sources, including irrigation water, animal manure, fertilizers, plant residues, rainwater, and dust [140]. Despite being required in small amounts, Cl is critical for several key physiological processes in plants. It plays an essential role in photosynthesis, specifically as a cofactor in the oxygen-evolving complex of photosystem II. Furthermore, Cl is vital for osmoregulation and maintaining turgor, acting as a major mobile anion to balance the charge of cations such as potassium (K+) during stomatal opening and closing. This function directly impacts the plant's water relations and ability to respond to environmental stress [50]. Chlorine has a strong tendency to form anions due to its high electronegativity, and is therefore often found in the form of salts, such as chloride. It is a halogen, which actually means "salt maker" in Greek, and is ubiquitous in the soil environment [139]. Measuring Cl^- in soil extracts is a routine task in laboratories dealing with salinity problems. In drought-prone and semiarid areas of the United States, Cl^- is an important parameter used in irrigation management. For example, Cl^- is used to assess leaching fraction and salt balance. Determination of Cl^- along with NH_4^+ ions in soil extracts is the basis for measuring soil cation exchange capacity [140]. Due to its solubility, chloride generally occurs as an exchangeable ion in water that adheres to soil particles and as a free ion that accompanies water movement through soil. In tropical and subtropical regions, high evapotranspiration occasionally leads to the formation of salt crystals. All organic matter is chlorinated, although the degree of chlorination varies [139]. Research has shown that organic Cl is ubiquitous in soil and that organic matter contains Cl in amounts similar to P, which is only one order of magnitude smaller than N and S [141]. The study found that 20–50% of Cl is organically bound. The concentration of both organic C and organic Cl in leachate was extremely high compared to values generally observed in runoff, suggesting that organic matter is deposited or mineralized on its way through the soil. It has been documented that organic matter in temperate areas is transported downwards with water in the soil, with most of it deposited lower in the soil profile [142].

4. Conclusions and Future Perspective

As the global population continues to grow, the demand for food is also increasing, putting a strain on agricultural land and resources. This presents a significant challenge for agricultural production that must be addressed urgently. Microelement deficiencies are prevalent among populations, resulting in a range of health disorders and diseases, impact-

ing vitality and longevity. To move towards a more precise and effective management of microelements, future research should focus on the following key areas:

1. Integrative modeling: There is a pressing need to develop and validate predictive models that go beyond simple correlations. Future models should integrate multi–layered data: high-resolution soil maps (e.g., pH, texture, and SOC), climate data, crop genetics (e.g., genes for specific metal transporters), and data on soil microbial communities, which play a crucial role in nutrient cycling.
2. Quantifying interactions: While many antagonisms (e.g., P–Zn, S–Se) are known, their quantitative impact under field conditions is poorly understood. Research should focus on developing dynamic models of nutrient interactions in the rhizosphere to predict the net effect of multi-nutrient fertilization on the final crop nutritional profile.
3. Harnessing the rhizosphere: The role of root exudates and the soil microbiome in mobilizing microelements is a major knowledge gap. Future work should aim to identify microbial strains or plant–microbe combinations that can act as "bio-fertilizers" for specific microelements, offering a sustainable alternative to chemical inputs.
4. Closing the loop from soil to health: Most studies end at crop analysis. There is a need for more integrated, long-term studies that follow the chain from soil management to crop biofortification to food processing to bioavailability in humans. This requires interdisciplinary collaboration between soil scientists, agronomists, nutritionists, and public health experts.

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