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REVIEW

Metallic trace elements in cereal grain – a review: how much metal do we eat?

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Abstract

Plants are the first step of a metal's pathway from the soil to heterotrophic organisms such as animals and humans, so the content of metallic trace elements in edible parts of a plant represent available load of these metals that may enter the food chain through plants. Among metal elements, Cu, Fe, Mn, and Zn are micronutrients as they are essential in trace amounts for physiological processes in living organisms and therefore are a significant component of the soil–plant–food continuum. Billions of people around the world suffer from micronutrient malnutrition. This review is aimed at giving an overview of the data pertaining to the Fe, Mn, Zn, and Cu content of the grains of the globally most important cereals – wheat, rice, and maize, reported mostly during the last two decades. The prevailing opinions on their importance in the food chain, and current strategies for enrichment of cereal grains with those essential microelements are briefly summarized.

Introduction

Metals have important and wide-ranging roles in biochemistry, being both essential and toxic (Guengerich 2009). It is well known that essential transition metals are required in all plant organs for the activities of numerous metal-dependent enzymes and proteins (Krämer et al. 2007), and they have similar roles in other organisms. The concentration of individual transition metals in plant tissues varies over several orders of magnitude, with Fe being the most prevalent (~100 mg g^{-1}) and Mo being the least abundant (Merchant 2010). Among metal elements, Cu, Fe, Mn, Mo, Ni, and Zn are considered plant micronutrients because they are essential for physiological processes in trace amounts (Vincevica-Gaile and Klavins 2012). Historically, their physiological roles were first described on the basis of deficiency symptoms in plants (Hänsch and Mendel 2009). Deficiency of micronutrients in soils and plants is a global nutritional problem as the major food staples are highly susceptible to such deficits (Imtiaz et al. 2010). For example, essentiality of Zn in the diet and its deficiency in humans was recognized in 1963 (Prasad 2012). During the past 50 years, it has become apparent that deficiency of Zn in humans is prevalent with nearly 40% of the global population suffering from Zn malnutrition.

If the availability of a micronutrient in the external medium is insufficient to cover the demand of the plant, physiological, and/or morphological responses are upregulated to improve micronutrient acquisition and increase internal utilization (Giehl et al. 2009). Furthermore, coordinated uptake, buffering, translocation, and storage processes regulate metal ion concentrations within narrow physiological limits (Clemens et al. 2002; Bhullar and Gruissem 2013). However, among all the environmental stresses, the effect of metal accumulation has been considered one of the most disturbing factors arising in the late 19th and early 20th centuries (Azevedo et al. 2012). In addition to their essentiality for plant growth and human nutrition, some micronutrients may also be toxic to animals, including humans, at high concentrations (Wang et al. 2008), for example, Cu or Zn. Even though Zn is not redox active, Zn toxicity occurs at too high levels because Zn can displace other metals in the cell (Pilon et al. 2009). Transport to grain of Cd and Zn are somewhat independent, so it is possible to achieve both higher Zn and Cd uptake into the plant but only higher Zn movement to grain. However, breeding programs to improve grain Zn and Fe content should ensure that Cd is not being increased along with Zn (Khoshgoftarmanesh et al. 2010).

Plant seeds are among the major sources of animal and human foods, and also the input material for cultivating most agricultural crops. An important component of seed quality is its chemical composition, including the concentration of micronutrients such as Fe, Zn, and Cu (Waters and Sankaran 2011). Plants face major variations in transition metals, and also concentrations of Fe, Zn, Cu, and Mn within the rhizosphere (Puig and Peñarrubia 2009). The propensity for plants to accumulate and translocate these essential elements to edible and harvested parts depends to a large extent on soil and climatic factors, plant genotype, and agronomic management (McLaughlin et al. 1999). For example, delaying the seeding date of spring wheat decreased subsequent grain Fe by 10–30% and Zn content by 7–22% as shown by Gao et al. (2012). Quantitative data on micronutrient density of food crops grown on different types of soils are limited. Nubé and Voortman (2006) stated that the focus in agricultural research has been more on yields, and consequently there is much literature on the relationships between micronutrient availability in soils and associated yields, but little information on crop micronutrient concentration in the edible parts of crops. The term "micronutrient density" is commonly used in literature (Graham et al. 1999; Bouis et al. 2000; Welch and Graham 2002; Bouis 2003; Nubé and Voortman 2006; Yang et al. 2007; Alloway 2008; Cakmak et al. 2010a; Depar et al. 2011; Husted et al. 2011; Waters and Sankaran 2011; Hansen et al. 2012) as a synonym for concentration, expressed as the amount of micronutrient per unit of plant dry weight, which is – as an example – a more important measure of Zn supply in the grain destined for human food than Zn content, or the total amount of Zn per seed or plant (Rengel 2002).

Clearly, plants are the first step of a metal's pathway from the soil to heterotrophic organisms such as animals and humans, so the micronutrient content in their edible parts makes a major contribution to human intake. As many of the metals that can be hyperaccumulated are also essential nutrients, phytoremediation and food fortification can be considered two sides of the same coin (Guerinot and Salt 2001) for improved food quality and safety. Zhao and McGrath (2009) suggested that micronutrient malnutrition in humans and environmental contamination with heavy metals or metalloids are both global and challenging problems that require concerted efforts from researchers in multiple disciplines, including plant biology, plant breeding as well as biotechnology, nutrition and environmental sciences, such as soil fertility and chemistry.

In this review, our aim is to provide an overview of data regarding Fe, Mn, Zn, and Cu concentration in the grain of the most important cereals, that is, wheat, rice, and maize, published in the last two decades, as well as the prevailing opinions on their plant-driven entry into the food chain.

"Hidden Hunger"

Agriculture performs a vital public function: it feeds the people of the world (Dudal 1996). Plants are the major source of food both for human consumption and as feed for animals. According to Welch and Graham (2005), advances in crop production, incurred during the "green revolution", were dependent mostly on improvements in cereal cropping systems (i.e., rice, wheat, and maize) and resulted in greatly increased food supplies. However, the gap between actual and potential yield must be addressed. This gap is 15–95% of the potential yield, depending on the crop and agricultural system (White et al. 2012). The results of Neumann et al. (2010) show that on average the present actual yields of wheat, maize, and rice are 64%, 50%, and 64% of their potential yields, respectively. Since the "green revolution", intensive cropping, cultivation of high-yielding genotypes, improved agricultural mechanization, production of macronutrient fertilizers with low impurities such as trace elements, and the use of modern irrigation systems have resulted in higher crop production per unit area and greater depletion of soil phytoavailable micronutrients (Nubé and Voortman 2006; Khoshgoftarmanesh et al. 2010; Zhao and Shewry 2011).

Micronutrient deficiencies in humans exist in both developing and developed countries (Genc et al. 2005; Thompson 2011) and may be considered as "hidden hunger". Poor dietary intake, in terms of both total quantity of food and micronutrient-deficient food, is often the major cause of micronutrient malnutrition. There is a plethora of research and review papers where the term "hidden hunger" has been used to describe the micronutrient malnutrition inherent in human diets, especially with regard to Zn, Fe, and I (Cakmak and Braun 2001; Welch and Graham 2004; Liu et al. 2006; Mayer et al. 2008; White and Broadley 2008; Bouis 2011; Depar et al. 2011). Micronutrient malnutrition affects over 2 billion people in the developing world (Cakmak et al. 2010b; Depar et al. 2011). Some other reports mention that microelement deficiencies affect more than 3 billion of the world's population (Welch 2003; Šramková et al. 2009; Nagy et al. 2012). In developing countries, a large percentage of the population has no access to meat in their diet; the daily food intake is mostly cereal-based and does not support the microelement and vitamin needs of the population, as well as the biochemical diversity of food needed for a healthy life (Mayer et al. 2008). As emphasized by Nubé and Voortman (2006), among poor populations overall food intakes are often below requirements, resulting in inadequate macro- and micronutrient intake. Moreover, their diets are often highly monotonous, which increases the risk that the dietary intake of one or more micronutrients is insufficient. Diets low in foods from animal sources are also low in dietary components which may enhance micronutrient absorption, whereas diets containing high amounts of unrefined cereals and legumes are high in inhibitors such as phytate and polyphenols (Gibson 2005). Minerals such as Fe and Zn are found in low amounts in cereal- and tuber-based diets – and the bioavailability of non-hem Fe is low. Therefore, it is not possible to meet the recommended levels of Fe in the staple-based diets through a food-based approach unless some meat or fish is included (FAO 2012). Globally, Fe deficiency has grown from about 30% in the 1960s to over 40% in the mid-1990s (Cakmak et al. 2002). Currently, it is estimated that over 60% of the world's six billion people are Fe deficient and over 30% are Zn deficient. In addition, Cu deficiency occurs in many developed and developing countries (White et al. 2012).

Ekholm et al. (2007) reported significant changes in food composition in comparison to similar previous data in Finland, where the calculated daily intakes of Zn, Fe, Co, Ni, and Cd were 25% or lower in the 2000s than in the 1970s. Recent publications using data from food composition tables indicate a downward trend in the mineral content (Fe, Zn, Cu, and Mg) of foods in the United Kingdom (Fan et al. 2008), because of a combination of reduced energy requirements associated with sedentary lifestyles and dietary changes associated with lower micronutrient density in the food. Yang et al. (2007) reported that ~40% of the total land area in China is deficient in Fe and Zn.

Contrary to many other parts of the world, the overall nutritional situation in Europe is characterized by abundance and variety, in the opinion of Meyer and Elmadfa (2012). The authors stated that foods of high quality are available throughout the year; however, surveys of dietary intake and nutrient status keep revealing suboptimal supply and body stores for some minerals despite the high prevalence of obesity. A major reason for malnutrition is seen in the preference for highly processed foods as part of the so-called Western diet. The authors pointed out that these energy-dense but micronutrient-poor foods are major sources of fat and sugar, which promote weight gain without supplying required amounts of essential minerals. Accordingly, Waters and Sankaran (2011) underlined the need to improve the mineral concentrations of important seed crops such as rice, wheat, and maize, as well as bean and other legumes.

The daily dietary intake of young adults ranges from 10 to 60 mg for Fe, 2–3 mg for Cu and ~15 mg for Zn (Imtiaz et al. 2010). Recommended daily intake for Zn is in the range 3–16 mg day^{-1}, depending on age, gender, type of diet, and other factors (Alloway 2009; Sharma et al. 2013). As for Fe, the RDA (Recommended Dietary Allowance) is set at 10–15 mg for adults (Gebhardt and Thomas 2002). The Western diet is often inadequate in Cu, based on criteria of low-Cu concentrations in body fluids, low activities of enzymes dependent on Cu, and beneficial effects of Cu supplements (Klevay 2011). The recommended value for Cu intake in the United Kingdom (since 1991) is 1.2 mg daily and that of the EU is 1.1 mg daily (since 1993). A more recent value for Australia and New Zealand is >1.2 mg daily.

The total intake of a mineral is not the only issue regarding the nutritional value of a food or diet. Absorption of minerals depends on a number of variables which determine its bioavailability (Welch 2005; Fan et al. 2008). Soetan et al. (2010) stated that there is a need to revisit such studies/investigations/assessments/evaluations, so as to revalidate the data on the mineral element composition of human and animal diets, especially in the developing countries.

Strategies to Overcome Micronutrient Deficiency in Cereals

Worldwide, more than 600 million metric tonnes of wheat and maize flours are milled annually by commercial roller mills and consumed as noodles, breads, pasta, and other flour products by people in many countries (WHO, FAO, UNICEF, GAIN, MI, and FFI 2009). Fortification of industrially processed wheat and maize flour may be considered an effective, simple, and inexpensive strategy for supplying vitamins and minerals to the diets on a large scale. However, Imtiaz et al. (2010) consider food fortification and supplementation as too expensive, unpractical, and not easily accessible by poor populations.

There are possibilities, but also limits, for increasing the content and bioavailability of Fe, Zn, and Ca in the edible parts of staple crops, such as cereals, pulses, roots, and tubers (Frossard et al. 2000). Theoretically, this could be achieved by increasing the total level of these metals in the plant foods, together with increasing the concentration of compounds that promote their uptake from the diet (House 1999) and/or by decreasing the concentration of compounds that inhibit their absorption in the human digestive system. In other words, micronutrient biofortification in the soil–plant system can be defined as increasing the concentration and bioavailability of micronutrients in the edible parts of crop plants, through both plant biotechnology and nutritional management of the soil–plant system, with the aim of improving human nutrition and health (Yang et al. 2007).

The micronutrient content (trace elements and minerals) in foods are partially determined by the micronutrient level and availability in the soils on which the crops are grown (Nubé and Voortman 2006). In the case of mineral composition of cereal grain, Anglani (1998) considers as important factors the type of cereal, soil conditions, and fertilizing practices. To a lesser extent, there are the influences of the season and variety. It is well known that crops grown on micronutrient-deficient soil frequently produce grain with low micronutrient – such as Zn – concentration (Rengel 2002). In general, under conditions of soil micronutrient deficiency, the micronutrient content in food crops can be increased by the application of micronutrients as fertilizer (Frossard et al. 2000; Nubé and Voortman 2006). As a specific problem with micronutrients, Nubé and Voortman (2006) stressed the chemical and physiological interactions, mutually between them and between micronutrients and other substances. A complex interaction of P with cations such as Mn, Fe, and especially Zn are known to occur so that P applications may significantly decrease grain Zn concentration in wheat, as reported by Zhang et al. (2012a). Erenoglu et al. (2011) suggested that a special attention in biofortification of food crops with Zn should be given to N, for its critical role in the uptake and accumulation of Zn in plants. In their research, N-nutritional status of wheat affected major steps in the route of Zn from the growth medium (nutrient solution) to the grain, including its uptake, xylem transport, and remobilization via phloem. Most of the grain Zn originates from Zn remobilized from vegetative tissues under field conditions, whereas optimal N management of a wheat crop can improve shoot Zn accumulation and support Zn remobilization (Xue et al. 2012). The authors assumed that the sufficient N supply during the vegetative growth period combined with foliar Zn fertilization may maximize Zn accumulation in the grain, due to possible high sink activity for Zn during the grain-filling period. The results of Cakmak et al. (2010a) show that a large pool of Zn in vegetative tissues in the period of grain filling (e.g., via foliar Zn spray) is necessary for grain Zn increment. In the case of restricted Zn availability in that period, the remobilization is critical for grain accumulation (Kutman et al. 2012). However, in conditions of continued root uptake net remobilization is overshadowed by concurrent Zn uptake, which is favored by a higher N supply, feasibly through promoted tillering and extension of the grain-filling period. The positive effect of N fertilization on grain micronutrients concentrations in wheat was also observed in the research of Shi et al. (2010) and Cakmak et al. (2010a), confirming the importance of proper management of N fertilization. The combination of high N and foliar Zn application may give an increase in wheat Zn concentration even in locations without soil Zn deficiency, as reported by Zou et al. (2012).

Rengel et al. (1999) consider the soil application of $ZnSO_4$ as a cheap and effective method of increasing yields and grain Zn concentration. In the case of Fe deficiency, they stated that foliar fertilization with $FeSO_4$ may be the only fertilizer option; however, increasing Cu in grain may be economically achievable by a change in agricultural practice only on highly Cu-deficient soils. The results of Wang et al. (2008) show that micronutrient fertilization can have positive effects on wheat yield and grain quality, but additional research is needed in order to establish the most effective application methods. Foliar Zn application at the early grain-filling stage increased grain Zn concentration and bioavailability in wheat grown on potential Zn-deficient calcareous soils, as reported by Yang et al. (2011). In the research of Wang et al. (2012), soil Zn application was not effective for Zn deficiency in maize. Foliar application was more efficient, resulting in a significant increase of the grain Zn in maize and wheat, as well as with increased grain Fe concentration in maize. Ghasemi et al. (2013) tested the effects of foliar application of Zn in the form of Zn-amino acid chelates, including Zn-arginine, Zn-glycine, and Zn-histidine, on wheat yield and grain quality. On the basis of the positive effects of these treatments on grain Zn, Fe and protein concentration, and lower phytic acid content in wheat grain, the authors consider Zn-amino acid chelates as new Zn fertilizer sources for improving yield as well as total and bioavailable Zn in wheat grain. However, combined soil and foliar Zn application is recommended if a high concentration of grain Zn is the aim in addition to a high grain yield (Cakmak 2008).

According to White and Broadley (2012), Zn concentration in edible crop parts can be increased through a combination of agronomic and genetic approaches. Zhu et al. (2012) gave an overview of current strategies for the biofortification of crops, including mineral fertilization and conventional breeding but with a focus on transgenic approaches, which they suggest as the most rapid way to develop high-nutrient commercial cultivars. Bhullar and Gruissem (2013) also reviewed genetic engineering approaches that have been successful in the nutritional enhancement of rice endosperm. They stated that conventional breeding alone is not an option for micronutrient biofortification in many circumstances, with micronutrient improvement of rice endosperm remaining a considerable challenge. In the case of Zn deficiency in plants and humans, Ishimaru et al. (2011) suggested that traditional breeding, marker-assisted breeding, plant transformation techniques, and combinations of these techniques can be further exploited. By the opinion of Halford (2012), the era of cheap food and global food surpluses has already ended, so that plant breeders will have to be able to use every available tool including biotechnology. A more comprehensive insight into the achievements in genetic engineering strategy for nutritional enhancement of cereals can be found in the above mentioned reviews.

Some success in increasing the mineral content of staples can be achieved in the short term through conventional breeding techniques, because of the inherent compatibility of high yields and trace mineral density in the seeds (Datta and Bouis 2000; Bouis 2003). A strategy of breeding plants that load high amounts of minerals and vitamins into their edible parts can substantially reduce the recurrent costs of other strategies, such as fortification and supplementation (Bouis et al. 2000; Genc et al. 2005). Gregorio (2002) stated that the results obtained under the Consultative Group on International Agricultural Research Micronutrient Project indicate that breeding parameters are not difficult and are highly likely to be low cost, and micronutrient/density traits are stable across environments. One of the current promising strategies for crops biofortification is undoubtedly the application of plant growth promoting rhizobacteria (PGPR). The research of Rana et al. (2012a,b) shows clear beneficial effects of wheat seed treatment with several rhizobacterial and cyanobacterial strains, both on plant growth in general and on grain micronutrient concentration. Accordingly, Nain et al. (2010) consider screening for the selection of effective PGPR strains as highly important.

The identification and propagation of agricultural methods that enhance the yield, and biological value, of micronutrient-rich foods was considered the one of the research priorities by FAO (2012), in order to facilitate the implementation of food-based approaches in the prevention of micronutrient deficiencies. As for ecological concerns, cultivation and breeding of micronutrient-efficient genotypes in combination with proper agronomic management practices appear as the most sustainable and cost-effective solution (Khoshgoftarmanesh et al. 2010). Micronutrient-efficient genotypes could provide a number of benefits such as the reduction in the use of fertilizers, improvements in seedling vigor, and resistance to abiotic and biotic stresses.

Kutman et al. (2011) suggested that in cereal biofortification efforts, endosperm analysis should be recommended in addition to whole grain analysis. Rengel et al. (1999) stated that the advantages accrued through increasing micronutrient density in grains via agricultural means may need to be accompanied by changes in the milling practices (e.g., reduction in the degree of milling with a resulting higher flour extraction), if the full benefits of field fortification of staple crops are to be achieved. Bioavailability in the human digestive system has to be considered when employing plant breeding and/or transgenic approaches to reduce micronutrient malnutrition. Welch and Graham (2004) suggested that enhancing substances (e.g., ascorbic acid, S-containing amino acids) that promote micronutrient bioavailability, or decreasing anti-nutrient substances (e.g., phytate, polyphenolics) that inhibit micronutrient bioavailability, are both options that could be pursued, but that the latter approach should be used with caution.

Seed biofortification will likely require simultaneous enhancement of several physiological processes, such as uptake from the rhizosphere, translocation from roots to shoots, phloem loading, and remobilization (Waters and Sankaran 2011). Ultimately, an interdisciplinary approach integrating molecular, genetic, physiological, and biochemical approaches holds much promise for improving both plant and human nutrition (Hacisalihoglu and Kochian 2003).

Cereal Grains – An Important Source of Micronutrients

The most important crop species which supply the majority of the world population's nutritional needs are the graminaceous cereals such as rice, maize, wheat, barley, and sorghum (Alloway 2008). Seeds or grains from cereals are a main resource for human nutrition and animal feed throughout the world (Chen et al. 2012). The nutritional relevance of cereals, and particularly of wheat, has been widely recognized as a symbol of the Mediterranean diet, and diets including enriched cereal products are encouraged by nutritionists in Western Europe in order to improve cereal nutritional contribution (Hernández Rodríguez et al. 2011). The world cereal utilization forecast in the 2012/13 marketing season was 2314 million tonnes (FAO 2012). Total consumption of cereals for food is forecast to rise by 1.3% in 2012/13, keeping pace with world population growth and therefore resulting in stable *per capita* consumption of 153 kg year^{-1} for the world as a whole. As the primary staple food of humankind, cereals are accordingly central in strategies for alleviating micronutrient deficiencies by biofortification (Brinch-Pedersen et al. 2007; Shi et al. 2010). High levels of minerals and proteins are usually considered indicators of a high dietary quality of cereal products for humans and farm animals (Feil et al. 2005). On the other hand, micronutrient deficiency in many cereal crops leads to human malnutrition (Williams and Salt 2009). Zn deficiency is probably the most widespread micronutrient deficiency in cereals (Bouis et al. 2000) and biofortification of cereal grains with Zn and Fe is considered a global challenge (Kutman et al. 2011), so there is an urgent need to increase the density and bioavailability of Fe and Zn in the edible parts of cereals (Husted et al. 2011).

The increase of cereals and cash crops in modern farming systems and full adoption of high-yielding cultivars have resulted in a dramatic reduction in food diversity and micronutrient intake (Cakmak et al. 2010b). Khoshgoftarmanesh et al. (2010) stated that the most modern cultivars of wheat and rice have a lower concentration of micronutrients in grain than traditional cultivars because breeders generally focused on increasing yield, without attention to the micronutrient concentrations in grain. Mineral content varies significantly among wheat samples due to a variety of environmental and genetic factors, and their interactions (Anglani 1998). In general, there are some controversial opinions considering the mineral composition of cereal grain. Demirbas (2005) stated that they are excellent sources of Zn, highly available Fe, Cu, Mn, Mo, and B, which also provide significant amounts of P, K, Ca, Mg, and N. According to Dewettinck et al. (2008), wheat, rye, barley, and oats are classified as moderate sources of Fe, Zn, and Cu. Fardet et al. (2008) gave an overview of the content of micronutrients in whole grain cereals (based on literature data, in mg kg^{-1}): wheat Zn 26, Fe 32, Cu 3.7, Mn 31; maize Zn 17, Fe 15, Cu 2.4, Mn 4; rice Zn 16, Fe 32, Cu 2.9, Mn 21. According to Ortiz-Monasterio et al. (2007), tentative targets of increasing the concentration of Fe in maize grain by 40 mg kg^{-1} and of Zn by 15 mg kg^{-1} above the concentrations present in the most widely grown variety are set, for individuals consuming 200 g of maize daily. In the case of wheat, targets were set for increasing the grain concentration of Fe by 22 mg kg^{-1} and of Zn by 10 mg kg^{-1}, for individuals consuming 400 g of wheat daily. Zhao et al. (2009) stated that the targets for Zn and Fe biofortification in wheat grain are around 40 and 60 mg kg^{-1}, assuming current mean Zn and Fe concentrations of 30 and 35 mg kg^{-1}, respectively. The target Zn concentrations set by the HarvestPlus program are 28 mg kg^{-1} in polished rice, and 38 mg kg^{-1} in wheat and maize grain (Bouis and Welch 2010; White and Broadley 2011). On the basis of RDA and bioavailability values, 22 mg kg^{-1} Zn in the polished rice grain have been set as the desirable target, but current status of consumable rice shows that it has only around 20% of this value, as stated by Sharma et al. (2013).

Wheat

In many micronutrient-deficient regions, wheat is the dominant staple food making up >50% of the diet, having a particularly important role in daily energy intake especially in the developing world (Cakmak et al. 2010b). As well as being at low concentrations, genetic variation for micronutrients such as Zn and Fe in modern wheat cultivars is very small (Zhao et al. 2011). However, analyses of multiple grain samples from maize and wheat that have been collected by the International Maize and Wheat Improvement Center (CIMMYT) across a variety of environments and genotypes suggest that the levels of Fe and Zn are higher in wheat than in maize (Ortiz-Monasterio et al. 2007).

However, Hernández Rodríguez et al. (2011) consider wheat as, in general, a good source of nutrients, particularly of minerals and trace elements. Lončarić et al. (2012) quoted that efficient genotypes offer a potential for grain production for human consumption with higher concentrations of Fe, Zn, and Cu. In their research, large yield differences among the most grown Croatian wheat genotypes affected the concentrations of essential metals in the grain differently, as the higher yield was associated with the lower concentrations of Fe, Mn, Zn, and Cu.

Most of the literature related to wheat grain taken into account in this review (Table 1) provide mean concentrations or the concentration ranges for Fe and Zn, the metals which are most often considered deficient in plants, and consequently, in human diet. The reports containing data on all four metals (Fe, Mn, Zn, Cu) in wheat grain are scarce. Mean Fe concentration in bread wheat grain (*Triticum aestivum*) is 39.4 mg kg^{-1}. Mean concentrations of Mn, Zn, and Cu were 29.0, 32.3, and 4.7 mg kg^{-1}, respectively. In comparison with values reported by Fardet et al. (2008), mean Fe, Zn, and Cu concentrations are slightly higher.

Given the widespread occurrence of Zn deficiency in plants, particularly wheat, it is of great importance to breed bread wheat genotypes with high Zn efficiency (Cakmak and Braun 2001). It appears that, with the domestication and modern cultivation of wheat, seed Zn concentration has decreased (Cakmak et al. 1999). There is sufficient genetic variability to develop wheat varieties with increased Zn (Welch et al. 2005; Ortiz-Monasterio et al. 2007), as well as Fe (Welch and Graham 2002) levels in the grain. Due to the lower bioavailability of Fe as compared to Zn, target levels for Fe are significantly higher and meeting them will be more challenging (Ortiz-Monasterio et al. 2007).

As stated by Xu et al. (2011), many researchers have reported significant differences in the concentrations of mineral elements in the grain of wheat and its relatives.

Table 1. Concentration range of essential metals – Fe, Mn, Zn, and Cu in bread wheat (*Triticum aestivum* L.) grain.

Fe	Mn	Zn	Cu	
mg kg^{-1}				Literature source
51.4–60.5	34.9–49.8	10.1–17.1	4.7–9.0	Al-Gahri and Almussali (2008)
24.0–51.0	–	8.0–61.0	–	Cakmak et al. (2000)
33.6–65.6	–	28.5–46.3	–	Ficco et al. (2009)
45.0	–	35.0		Frossard et al. (2000)
37.2	–	37.4	–	Gao et al. (2012)
40.1	42.8	19.2	6.84	Genc et al. (2001)
–	–	25.0–53.0	–	Genc et al. (2005)
28.8–56.5	–	25.2–53.3	–	Graham et al. (1999)
32.6–46.6	15.1–27.6	26.6–36.5	0.7–4.1	Hernández Rodríguez et al. (2011)
33.3	23.3	36.2	4.5	Hussain et al. (2010)
13.0–52.4	–	12.7–46.7	2.9–6.1	Imtiaz et al. (2005, 2010)
8.5–84.1	–	4.6–41.4	–	Khoshgoftarmanesh et al. (2010)
22.6–27.7	4.8–5.3	26.0–28.0	1.9	Kovacevic et al. (2013)
22.9–67.6	–	16.2–32.4	–	Liu et al. (2006)
35.2	36.2	41.6	5.5	Nuss and Tanumihardjo (2010)
19.3–29.8	25.9–45.2	21.7–47.1	3.2–4.9	Shar et al. (2004)
34.0–41.0	24.0–28.0	35.0	3.5–4.4	Suchowilska et al. (2012)
21.6–33.8	19.7–36.8	21.2–34.8	5.2–8.1	Tang et al. (2008)
33.0–73.0	–	27.0–85.0	–	Welch (2003)
28.8–50.8	–	13.5–34.5	–	Zhao et al. (2009)

Compared with cultivated wheat, wild wheats are potential genetic resources for enhancing micronutrient in wheat grain (Cakmak et al. 2000; Monasterio and Graham 2000; Rawat et al. 2009) and current breeding efforts at CIMMYT have focused on transferring genes governing increased Zn and Fe from *T. spelta*, *T. dicoccon*-based synthetics, landraces, and other reported high Zn and Fe sources to high-yielding elite wheat backgrounds (Velu et al. 2011).

Liu et al. (2006) quoted three major factors affecting the utilization of Fe and Zn in wheat grains: the content of Fe and Zn, the content of phytate and the activity of endogenous phytase (EC 3.1.3.26). From a nutritional viewpoint, higher flour yields will provide better mineral element nutrition. However, much more information is needed to confirm the associations between flour yield and bioavailability (Tang et al. 2008).

Rice

Rice (*Oryza sativa* L.) is one of the most important cereals worldwide, it is a staple food for more than half of the world's human population, and polished rice is an important staple food for the majority of people in Asia (Meng et al. 2005; Wang et al. 2011; Jeng et al. 2012; Zhang et al. 2012b). In countries where rice is used as staple food, the *per capita* consumption of this "global grain" (Sharma et al. 2013) is very high, ranging from 62 to 190 kg year^{-1} (Lu et al. 2008). Recognizing the importance of rice-based systems in the fight against hunger and poverty, the United Nations General Assembly named 2004 the International Year of Rice (Fresco 2005). Rice is the lowest of all cereals in Fe, often containing only 5 or 6 mg of Fe kg^{-1} after milling (Gregorio et al. 2000). Although rice is not considered a major mineral source in the diet, any increase in its mineral concentration could significantly help reduce Fe and Zn deficiency in humans because of the high levels of rice consumption among the poor in Asia.

In comparison with wheat, rice is not usually ground into flour so that fortification is a less applicable option (Impa and Johnson-Beebout 2012). Improved intake of mineral elements by rice consumers may be achieved by minimizing the substantial losses that result from polishing (Hansen et al. 2012). In this process, the bran – the outer grain layers (i.e., the germ/embryo and the aleurone/pericarp) – which makes 8–10% of the rough rice kernel mass and is much denser in minerals than the inner parts, is removed, resulting in white rice grains with significantly lower concentration of mineral elements such as Zn (Jiang et al. 2008a). The three main parameters in the evaluation of the quality and efficiency of the milling are the brown rice rate, milled rice rate, and head rice rate (Chen et al. 2012). Data presented by Welch (2005) show that 75% of Fe, 62% of Mn, 30% of Zn, and 12% of Cu are lost by polishing and milling. However, in the research of Heinemann et al. (2005), the milling process did not affect significantly the contents of Fe, Cu, and Zn, and the authors concluded that the intake of one single portion of raw rice (50 g) contributes significant amounts of Se, Cu, Zn, and Mn, reaching up to 35% of the RDA. According to the presented literature data (Table 2), rice grain has a mean Fe, Mn, Zn, and Cu content 22.0, 29.3, 26.5, and 7.2 mg kg^{-1}, respectively, so notably higher than those reported by Fardet et al. (2008), with exception of Fe.

Considerable genotypic differences in the concentrations of Zn, Fe, Cu, and Mn in polished rice grains have been found, with the differences being as high as 10-fold for Zn and sevenfold for Fe (Yang et al. 1998, 2007). Depar et al. (2011) reported considerable genetic variation in different rice genotypes, where 53% of the observed variability was associated with Zn uptake and translocation from roots, shoots, and seed Zn content. The results from IRRI (International Rice Research Institute) indicate that there is significant genetic diversity in the rice genome to potentially increase Fe and Zn concentrations

Table 2. Concentration range of essential metals – Fe, Mn, Zn, and Cu in rice (*Oryza sativa* L.) grain.

Fe	Mn	Zn	Cu	
	mg kg^{-1}			Literature source
31.6–65.1	34.8–64.2	12.5–26.3	5.9–14.3	Depar et al. (2011)
–	–	30.0	–	Fageria (2007)
9.0–20.0	–	11.0–20.0	–	Frossard et al. (2000)
9.6	11.6	32.4	15.7	Genc et al. (2001)
–	–	15.9–58.4	–	Graham et al. (1999)
6.3–24.4	–	13.5–58.4	–	Gregorio et al. (2000)
–	–	12.0–29.6	–	Jiang et al. (2008b)
40.0	45.0	20.9	1.8	Heinemann et al. (2005)
8.0	11.0	11.6	1.1	Nuss and Tanumihardjo (2010)
–	–	14.0–26.0	–	Virk et al. (2007)
13.3–22.4	–	35.1–60.5	–	Welch et al. (2000)

substantially in rice grain. This is confirmed by the successful breeding of a high-Fe rice variety with four to five-fold higher Fe concentration after processing than conventional varieties (Gregorio 2002).

According to Impa and Johnson-Beebout (2012), the priority knowledge gap in rice Zn physiology is the lack of information about the relationship between Zn-deficiency tolerance mechanisms and grain Zn accumulation, as well as on the relative importance of the different uptake and mobilization mechanisms. Foliar application of Zn in rice is definitely a practical and useful approach to improve bioavailable Zn in rice, as stated by Wei et al. (2012), who recommended both Zn-amino acid and $ZnSO_4$ as excellent foliar Zn forms for agronomic biofortification. For successful Fe biofortification, Bhullar and Gruissem (2013) found that coordination between effective uptake of Fe by the roots, effective translocation within the plant, storage in the endosperm and bioavailability upon human ingestion was necessary. The authors concluded that it is important to complement rice breeding with functional genomics technologies, including transcript, protein, and metabolite profiling, as well as with biotechnological approaches for trait improvement. These modern technologies can result in Zn-efficient genotypes, which should be used in conjunction with judicious fertilization to optimize rice grain yield and Zn content (Rehman et al. 2012).

Maize

Corn or maize (*Zea mays* L.) is one of the world's leading cereal crops along with rice and wheat (Nuss and Tanumihardjo 2010). The importance of maize as a crop is based on its diverse functionality as a food source for both humans and animals. It is a staple food for large groups of people in Latin America, Asia, and Africa (Ortiz-Monasterio et al. 2007; Prasanna et al. 2008) and the only kind of food commodity which can be used in the form of grains with or without heat treatment, as well as in many bread and bakeries products (Shar et al. 2011). Similar to other cereals, grain processing after harvest, such as drying, can have a negative impact on maize grain micronutrient content, as seen in the research of Bhuiyan et al. (2010), where drying maize at 100°C resulted in lower Mn, Zn, and Fe concentrations than drying at 90°C and 80°C.

Even though maize grains supply many macro- and micronutrients necessary for human metabolic needs, the amounts of some essential nutrients are low and inadequate for consumers that use maize as a major food source. Maize provides a large proportion of the daily intake of energy and other nutrients, including micronutrients for poor populations in many areas of South East Asia and sub-Saharan Africa (Chakraborti et al. 2009). Data collected by CIMMYT suggest that the range in Fe and Zn concentrations in maize kernels is much lower in comparison with other cereal crops (Welch and Graham 2002). Mean concentrations in maize grain, as seen from the available literature (Table 3), are as follows: Fe 28.4, Mn 7.0, Zn 24.7, and Cu 3.5 mg kg^{-1}, which is much higher than those reported by Fardet et al. (2008).

Raboy (2000) stated that the primary goal of the maize-breeding community in the United States is to improve this crop as a feed grain. Maize breeders seek to combine or "stack" nutritional quality traits to produce an optimal feed grain. This approach might have applications in the improvement of grains as human foods as well, considering food quality from a mineral nutrients content viewpoint. Šimić et al. (2009b) established generally positive correlations among concentrations of various micronutrients in maize grain, suggesting possible improvements regarding increased concentrations of various micronutrient in maize grain could be done simultaneously.

Conclusion

Among many trace elements, Cu, Fe, Mn, and Zn are defined as micronutrients because they are essential for physiological processes in living organisms; therefore, they make significant components of the soil–plant–food continuum, or the food chain. Considering that microelement malnutrition is recognized as a global nutritional problem, the role of plants as the first link of the food chain has received substantial public attention in the last few decades. Deficiency of micronutrients in soil and

Table 3. Concentration range of essential metals – Fe, Mn, Zn, and Cu in maize (*Zea mays* L.) grain

Fe	Mn	Zn	Cu	
mg kg^{-1}				Literature source
9.6–63.2	–	12.9–57.6	–	Banzinger and Long (2000)
13.6–30.3	6.4–11.0	16.0–23.6	0.6–3.0	Brkić et al. (2003)
11.0–60.7	4.7–14.8	11.9–33.2	0.5–3.4	Brkić et al. (2004)
10.1–26.7	–	21.3–34.7	–	Chakraborti et al. (2009)
17.0–20.0	4.0–6.0	19.0–25.0	1.0–3.0	de Oliveira Guimarães et al. (2007)
–	–	18.0	–	Fageria (2007)
17.0–41.0	5.0–13. 0	22.0–39.0	0.7–9.6	Ferreira et al. (2012)
30.0	–	25.0	–	Frossard et al. (2000)
24.2	19.5	17.0	15.3	Genc et al. (2001)
20.4	4.5	25.9	4.1	Gumze et al. (2012)
9.0–89.5	1.0–9.8	15.0–34.5	1.0–5.8	Heckman et al. (2003)
–	–	21.8–30.7	–	Kanval (2009), Kanval et al. (2010)
17.8–18.8	3.3–3.8	17.8–18.8	1.8–2.3	Komljenovic et al. (2006)
19.8–20.7	3.5–4.6	16.5–20.1	–	Kovacevic et al. (2010)
13.6–159.4	–	11.7–95.6	–	Maziya-Dixon et al. (2000)
27.1	4.9	22.1	3.1	Nuss and Tanumihardjo (2010)
11.3–60.1	–	15.1–53.0	–	Prasanna et al. (2011)
15.0–27.0	3.5–7.5	13.0–15.0	0.6–2.6	Sager and Hoesch (2005)
6.3–10.7	3.6–9.3	16.3–31.2	1.1–2.0	Shar et al. (2011)
–	–	15.5–34.4	–	Šimić et al. (2007)
16.6–33.6	–	16.4–28.6	–	Šimić et al. (2009a)
24.9	8.0	21.8	1.0	Šimić et al. (2009b)
15.9–24.7	–	19.2–24.1	–	Vragolovic et al. (2007)
–	2.9–4.6	13.1–17.1	1.2–4.6	Vyn and Tollenaar (1998)
15.7–33.9	–	27.7–35.9	–	Yazdani and Pirdashti (2011)

plants, and consequently in the diet, leads to “hidden hunger” with serious health-related human and animal diseases. Therefore, the desirable micronutrient density in major staple foods, such as cereal grains, is an important issue and a matter of great concern in agricultural and food sciences. The knowledge on metal concentrations and genetic potential of cultivated and wild cereal species in the uptake of microelements, as well as their transport and storage, may help in breeding and growing high-efficient crops, containing satisfactory amounts of essential metals. Based on the literature reviewed in this study, there is a lot of genetic variability within the major grain cereals – wheat, rice, and maize – which could be exploited in attaining the desired amount of essential trace metals in food, taking into account our specific physiological requirements. Further interdisciplinary research and development of agricultural methods that will enhance not only the yield but also the concentration and biological value, of micronutrient-rich foods are required to accomplish controlled and sustainable metal content in the food chain.

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Conflict of Interest

None declared.

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